Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structural, phonon and optical properties of [CH3NH3]M0.5CrxAl0.5-x(HCOO)3 (M=Na, K; x=0, 0.025, 0.5) metal-organic framework perovskites for luminescence thermometry

by *Maciej Ptak,a Błażej Dziuk,b Dagmara Stefańskaa and Krzysztof Hermanowicza*

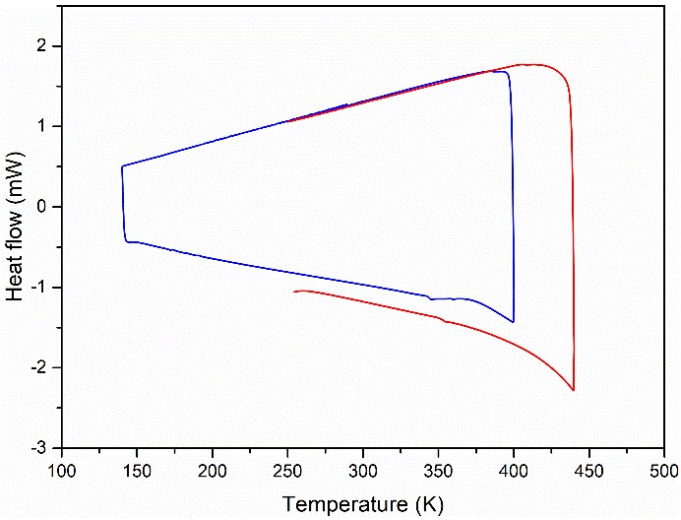


Fig. S1. The DSC traces for the MeANaCr crystals measured in the 140–300 K (blue line) and 250–440 K (red line) ranges at a rate of 5 °C min^{-1} under a nitrogen atmosphere.

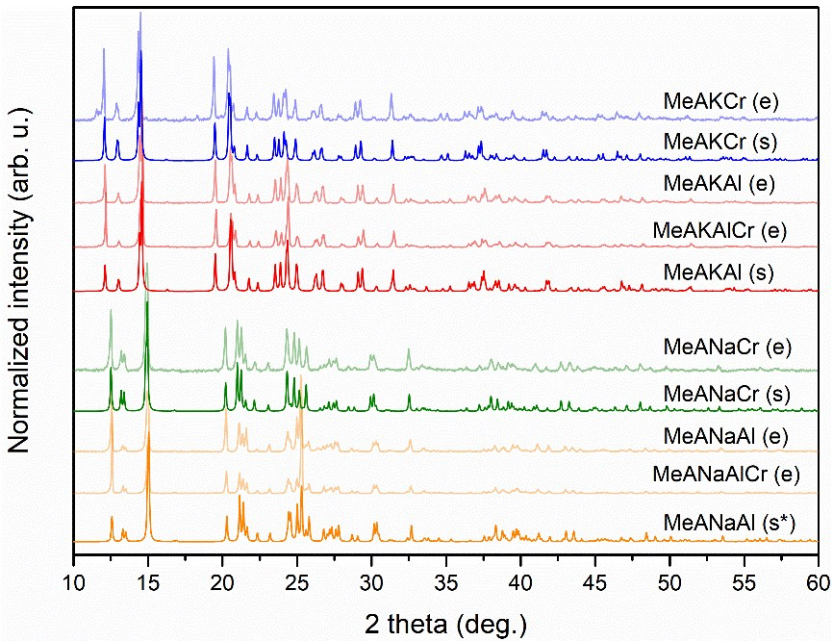
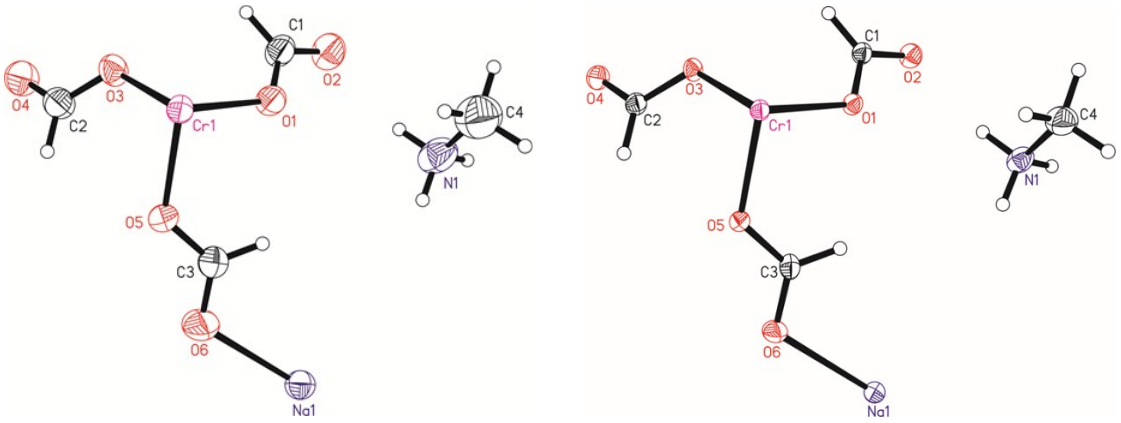
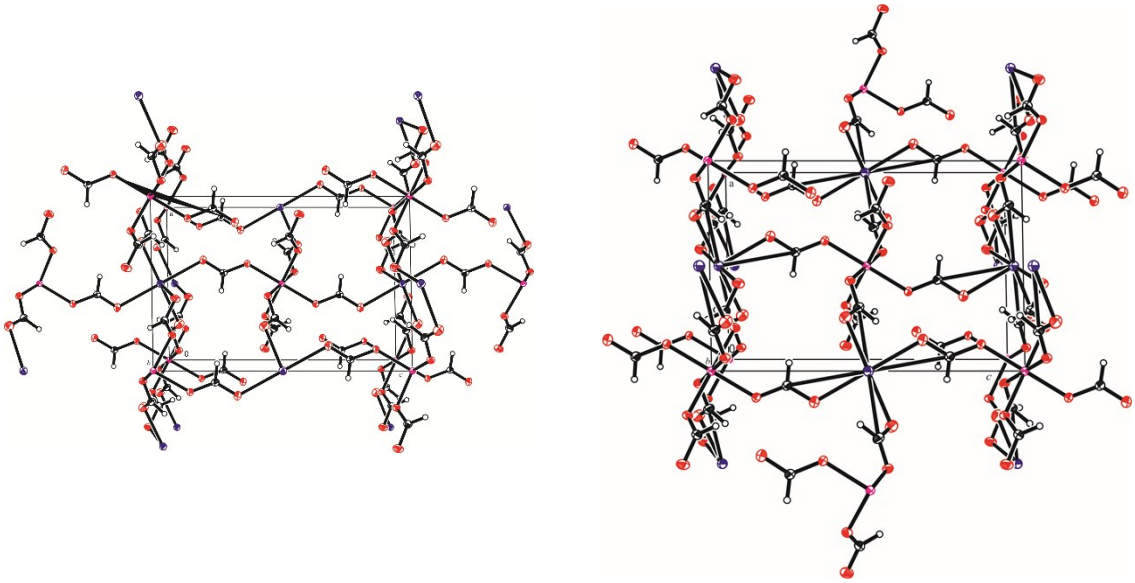


Fig. S2. Experimental (e) and simulated (s) powder XRD based on the single-crystal data for all studied perovskites. The simulated pattern for MeANaAl (s*) is taken from literature.[1]



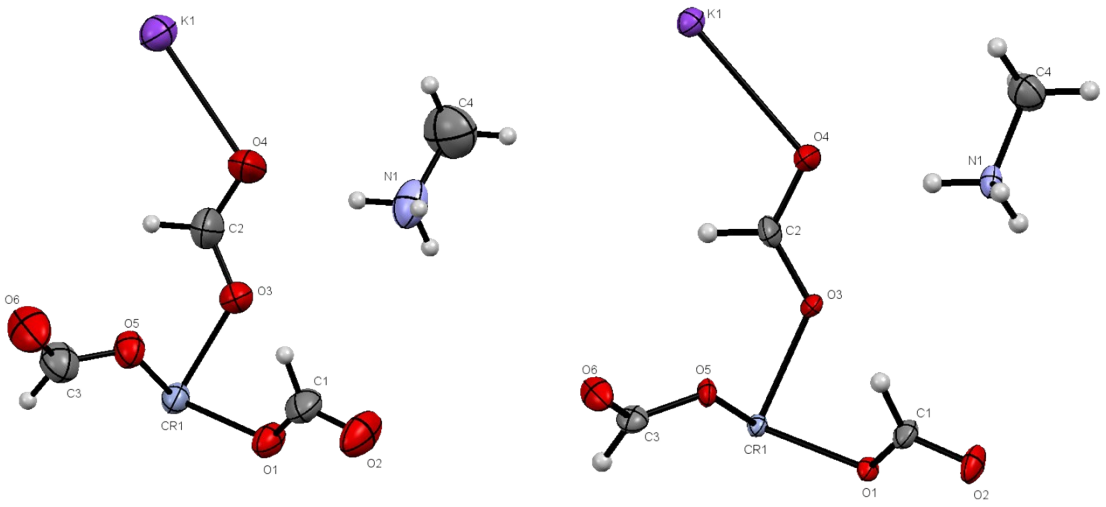
(a) (b)

Fig. S3. Asymmetric part of unit cell for MeANaCr at (a) 295 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.



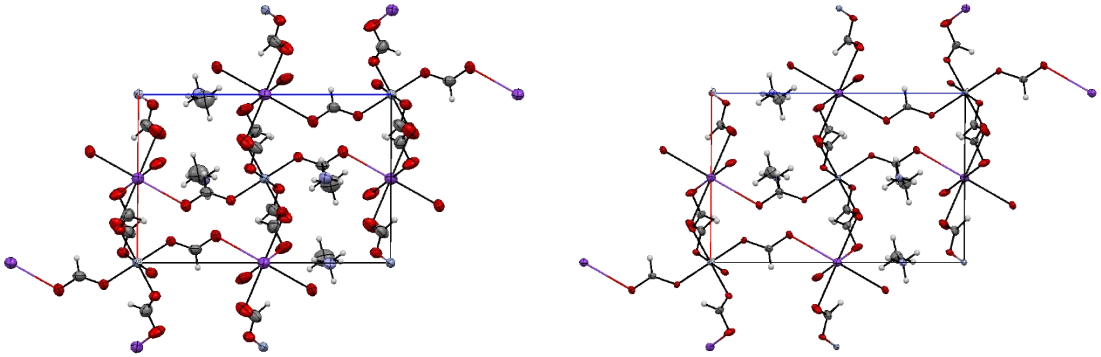
(a) (b)

Fig. S4. Packing diagrams for MeANaCr at (a) 295 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.



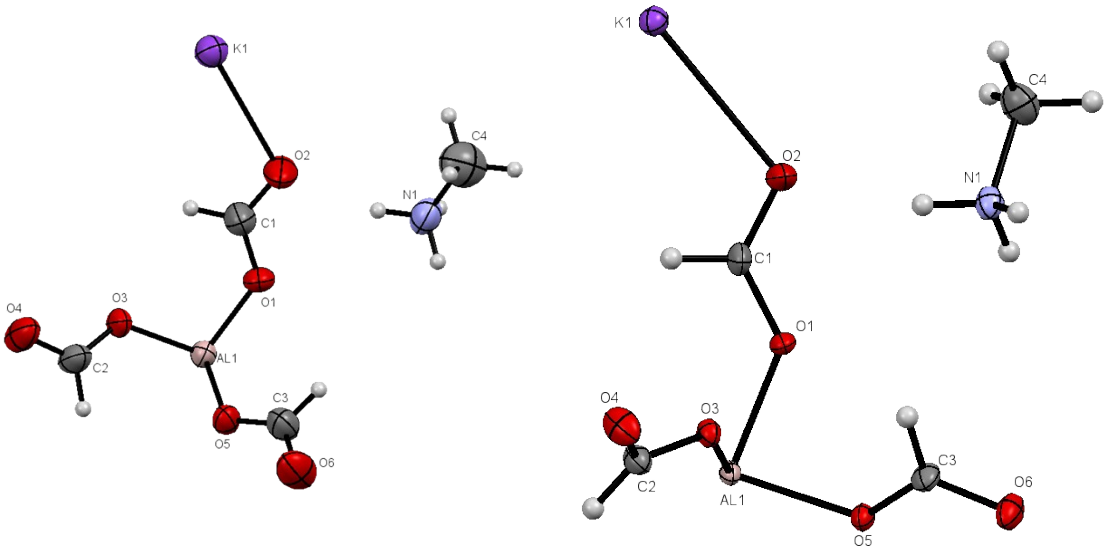
(a) (b)

Fig. S5. Asymmetric part of unit cell for MeAKCr at (a) 293 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.



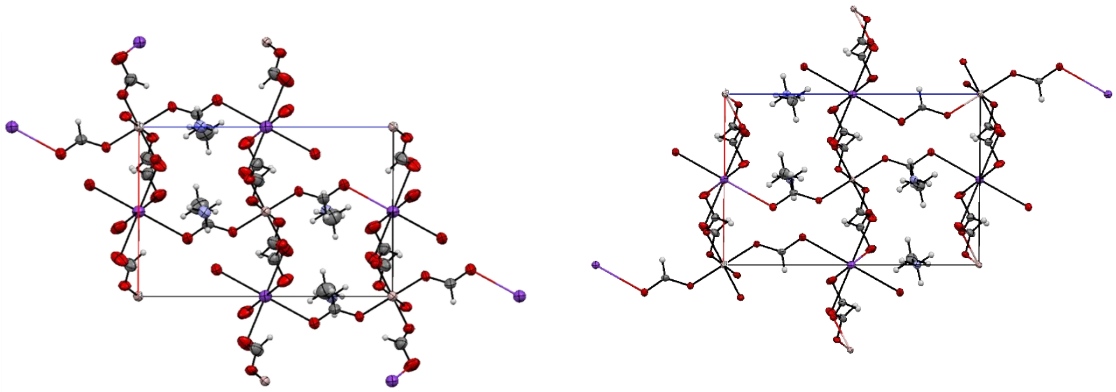
(a) (b)

Fig. S6. Packing diagrams for MeAKCr at (a) 293 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.



(a) (b)

Fig. S7. Asymmetric part of unit cell for MeAKAl at (a) 293 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.



(a) (b)

Fig. S8. Packing diagrams for MeAKAl at (a) 293 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.

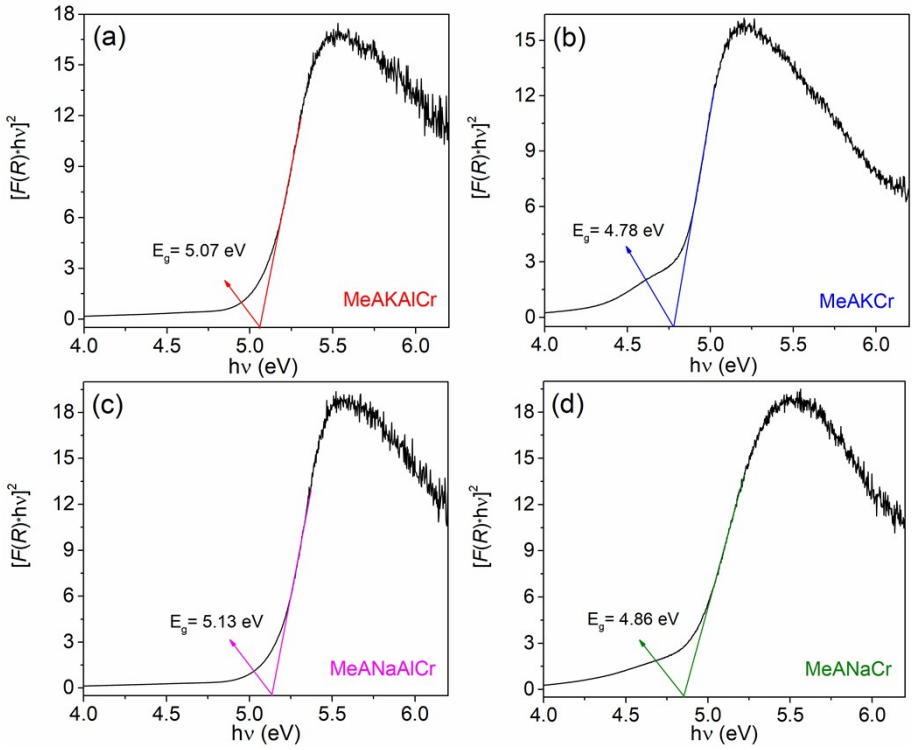


Fig. S9. The energy of band gaps for investigated compounds determined using Kubelka-Munk function.

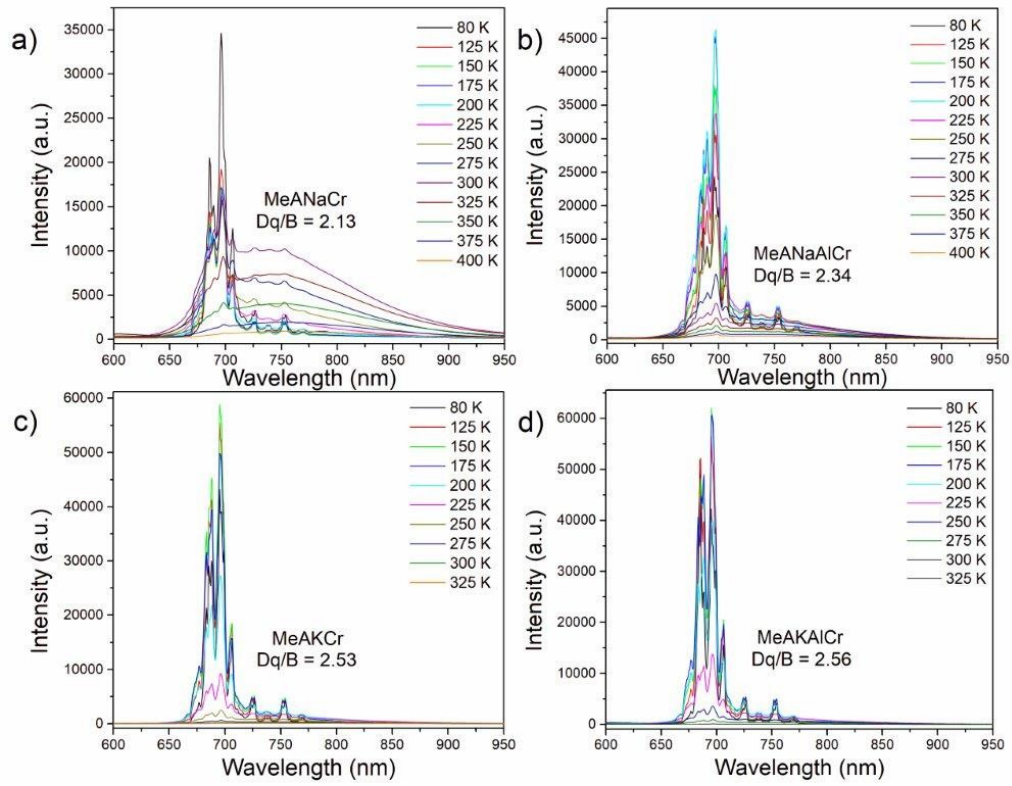


Fig. S10. The temperature-dependent emission spectra of (a) MeANaCr, (b) MeANaAlCr, (c) MeAKCr and (d) MeAKAlCr recorded under 450 nm excitation line in the range of 77 to 400 K.

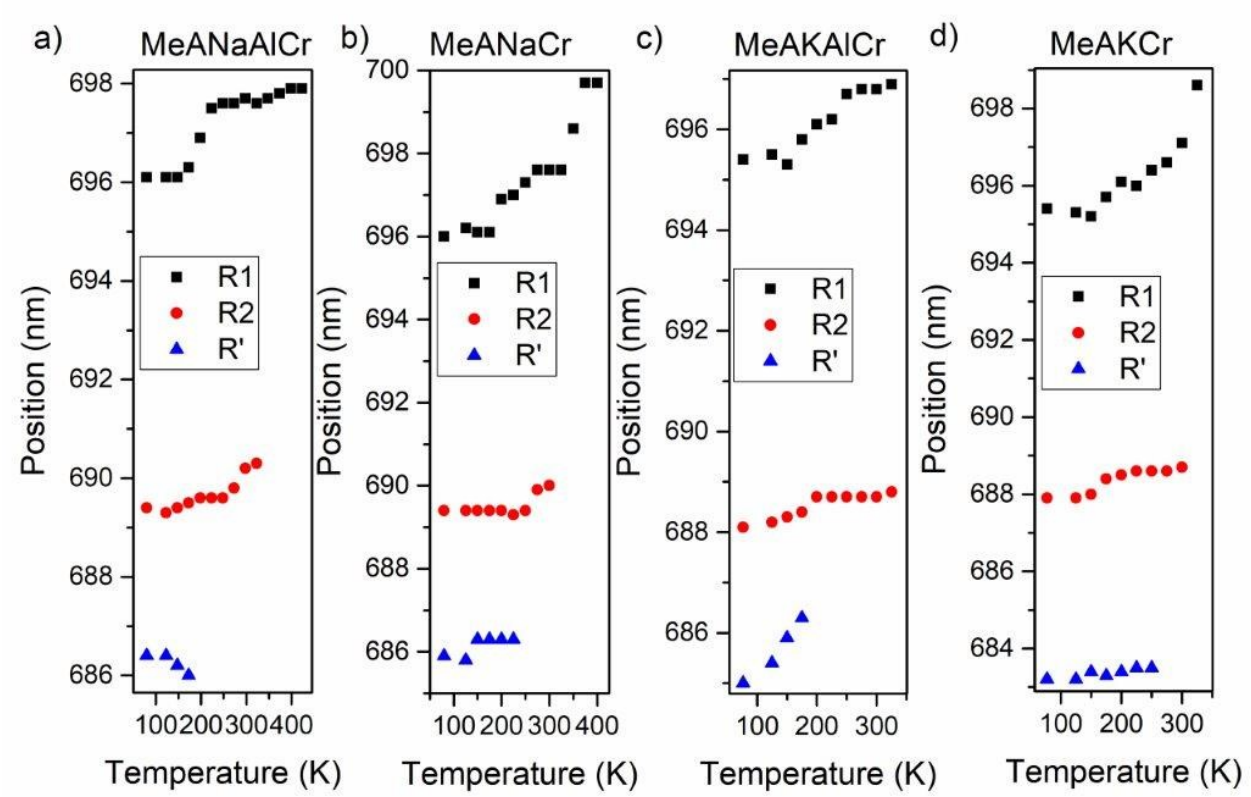


Fig. S11. The temperature dependents of R-lines positions in investigated compounds.

Tab. S1. Crystallographic details of MeANaCr, MeAKCr and MeAKAl at room-temperature and 100 K.

Crystal data	MeANaCr		MeAKAl		MeAKCr	
Chemical formula	$(CH_3NH_3)_2NaCr(HCOO)_6$		$(CH_3NH_3)_2KAl(HCOO)_6$		$(CH_3NH_3)_2KCr(HCOO)_6$	
M	409.23		400.32		425.34	
Crystal system, sg	Monoclinic, $P2_1/n$		Monoclinic, $P2_1/n$		Monoclinic, $P2_1/n$	
Temperature (K)	295(2)	100.0(1)	293(2)	100.0(1)	293(2)	100.0(1)
a, *b*, *c* (Å)	8.0317(4), 8.7854(5), 11.9391(7)	7.9504(9), 8.7582(10), 11.8530(14)	8.1644(8), 9.0972(10), 12.2715(13)	8.1568(4), 9.0289(4), 12.2380(6)	8.2054(9), 9.1089(13), 12.3423(15)	8.1907(5), 9.0549(7), 12.2909(8)
α, β, γ (°)	90.000(0), 90.923(5), 90.000(0)	90.000, 90.989(10), 90.000	90.000(0), 90.289(10), 90.000(0)	90.000, 90.509(4), 90.000	90.000, 90.377(10), 90.000	90.000, 90.410(6), 90.000
V (Å^3)	842.33(8)	825.22(16)	911.43(17)	901.26(7)	922.5(2)	911.54(11)
Z	2		2		2	
Radiation type	MoKα		MoKα		MoKα	
μ (mm^{-1})	0.77	0.78	0.40	0.40	0.90	0.91
Crystal size (mm)	0.20 × 0.20 × 0.10		0.20 × 0.20 × 0.10		0.20 × 0.20 × 0.10	
Data collection						
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	5502, 1629, 1056	5450, 1614, 1066	5975, 1773, 720	5822, 1741, 1234	5947, 1798, 922	5936, 1779, 992
R_{int}	0.043	0.051	0.144	0.048	0.098	0.083
(sinθ/λ$_{max}$ (Å^{-1})	0.617		0.616	0.617	0.617	
Refinement						
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.065, 0.86	0.033, 0.068, 0.86	0.061, 0.153, 0.91	0.037, 0.083, 0.87	0.065, 0.131, 1.11	0.044, 0.086, 0.97
No. of reflections	1629	1614	1773	1741	1798	1779
No. of parameters	114		114		114	
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement					
Δρ$_{max}$,Δρ$_{min}$(eÅ^{-3})	0.18, −0.27	0.28, −0.40	0.31, −0.28	0.33, −0.31	0.35, −0.45	0.35, −0.52

Tab. S2. The parameters of selected HBs created between the MeA^+ cation and metal-formate framework for studied MOFs at room temperature and at 100 K (in square brackets). Data for MeANaAl are taken from literature[1] and refer to single crystal data at room temperature and at 180 K (at square brackets).

	D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
MeANaCr					
	N1—H1A···O2	0.89 [0.89]	2.00 [1.96]	2.862(3) [2.832(3)]	164.2 [165.4]
NaO_6	N1—H1B···O4^{i}	0.89 [0.89]	1.99 [1.99]	2.875(3) [2.877(3)]	173.6 [172.2]
	N1—H1C···O6^{ii}	0.89 [0.89]	2.09 [2.01]	2.940(3) [2.884(3)]	160.3 [165.7]
CrO_6	N1—H1C···O5^{ii}	0.89 [0.89]	2.36 [2.41]	3.097(3) [3.104(3)]	140.7 [135.5]
MeAKCr					

	N1—H1B···O2^{ii}	0.89 [0.89]	1.95 [1.95]	2.828(6) [2.821(4)]	167.1 [167.3]
KO_6	N1—H1A···O6^{i}	0.89 [0.89]	1.95 [1.94]	2.832(6) [2.833(4)]	172.2 [176.9]
	N1—H1C···O4	0.89 [0.89]	1.95 [1.92]	2.820(5) [2.795(4)]	166.8 [166.5]
CrO_6	N1—H1C···O3	0.89 (0.89)	2.57 [2.58]	3.273(6) [3.283(4)]	136.9 [136.1]
MeNaAl[1]					
	N1—H6···O2	0.91 [0.89]	1.99 [1.96]	2.8577(16) [2.8454(17)]	163.0 [163.5]
NaO_6	N1—H4···O5	0.91 [0.89]	1.97 [1.95]	2.8544(16) [2.8520(19)]	174.5 [174.5]
	N1—H5···O4	0.91 [0.89]	2.04 [1.99]	2.9035(17) [2.8748(18)]	161.7 [163.9]
AlO_6	N1—H5···O3	0.91 [0.89]	2.42 [2.42]	3.1444(16) [3.1453(18)]	139.3 [136.7]
MeAKAl					
	N1—H1B···O6^{v}	0.89 [0.89]	1.96 [1.95]	2.832(6) [2.822(3)]	166.4 [167.5]
KO_6	N1—H1A···O4^{iv}	0.89 [0.89]	1.93 [1.93]	2.823(6) [2.822(3)]	175.9 [175.3]
	N1—H1C···O2	0.89 [0.89]	1.94 [1.93]	2.810(6) [2.801(3)]	165.2 [167.2]
AlO_6	N1—H1B···O1	0.89 [0.89]	2.61 [2.63]	3.331(6) [3.342(3)]	138.7 [137.2]

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

Tab. S3. Selected geometric parameters (Å, °) for MeANaCr at 295 and 100 K.

295 K

Cr1—O5	1.9695 (15)	Na1—O2^{iii}	2.4162 (17)
Cr1—O5^{i}	1.9695 (15)	Na1—O2^{iv}	2.4162 (17)
Cr1—O3^{i}	1.9738 (16)	Na1—O4^{v}	2.4614 (17)
Cr1—O3	1.9738 (16)	Na1—O4^{vi}	2.4614 (17)
Cr1—O1^{i}	1.9740 (16)	C3—O6	1.209 (3)
Cr1—O1	1.9740 (16)	C3—O5	1.263 (3)
O1—C1	1.261 (3)	C3—H3	0.9300
N1—C4	1.452 (4)	O3—C2	1.254 (3)
N1—H1A	0.8900	C2—O4	1.227 (3)
N1—H1B	0.8900	C2—H2	0.9300
N1—H1C	0.8900	O2—Na1^{vii}	2.4162 (17)
C1—O2	1.226 (3)	O4—Na1^{viii}	2.4614 (17)
C1—H1	0.9300	C4—H4A	0.9600
Na1—O6^{ii}	2.3944 (17)	C4—H4B	0.9600
Na1—O6	2.3944 (17)	C4—H4C	0.9600
O5—Cr1—O5^{i}	180.0	O6—Na1—O2^{iv}	87.39 (6)
O5—Cr1—O3^{i}	88.63 (6)	O2^{iii}—Na1—O2^{iv}	180.0
O5^{i}—Cr1—O3^{i}	91.37 (6)	O6^{ii}—Na1—O4^{v}	91.63 (6)
O5—Cr1—O3	91.37 (6)	O6—Na1—O4^{v}	88.37 (6)
O5^{i}—Cr1—O3	88.63 (6)	O2^{iii}—Na1—O4^{v}	86.73 (6)
O3^{i}—Cr1—O3	180.0	O2^{iv}—Na1—O4^{v}	93.27 (6)
O5—Cr1—O1^{i}	88.91 (6)	O6^{ii}—Na1—O4^{vi}	88.37 (6)
O5^{i}—Cr1—O1^{i}	91.09 (6)	O6—Na1—O4^{vi}	91.63 (6)
O3^{i}—Cr1—O1^{i}	90.93 (7)	O2^{iii}—Na1—O4^{vi}	93.26 (6)
O3—Cr1—O1^{i}	89.07 (7)	O2^{iv}—Na1—O4^{vi}	86.74 (6)
O5—Cr1—O1	91.09 (6)	O4^{v}—Na1—O4^{vi}	180.0
O5^{i}—Cr1—O1	88.91 (6)	O6—C3—O5	125.1 (3)
O3^{i}—Cr1—O1	89.07 (7)	O6—C3—H3	117.5
O3—Cr1—O1	90.93 (7)	O5—C3—H3	117.5
O1^{i}—Cr1—O1	180.0	C2—O3—Cr1	126.70 (17)
C1—O1—Cr1	126.74 (16)	O4—C2—O3	126.2 (3)
C4—N1—H1A	109.5	O4—C2—H2	116.9
C4—N1—H1B	109.5	O3—C2—H2	116.9
H1A—N1—H1B	109.5	C1—O2—Na1^{vii}	116.46 (16)
C4—N1—H1C	109.5	C2—O4—Na1^{viii}	114.86 (18)
H1A—N1—H1C	109.5	N1—C4—H4A	109.5
H1B—N1—H1C	109.5	N1—C4—H4B	109.5
O2—C1—O1	124.6 (2)	H4A—C4—H4B	109.5
O2—C1—H1	117.7	N1—C4—H4C	109.5
O1—C1—H1	117.7	H4A—C4—H4C	109.5
O6^{ii}—Na1—O6	180.0	H4B—C4—H4C	109.5
O6^{ii}—Na1—O2^{iii}	87.39 (6)	C3—O6—Na1	116.73 (18)
O6—Na1—O2^{iii}	92.61 (6)	C3—O5—Cr1	127.66 (17)

O6^{ii}—Na1—O2^{iv}	92.61 (6)		
Cr1—O1—C1—O2	−176.10 (19)	O3—C2—O4—Na1^{viii}	170.6 (2)
Cr1—O3—C2—O4	176.1 (2)	O5—C3—O6—Na1	179.7 (2)
O1—C1—O2—Na1^{vii}	179.82 (19)	O6—C3—O5—Cr1	176.2 (2)

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

100 K

Cr1—O5^{i}	1.9708 (17)	Na1—O4^{vi}	2.4469 (18)
Cr1—O5	1.9708 (17)	Na1—O4^{vii}	2.4469 (18)
Cr1—O3	1.9743 (17)	Na1—C3	3.099 (3)
Cr1—O3^{i}	1.9743 (17)	Na1—C3^{iii}	3.099 (3)
Cr1—O1	1.9770 (17)	Na1—C1^{v}	3.126 (3)
Cr1—O1^{i}	1.9770 (17)	Na1—C1^{iv}	3.126 (3)
O1—C1	1.270 (3)	C3—O6	1.223 (3)
N1—C4	1.467 (3)	C3—O5	1.265 (3)
N1—H1A	0.8900	C3—H3	0.9300
N1—H1B	0.8900	O3—C2	1.272 (3)
N1—H1C	0.8900	C2—O4	1.227 (3)
C1—O2	1.232 (3)	C2—H2	0.9300
C1—Na1^{ii}	3.126 (3)	O2—Na1^{ii}	2.3925 (18)
C1—H1	0.9300	O4—Na1^{viii}	2.4469 (18)
Na1—O6^{iii}	2.3725 (18)	C4—H4A	0.9600
Na1—O6	2.3725 (18)	C4—H4B	0.9600
Na1—O2^{iv}	2.3925 (18)	C4—H4C	0.9600
Na1—O2^{v}	2.3925 (18)		
O5^{i}—Cr1—O5	180.0	O4^{vi}—Na1—C3	107.88 (7)
O5^{i}—Cr1—O3	88.96 (7)	O4^{vii}—Na1—C3	72.12 (7)
O5—Cr1—O3	91.04 (7)	O6^{iii}—Na1—C3^{iii}	20.89 (7)
O5^{i}—Cr1—O3^{i}	91.04 (7)	O6—Na1—C3^{iii}	159.11 (7)
O5—Cr1—O3^{i}	88.96 (7)	O2^{iv}—Na1—C3^{iii}	79.17 (7)
O3—Cr1—O3^{i}	180.0	O2^{v}—Na1—C3^{iii}	100.83 (7)
O5^{i}—Cr1—O1	88.81 (7)	O4^{vi}—Na1—C3^{iii}	72.12 (7)
O5—Cr1—O1	91.19 (7)	O4^{vii}—Na1—C3^{iii}	107.88 (7)
O3—Cr1—O1	90.94 (7)	C3—Na1—C3^{iii}	180.0
O3^{i}—Cr1—O1	89.06 (7)	O6^{iii}—Na1—C1^{v}	77.14 (7)
O5^{i}—Cr1—O1^{i}	91.19 (7)	O6—Na1—C1^{v}	102.86 (7)
O5—Cr1—O1^{i}	88.81 (7)	O2^{iv}—Na1—C1^{v}	159.15 (6)
O3—Cr1—O1^{i}	89.06 (7)	O2^{v}—Na1—C1^{v}	20.85 (6)
O3^{i}—Cr1—O1^{i}	90.94 (7)	O4^{vi}—Na1—C1^{v}	107.28 (7)
O1—Cr1—O1^{i}	180.0	O4^{vii}—Na1—C1^{v}	72.72 (7)
C1—O1—Cr1	125.60 (17)	C3—Na1—C1^{v}	90.18 (7)
C4—N1—H1A	109.5	C3^{iii}—Na1—C1^{v}	89.82 (7)
C4—N1—H1B	109.5	O6^{iii}—Na1—C1^{iv}	102.86 (7)
H1A—N1—H1B	109.5	O6—Na1—C1^{iv}	77.14 (7)
C4—N1—H1C	109.5	O2^{iv}—Na1—C1^{iv}	20.85 (6)
H1A—N1—H1C	109.5	O2^{v}—Na1—C1^{iv}	159.15 (6)
H1B—N1—H1C	109.5	O4^{vi}—Na1—C1^{iv}	72.72 (7)
O2—C1—O1	124.0 (3)	O4^{vii}—Na1—C1^{iv}	107.28 (7)
O2—C1—Na1^{ii}	43.73 (13)	C3—Na1—C1^{iv}	89.82 (7)
O1—C1—Na1^{ii}	167.69 (19)	C3^{iii}—Na1—C1^{iv}	90.18 (7)
O2—C1—H1	118.0	C1^{v}—Na1—C1^{iv}	180.000 (17)
O1—C1—H1	118.0	O6—C3—O5	123.9 (3)
Na1^{ii}—C1—H1	74.3	O6—C3—Na1	43.78 (13)
O6^{iii}—Na1—O6	180.0	O5—C3—Na1	167.7 (2)
O6^{iii}—Na1—O2^{iv}	86.86 (7)	O6—C3—H3	118.0
O6—Na1—O2^{iv}	93.14 (7)	O5—C3—H3	118.0
O6^{iii}—Na1—O2^{v}	93.14 (7)	Na1—C3—H3	74.3
O6—Na1—O2^{v}	86.86 (7)	C2—O3—Cr1	125.10 (18)
O2^{iv}—Na1—O2^{v}	180.0	O4—C2—O3	124.6 (3)
O6^{iii}—Na1—O4^{vi}	91.86 (6)	O4—C2—H2	117.7
O6—Na1—O4^{vi}	88.14 (6)	O3—C2—H2	117.7
O2^{iv}—Na1—O4^{vi}	86.28 (6)	C1—O2—Na1^{ii}	115.42 (17)
O2^{v}—Na1—O4^{vi}	93.72 (6)	C2—O4—Na1^{viii}	113.48 (18)
O6^{iii}—Na1—O4^{vii}	88.14 (6)	N1—C4—H4A	109.5
O6—Na1—O4^{vii}	91.86 (6)	N1—C4—H4B	109.5
O2^{iv}—Na1—O4^{vii}	93.72 (6)	H4A—C4—H4B	109.5
O2^{v}—Na1—O4^{vii}	86.28 (6)	N1—C4—H4C	109.5
O4^{vi}—Na1—O4^{vii}	180.0	H4A—C4—H4C	109.5
O6^{iii}—Na1—C3	159.11 (7)	H4B—C4—H4C	109.5
O6—Na1—C3	20.89 (7)	C3—O6—Na1	115.34 (18)
O2^{iv}—Na1—C3	100.83 (7)	C3—O5—Cr1	126.85 (18)

O2^{v}—Na1—C3	79.17 (7)		
Cr1—O1—C1—O2	−175.23 (19)	O3—C2—O4—Na1^{viii}	170.8 (2)
Cr1—O1—C1—Na1^{ii}	−171.4 (7)	O5—C3—O6—Na1	179.7 (2)
Cr1—O3—C2—O4	174.73 (19)	O6—C3—O5—Cr1	175.2 (2)
O1—C1—O2—Na1^{ii}	178.8 (2)	Na1—C3—O5—Cr1	176.1 (8)

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

The Cr–O distances are in the 1.9708(17)–1.9770(17) Å range, while Na–O in the 2.3725(18)–2.4469(18) Å range (1.9695(15)–1.9740(16) Å and 2.3944(17)–2.4614(17) Å for room temperature structure, respectively). Taking into account the valence angles, the O–Cr–O ones involving oxygen atoms *cis* to each other range from 88.96(7)° to 91.19(7)°, while those located *trans* amount to 180.0° (88.63(6)° to 91.37(6) and 180° for room temperature structure). The octahedral geometry of the NaO_6 moiety is more distorted as the O–Na–O angles involving oxygen atoms mutually *cis* range from 86.28(6)° to 93.72(6)°, while those located trans amount to 180° (86.73(6)° to 93.27(6) and 180° for room temperature structure).

Tab. S4. Selected geometric parameters (Å, °) for MeAKCr at 293 and 100 K.

293 K

Cr1—O3^{i}	1.961 (3)	K1—C1^{v}	3.413 (6)
Cr1—O3	1.961 (3)	K1—C3^{vii}	3.413 (6)
Cr1—O5^{i}	1.970 (3)	K1—C3^{vi}	3.413 (6)
Cr1—O5	1.970 (3)	N1—C4	1.451 (8)
Cr1—O1	1.971 (3)	N1—H1A	0.8900
Cr1—O1^{i}	1.971 (3)	N1—H1B	0.8900
O1—C1	1.257 (6)	N1—H1C	0.8900
C1—O2	1.227 (6)	O3—C2	1.254 (6)
C1—K1^{ii}	3.413 (6)	C3—O6	1.228 (6)
C1—H1	0.9300	C3—O5	1.257 (6)
K1—O4^{iii}	2.691 (4)	C3—K1^{viii}	3.413 (6)
K1—O4	2.691 (4)	C3—H3	0.9300
K1—O2^{iv}	2.711 (4)	C2—O4	1.220 (6)
K1—O2^{v}	2.711 (4)	C2—H2	0.9300
K1—O6^{vi}	2.747 (4)	O2—K1^{ii}	2.712 (4)
K1—O6^{vii}	2.747 (4)	C4—H4A	0.9600
K1—C2	3.375 (6)	C4—H4B	0.9600
K1—C2^{iii}	3.375 (6)	C4—H4C	0.9600
K1—C1^{iv}	3.413 (6)	O6—K1^{viii}	2.747 (4)
O3^{i}—Cr1—O3	180.0	O4—K1—C1^{v}	77.85 (13)
O3^{i}—Cr1—O5^{i}	88.41 (14)	O2^{iv}—K1—C1^{v}	160.96 (11)
O3—Cr1—O5^{i}	91.59 (14)	O2^{v}—K1—C1^{v}	19.04 (11)
O3^{i}—Cr1—O5	91.59 (14)	O6^{vi}—K1—C1^{v}	104.48 (13)
O3—Cr1—O5	88.41 (14)	O6^{vii}—K1—C1^{v}	75.52 (13)
O5^{i}—Cr1—O5	180.0	C2—K1—C1^{v}	88.95 (15)
O3^{i}—Cr1—O1	91.43 (14)	C2^{iii}—K1—C1^{v}	91.05 (15)
O3—Cr1—O1	88.57 (14)	C1^{iv}—K1—C1^{v}	180.0
O5^{i}—Cr1—O1	88.91 (14)	O4^{iii}—K1—C3^{vii}	99.05 (13)
O5—Cr1—O1	91.09 (14)	O4—K1—C3^{vii}	80.95 (13)
O3^{i}—Cr1—O1^{i}	88.57 (14)	O2^{iv}—K1—C3^{vii}	75.15 (13)
O3—Cr1—O1^{i}	91.43 (14)	O2^{v}—K1—C3^{vii}	104.85 (13)
O5^{i}—Cr1—O1^{i}	91.09 (14)	O6^{vi}—K1—C3^{vii}	160.60 (12)
O5—Cr1—O1^{i}	88.91 (14)	O6^{vii}—K1—C3^{vii}	19.40 (12)
O1—Cr1—O1^{i}	180.0	C2—K1—C3^{vii}	96.55 (15)
C1—O1—Cr1	126.8 (3)	C2^{iii}—K1—C3^{vii}	83.45 (15)
O2—C1—O1	125.6 (5)	C1^{iv}—K1—C3^{vii}	89.54 (14)
O2—C1—K1^{ii}	46.2 (3)	C1^{v}—K1—C3^{vii}	90.46 (14)
O1—C1—K1^{ii}	171.7 (4)	O4^{iii}—K1—C3^{vi}	80.95 (13)
O2—C1—H1	117.2	O4—K1—C3^{vi}	99.05 (13)
O1—C1—H1	117.2	O2^{iv}—K1—C3^{vi}	104.85 (13)

K1^{ii}—C1—H1	71.1	O2^{v}—K1—C3^{vi}	75.15 (13)
O4^{iii}—K1—O4	180.0	O6^{vi}—K1—C3^{vi}	19.40 (12)
O4^{iii}—K1—O2^{iv}	92.53 (13)	O6^{vii}—K1—C3^{vi}	160.60 (12)
O4—K1—O2^{iv}	87.47 (13)	C2—K1—C3^{vi}	83.45 (15)
O4^{iii}—K1—O2^{v}	87.47 (13)	C2^{iii}—K1—C3^{vi}	96.55 (15)
O4—K1—O2^{v}	92.53 (13)	C1^{iv}—K1—C3^{vi}	90.46 (14)
O2^{iv}—K1—O2^{v}	180.0	C1^{v}—K1—C3^{vi}	89.54 (14)
O4^{iii}—K1—O6^{vi}	89.95 (12)	C3^{vii}—K1—C3^{vi}	180.0 (2)
O4—K1—O6^{vi}	90.05 (12)	C4—N1—H1A	109.5
O2^{iv}—K1—O6^{vi}	87.39 (13)	C4—N1—H1B	109.5
O2^{v}—K1—O6^{vi}	92.61 (13)	H1A—N1—H1B	109.5
O4^{iii}—K1—O6^{vii}	90.05 (12)	C4—N1—H1C	109.5
O4—K1—O6^{vii}	89.95 (12)	H1A—N1—H1C	109.5
O2^{iv}—K1—O6^{vii}	92.61 (13)	H1B—N1—H1C	109.5
O2^{v}—K1—O6^{vii}	87.39 (13)	C2—O3—Cr1	127.1 (4)
O6^{vi}—K1—O6^{vii}	180.0	O6—C3—O5	126.4 (6)
O4^{iii}—K1—C2	160.71 (12)	O6—C3—K1^{viii}	48.0 (3)
O4—K1—C2	19.29 (12)	O5—C3—K1^{viii}	167.5 (4)
O2^{iv}—K1—C2	80.56 (14)	O6—C3—H3	116.8
O2^{v}—K1—C2	99.44 (14)	O5—C3—H3	116.8
O6^{vi}—K1—C2	71.87 (14)	K1^{viii}—C3—H3	70.1
O6^{vii}—K1—C2	108.13 (14)	O4—C2—O3	125.0 (6)
O4^{iii}—K1—C2^{iii}	19.29 (12)	O4—C2—K1	46.8 (3)
O4—K1—C2^{iii}	160.71 (12)	O3—C2—K1	171.7 (4)
O2^{iv}—K1—C2^{iii}	99.44 (14)	O4—C2—H2	117.5
O2^{v}—K1—C2^{iii}	80.56 (14)	O3—C2—H2	117.5
O6^{vi}—K1—C2^{iii}	108.13 (14)	K1—C2—H2	70.7
O6^{vii}—K1—C2^{iii}	71.87 (14)	C1—O2—K1^{ii}	114.8 (3)
C2—K1—C2^{iii}	180.0	N1—C4—H4A	109.5
O4^{iii}—K1—C1^{iv}	77.85 (13)	N1—C4—H4B	109.5
O4—K1—C1^{iv}	102.15 (13)	H4A—C4—H4B	109.5
O2^{iv}—K1—C1^{iv}	19.04 (11)	N1—C4—H4C	109.5
O2^{v}—K1—C1^{iv}	160.96 (11)	H4A—C4—H4C	109.5
O6^{vi}—K1—C1^{iv}	75.52 (13)	H4B—C4—H4C	109.5
O6^{vii}—K1—C1^{iv}	104.48 (13)	C2—O4—K1	113.9 (4)
C2—K1—C1^{iv}	91.05 (15)	C3—O6—K1^{viii}	112.6 (4)
C2^{iii}—K1—C1^{iv}	88.95 (15)	C3—O5—Cr1	126.5 (4)
O4^{iii}—K1—C1^{v}	102.15 (13)		
Cr1—O1—C1—O2	178.5 (4)	O5—C3—O6—K1^{viii}	−165.6 (5)
Cr1—O3—C2—O4	175.7 (5)	O6—C3—O5—Cr1	−176.7 (4)
O1—C1—O2—K1^{ii}	−179.5 (4)	K1^{viii}—C3—O5—Cr1	124.7 (18)
O3—C2—O4—K1	178.3 (5)		

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

100 K

Cr1—O3^{i}	1.965 (2)	K1—C1^{v}	3.399 (4)
Cr1—O3	1.965 (2)	K1—C3^{vii}	3.399 (4)
Cr1—O1^{i}	1.969 (2)	K1—C3^{vi}	3.399 (4)
Cr1—O1	1.969 (2)	N1—C4	1.476 (5)
Cr1—O5^{i}	1.973 (2)	N1—H1A	0.8900
Cr1—O5	1.973 (2)	N1—H1B	0.8900
O1—C1	1.267 (4)	N1—H1C	0.8900
C1—O2	1.232 (4)	O3—C2	1.269 (4)
C1—K1^{ii}	3.399 (4)	C3—O6	1.229 (4)
C1—H1	0.9300	C3—O5	1.261 (4)
K1—O4	2.677 (3)	C3—K1^{viii}	3.399 (4)
K1—O4^{iii}	2.677 (3)	C3—H3	0.9300
K1—O2^{iv}	2.705 (3)	C2—O4	1.232 (4)
K1—O2^{v}	2.705 (3)	C2—H2	0.9300
K1—O6^{vi}	2.742 (3)	O2—K1^{ii}	2.705 (3)
K1—O6^{vii}	2.742 (3)	C4—H4A	0.9600

K1—C2	3.346 (4)	C4—H4B	0.9600
K1—C2^{iii}	3.346 (4)	C4—H4C	0.9600
K1—C1^{iv}	3.399 (4)	O6—K1^{viii}	2.742 (3)
O3^{i}—Cr1—O3	180.0	O4^{iii}—K1—C1^{v}	102.26 (9)
O3^{i}—Cr1—O1^{i}	88.60 (9)	O2^{iv}—K1—C1^{v}	160.67 (7)
O3—Cr1—O1^{i}	91.40 (9)	O2^{v}—K1—C1^{v}	19.33 (7)
O3^{i}—Cr1—O1	91.40 (9)	O6^{vi}—K1—C1^{v}	104.70 (9)
O3—Cr1—O1	88.60 (9)	O6^{vii}—K1—C1^{v}	75.30 (9)
O1^{i}—Cr1—O1	180.0	C2—K1—C1^{v}	89.24 (10)
O3^{i}—Cr1—O5^{i}	88.65 (10)	C2^{iii}—K1—C1^{v}	90.76 (10)
O3—Cr1—O5^{i}	91.35 (10)	C1^{iv}—K1—C1^{v}	180.0
O1^{i}—Cr1—O5^{i}	91.12 (10)	O4—K1—C3^{vii}	80.19 (9)
O1—Cr1—O5^{i}	88.88 (10)	O4^{iii}—K1—C3^{vii}	99.81 (9)
O3^{i}—Cr1—O5	91.35 (10)	O2^{iv}—K1—C3^{vii}	75.37 (9)
O3—Cr1—O5	88.65 (10)	O2^{v}—K1—C3^{vii}	104.63 (9)
O1^{i}—Cr1—O5	88.88 (10)	O6^{vi}—K1—C3^{vii}	160.42 (8)
O1—Cr1—O5	91.12 (10)	O6^{vii}—K1—C3^{vii}	19.58 (8)
O5^{i}—Cr1—O5	180.0	C2—K1—C3^{vii}	96.37 (10)
C1—O1—Cr1	125.5 (2)	C2^{iii}—K1—C3^{vii}	83.63 (10)
O2—C1—O1	124.6 (3)	C1^{iv}—K1—C3^{vii}	90.01 (10)
O2—C1—K1^{ii}	46.61 (18)	C1^{v}—K1—C3^{vii}	89.99 (10)
O1—C1—K1^{ii}	171.0 (3)	O4—K1—C3^{vi}	99.81 (9)
O2—C1—H1	117.7	O4^{iii}—K1—C3^{vi}	80.19 (9)
O1—C1—H1	117.7	O2^{iv}—K1—C3^{vi}	104.63 (9)
K1^{ii}—C1—H1	71.1	O2^{v}—K1—C3^{vi}	75.37 (9)
O4—K1—O4^{iii}	180.0	O6^{vi}—K1—C3^{vi}	19.58 (8)
O4—K1—O2^{iv}	87.23 (8)	O6^{vii}—K1—C3^{vi}	160.42 (8)
O4^{iii}—K1—O2^{iv}	92.77 (8)	C2—K1—C3^{vi}	83.63 (10)
O4—K1—O2^{v}	92.77 (8)	C2^{iii}—K1—C3^{vi}	96.37 (10)
O4^{iii}—K1—O2^{v}	87.23 (8)	C1^{iv}—K1—C3^{vi}	89.99 (10)
O2^{iv}—K1—O2^{v}	180.0	C1^{v}—K1—C3^{vi}	90.01 (10)
O4—K1—O6^{vi}	90.20 (8)	C3^{vii}—K1—C3^{vi}	180.00 (13)
O4^{iii}—K1—O6^{vi}	89.80 (8)	C4—N1—H1A	109.5
O2^{iv}—K1—O6^{vi}	87.24 (8)	C4—N1—H1B	109.5
O2^{v}—K1—O6^{vi}	92.76 (8)	H1A—N1—H1B	109.5
O4—K1—O6^{vii}	89.80 (8)	C4—N1—H1C	109.5
O4^{iii}—K1—O6^{vii}	90.20 (8)	H1A—N1—H1C	109.5
O2^{iv}—K1—O6^{vii}	92.76 (8)	H1B—N1—H1C	109.5
O2^{v}—K1—O6^{vii}	87.24 (8)	C2—O3—Cr1	126.1 (2)
O6^{vi}—K1—O6^{vii}	180.0	O6—C3—O5	125.9 (4)
O4—K1—C2	19.92 (8)	O6—C3—K1^{viii}	48.4 (2)
O4^{iii}—K1—C2	160.08 (8)	O5—C3—K1^{viii}	166.8 (3)
O2^{iv}—K1—C2	80.11 (9)	O6—C3—H3	117.1
O2^{v}—K1—C2	99.89 (9)	O5—C3—H3	117.1
O6^{vi}—K1—C2	71.40 (9)	K1^{viii}—C3—H3	70.1
O6^{vii}—K1—C2	108.60 (9)	O4—C2—O3	123.6 (4)
O4—K1—C2^{iii}	160.07 (8)	O4—C2—K1	47.8 (2)
O4^{iii}—K1—C2^{iii}	19.93 (8)	O3—C2—K1	170.9 (3)
O2^{iv}—K1—C2^{iii}	99.89 (9)	O4—C2—H2	118.2
O2^{v}—K1—C2^{iii}	80.11 (9)	O3—C2—H2	118.2
O6^{vi}—K1—C2^{iii}	108.60 (9)	K1—C2—H2	70.5
O6^{vii}—K1—C2^{iii}	71.40 (9)	C1—O2—K1^{ii}	114.1 (2)
C2—K1—C2^{iii}	180.0	N1—C4—H4A	109.5
O4—K1—C1^{iv}	102.26 (9)	N1—C4—H4B	109.5
O4^{iii}—K1—C1^{iv}	77.74 (9)	H4A—C4—H4B	109.5
O2^{iv}—K1—C1^{iv}	19.33 (7)	N1—C4—H4C	109.5
O2^{v}—K1—C1^{iv}	160.67 (7)	H4A—C4—H4C	109.5
O6^{vi}—K1—C1^{iv}	75.30 (9)	H4B—C4—H4C	109.5
O6^{vii}—K1—C1^{iv}	104.70 (9)	C2—O4—K1	112.3 (2)
C2—K1—C1^{iv}	90.76 (10)	C3—O6—K1^{viii}	112.0 (3)
C2^{iii}—K1—C1^{iv}	89.24 (10)	C3—O5—Cr1	125.2 (2)
O4—K1—C1^{v}	77.74 (9)		
Cr1—O1—C1—O2	177.6 (3)	O5—C3—O6—K1^{viii}	−164.7 (3)

Cr1—O3—C2—O4	175.4 (3)	O6—C3—O5—Cr1	−173.8 (3)
O1—C1—O2—K1^{ii}	−177.4 (3)	K1^{viii}—C3—O5—Cr1	126.4 (11)
O3—C2—O4—K1	176.1 (3)		

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

The Cr–O distances are slightly shorter in comparison to MeANaCr and range from 1.965(2) to 1.973(2) Å, while the K–O distances are as expected much longer and range from 2.677(3) to 2.742(3) Å (1.961(3)–1.971(3) Å and 2.691(4)–2.747(4) Å for room temperature structure, respectively). Taking into account the valence angles, the O–Cr–O angles involving oxygen atoms *cis* to each other range from 88.65(10)° to 91.40(9)°, while those located *trans* are equal to 180° (88.41(14)° to 91.59(14) and 180° for room temperature structure). The octahedral geometry of the KO_6 moiety is more distorted as the O–K–O angles involving oxygen atoms mutually *cis* range from 87.23(8)° to 92.77(8)°, while those located *trans* amount to 180° (87.39(13)° to 92.61(13) and 180° for room temperature structure).

Tab. S5. Selected geometric parameters (Å, °) for MeAKAl at 293 and 100 K.

293K

K1—O2	2.691 (4)	O1—Al1	1.885 (4)
K1—O2^{i}	2.691 (4)	Al1—O1^{vi}	1.885 (4)
K1—O4^{ii}	2.717 (4)	Al1—O3^{vi}	1.890 (3)
K1—O4^{iii}	2.717 (4)	Al1—O3	1.890 (3)
K1—O6^{iv}	2.748 (4)	Al1—O5^{vi}	1.898 (3)
K1—O6^{v}	2.748 (4)	Al1—O5	1.898 (3)
K1—C1^{i}	3.382 (7)	O3—C2	1.256 (6)
K1—C1	3.382 (7)	C3—O6	1.235 (6)
K1—C2^{ii}	3.405 (6)	C3—O5	1.250 (7)
K1—C2^{iii}	3.405 (6)	C3—K1^{vii}	3.416 (7)
K1—C3^{iv}	3.416 (7)	C3—H3	0.9300
K1—C3^{v}	3.416 (7)	C2—O4	1.221 (6)
N1—C4	1.468 (7)	C2—K1^{viii}	3.405 (6)
N1—H1A	0.8900	C2—H2	0.9300
N1—H1B	0.8900	O4—K1^{viii}	2.717 (4)
N1—H1C	0.8900	C4—H4A	0.9600
C1—O2	1.229 (6)	C4—H4B	0.9600
C1—O1	1.247 (7)	C4—H4C	0.9600
C1—H1	0.9300	O6—K1^{vii}	2.748 (4)
O2—K1—O2^{i}	180.00 (9)	O6^{iv}—K1—C3^{v}	160.48 (12)
O2—K1—O4^{ii}	92.45 (14)	O6^{v}—K1—C3^{v}	19.52 (12)
O2^{i}—K1—O4^{ii}	87.55 (14)	C1^{i}—K1—C3^{v}	96.94 (16)
O2—K1—O4^{iii}	87.55 (14)	C1—K1—C3^{v}	83.06 (16)
O2^{i}—K1—O4^{iii}	92.45 (14)	C2^{ii}—K1—C3^{v}	89.48 (15)
O4^{ii}—K1—O4^{iii}	180.0	C2^{iii}—K1—C3^{v}	90.52 (15)
O2—K1—O6^{iv}	90.31 (13)	C3^{iv}—K1—C3^{v}	180.0
O2^{i}—K1—O6^{iv}	89.69 (13)	C4—N1—H1A	109.5
O4^{ii}—K1—O6^{iv}	87.61 (13)	C4—N1—H1B	109.5
O4^{iii}—K1—O6^{iv}	92.39 (13)	H1A—N1—H1B	109.5
O2—K1—O6^{v}	89.69 (13)	C4—N1—H1C	109.5
O2^{i}—K1—O6^{v}	90.31 (13)	H1A—N1—H1C	109.5
O4^{ii}—K1—O6^{v}	92.39 (13)	H1B—N1—H1C	109.5
O4^{iii}—K1—O6^{v}	87.61 (13)	O2—C1—O1	125.9 (6)
O6^{iv}—K1—O6^{v}	180.0	O2—C1—K1	46.6 (3)
O2—K1—C1^{i}	160.61 (13)	O1—C1—K1	172.5 (5)
O2^{i}—K1—C1^{i}	19.39 (13)	O2—C1—H1	117.1
O4^{ii}—K1—C1^{i}	80.70 (14)	O1—C1—H1	117.1
O4^{iii}—K1—C1^{i}	99.30 (14)	K1—C1—H1	70.4

O6^{iv}—K1—C1^{i}	71.40 (15)	C1—O1—Al1	130.1 (4)
O6^{v}—K1—C1^{i}	108.60 (15)	O1—Al1—O1^{vi}	180.0
O2—K1—C1	19.39 (13)	O1—Al1—O3^{vi}	88.85 (15)
O2^{i}—K1—C1	160.61 (13)	O1^{vi}—Al1—O3^{vi}	91.15 (15)
O4^{ii}—K1—C1	99.30 (14)	O1—Al1—O3	91.15 (15)
O4^{iii}—K1—C1	80.70 (14)	O1^{vi}—Al1—O3	88.85 (15)
O6^{iv}—K1—C1	108.60 (15)	O3^{vi}—Al1—O3	180.0
O6^{v}—K1—C1	71.40 (15)	O1—Al1—O5^{vi}	88.72 (15)
C1^{i}—K1—C1	180.0	O1^{vi}—Al1—O5^{vi}	91.28 (15)
O2—K1—C2^{ii}	78.01 (14)	O3^{vi}—Al1—O5^{vi}	90.94 (16)
O2^{i}—K1—C2^{ii}	101.99 (14)	O3—Al1—O5^{vi}	89.06 (16)
O4^{ii}—K1—C2^{ii}	19.10 (11)	O1—Al1—O5	91.28 (15)
O4^{iii}—K1—C2^{ii}	160.90 (12)	O1^{vi}—Al1—O5	88.72 (15)
O6^{iv}—K1—C2^{ii}	75.45 (14)	O3^{vi}—Al1—O5	89.06 (16)
O6^{v}—K1—C2^{ii}	104.55 (14)	O3—Al1—O5	90.94 (16)
C1^{i}—K1—C2^{ii}	90.81 (15)	O5^{vi}—Al1—O5	180.00 (19)
C1—K1—C2^{ii}	89.19 (15)	C2—O3—Al1	129.6 (4)
O2—K1—C2^{iii}	101.99 (14)	O6—C3—O5	126.9 (6)
O2^{i}—K1—C2^{iii}	78.01 (14)	O6—C3—K1^{vii}	48.0 (3)
O4^{ii}—K1—C2^{iii}	160.90 (12)	O5—C3—K1^{vii}	168.5 (4)
O4^{iii}—K1—C2^{iii}	19.10 (11)	O6—C3—H3	116.6
O6^{iv}—K1—C2^{iii}	104.55 (14)	O5—C3—H3	116.6
O6^{v}—K1—C2^{iii}	75.45 (14)	K1^{vii}—C3—H3	69.6
C1^{i}—K1—C2^{iii}	89.19 (15)	C1—O2—K1	114.0 (4)
C1—K1—C2^{iii}	90.81 (15)	O4—C2—O3	126.0 (6)
C2^{ii}—K1—C2^{iii}	180.0	O4—C2—K1^{viii}	46.7 (3)
O2—K1—C3^{iv}	81.27 (14)	O3—C2—K1^{viii}	172.7 (4)
O2^{i}—K1—C3^{iv}	98.73 (14)	O4—C2—H2	117.0
O4^{ii}—K1—C3^{iv}	105.18 (14)	O3—C2—H2	117.0
O4^{iii}—K1—C3^{iv}	74.82 (14)	K1^{viii}—C2—H2	70.3
O6^{iv}—K1—C3^{iv}	19.52 (12)	C3—O5—Al1	129.3 (4)
O6^{v}—K1—C3^{iv}	160.48 (12)	C2—O4—K1^{viii}	114.2 (4)
C1^{i}—K1—C3^{iv}	83.06 (16)	N1—C4—H4A	109.5
C1—K1—C3^{iv}	96.94 (16)	N1—C4—H4B	109.5
C2^{ii}—K1—C3^{iv}	90.52 (15)	H4A—C4—H4B	109.5
C2^{iii}—K1—C3^{iv}	89.48 (15)	N1—C4—H4C	109.5
O2—K1—C3^{v}	98.73 (14)	H4A—C4—H4C	109.5
O2^{i}—K1—C3^{v}	81.27 (14)	H4B—C4—H4C	109.5
O4^{ii}—K1—C3^{v}	74.82 (14)	C3—O6—K1^{vii}	112.4 (4)
O4^{iii}—K1—C3^{v}	105.18 (14)		
O2—C1—O1—Al1	−176.6 (5)	Al1—O3—C2—O4	177.8 (4)
C1—O1—Al1—O3^{vi}	153.4 (5)	O6—C3—O5—Al1	−176.9 (5)
C1—O1—Al1—O3	−26.6 (5)	K1^{vii}—C3—O5—Al1	124 (2)
C1—O1—Al1—O5^{vi}	62.5 (5)	O1—Al1—O5—C3	−32.7 (5)
C1—O1—Al1—O5	−117.5 (5)	O1^{vi}—Al1—O5—C3	147.3 (5)
O1—Al1—O3—C2	−128.7 (5)	O3^{vi}—Al1—O5—C3	56.1 (5)
O1^{vi}—Al1—O3—C2	51.3 (5)	O3—Al1—O5—C3	−123.9 (5)
O5^{vi}—Al1—O3—C2	142.6 (5)	O3—C2—O4—K1^{viii}	−179.0 (5)
O5—Al1—O3—C2	−37.4 (5)	O5—C3—O6—K1^{vii}	−166.6 (5)
O1—C1—O2—K1	−179.2 (5)		

100K

K1—O2^{ix}	2.6812 (18)	O2—C1	1.235 (3)
K1—O2	2.6813 (18)	O3—C2	1.264 (3)
K1—O6^{x}	2.7045 (17)	O4—C2	1.236 (3)
K1—O6^{xi}	2.7045 (17)	O4—K1^{xiv}	2.7414 (18)
K1—O4^{xii}	2.7414 (18)	O5—C3	1.266 (3)
K1—O4^{xiii}	2.7414 (18)	O6—C3	1.236 (3)
K1—C1^{ix}	3.353 (3)	O6—K1^{xv}	2.7044 (17)
K1—C1	3.353 (3)	N1—C4	1.477 (4)
K1—C3^{x}	3.392 (3)	N1—H1A	0.8900
K1—C3^{xi}	3.392 (3)	N1—H1B	0.8900
K1—C2^{xii}	3.395 (3)	N1—H1C	0.8900
K1—C2^{xiii}	3.395 (3)	C1—H1	0.9300

Al1—O1	1.8888 (16)	C2—K1^{xiv}	3.395 (3)
Al1—O1^{vi}	1.8888 (16)	C2—H2	0.9300
Al1—O5^{vi}	1.8973 (16)	C3—K1^{xv}	3.392 (3)
Al1—O5	1.8973 (16)	C3—H3	0.9300
Al1—O3^{vi}	1.9011 (16)	C4—H4A	0.9600
Al1—O3	1.9011 (16)	C4—H4B	0.9600
O1—C1	1.261 (3)	C4—H4C	0.9600
O2^{ix}—K1—O2	180.0	O4^{xii}—K1—C2^{xiii}	160.21 (6)
O2^{ix}—K1—O6^{x}	92.76 (6)	O4^{xiii}—K1—C2^{xiii}	19.79 (6)
O2—K1—O6^{x}	87.24 (6)	C1^{ix}—K1—C2^{xiii}	96.61 (6)
O2^{ix}—K1—O6^{xi}	87.24 (6)	C1—K1—C2^{xiii}	83.39 (6)
O2—K1—O6^{xi}	92.76 (6)	C3^{x}—K1—C2^{xiii}	90.23 (6)
O6^{x}—K1—O6^{xi}	180.0	C3^{xi}—K1—C2^{xiii}	89.77 (6)
O2^{ix}—K1—O4^{xii}	89.89 (6)	C2^{xii}—K1—C2^{xiii}	180.00 (9)
O2—K1—O4^{xii}	90.11 (6)	O1—Al1—O1^{vi}	180.0
O6^{x}—K1—O4^{xii}	92.50 (6)	O1—Al1—O5^{vi}	91.11 (7)
O6^{xi}—K1—O4^{xii}	87.50 (6)	O1^{vi}—Al1—O5^{vi}	88.89 (7)
O2^{ix}—K1—O4^{xiii}	90.11 (6)	O1—Al1—O5	88.89 (7)
O2—K1—O4^{xiii}	89.89 (6)	O1^{vi}—Al1—O5	91.11 (7)
O6^{x}—K1—O4^{xiii}	87.50 (6)	O5^{vi}—Al1—O5	180.0
O6^{xi}—K1—O4^{xiii}	92.50 (6)	O1—Al1—O3^{vi}	91.20 (7)
O4^{xii}—K1—O4^{xiii}	180.0	O1^{vi}—Al1—O3^{vi}	88.80 (7)
O2^{ix}—K1—C1^{ix}	19.91 (6)	O5^{vi}—Al1—O3^{vi}	91.01 (7)
O2—K1—C1^{ix}	160.09 (6)	O5—Al1—O3^{vi}	88.99 (7)
O6^{x}—K1—C1^{ix}	99.90 (6)	O1—Al1—O3	88.80 (7)
O6^{xi}—K1—C1^{ix}	80.10 (6)	O1^{vi}—Al1—O3	91.20 (7)
O4^{xii}—K1—C1^{ix}	71.15 (6)	O5^{vi}—Al1—O3	88.99 (7)
O4^{xiii}—K1—C1^{ix}	108.85 (6)	O5—Al1—O3	91.01 (7)
O2^{ix}—K1—C1	160.09 (6)	O3^{vi}—Al1—O3	180.00 (6)
O2—K1—C1	19.91 (6)	C1—O1—Al1	128.80 (17)
O6^{x}—K1—C1	80.10 (6)	C1—O2—K1	112.42 (17)
O6^{xi}—K1—C1	99.90 (6)	C2—O3—Al1	127.26 (17)
O4^{xii}—K1—C1	108.85 (6)	C2—O4—K1^{xiv}	111.50 (17)
O4^{xiii}—K1—C1	71.15 (6)	C3—O5—Al1	128.20 (16)
C1^{ix}—K1—C1	180.0	C3—O6—K1^{xv}	113.46 (15)
O2^{ix}—K1—C3^{x}	77.80 (6)	C4—N1—H1A	109.5
O2—K1—C3^{x}	102.20 (6)	C4—N1—H1B	109.5
O6^{x}—K1—C3^{x}	19.53 (5)	H1A—N1—H1B	109.5
O6^{xi}—K1—C3^{x}	160.47 (5)	C4—N1—H1C	109.5
O4^{xii}—K1—C3^{x}	104.76 (6)	H1A—N1—H1C	109.5
O4^{xiii}—K1—C3^{x}	75.24 (6)	H1B—N1—H1C	109.5
C1^{ix}—K1—C3^{x}	89.41 (6)	O2—C1—O1	124.3 (2)
C1—K1—C3^{x}	90.59 (6)	O2—C1—K1	47.66 (13)
O2^{ix}—K1—C3^{xi}	102.20 (6)	O1—C1—K1	171.78 (19)
O2—K1—C3^{xi}	77.80 (6)	O2—C1—H1	117.8
O6^{x}—K1—C3^{xi}	160.47 (5)	O1—C1—H1	117.8
O6^{xi}—K1—C3^{xi}	19.53 (5)	K1—C1—H1	70.2
O4^{xii}—K1—C3^{xi}	75.24 (6)	O4—C2—O3	125.4 (3)
O4^{xiii}—K1—C3^{xi}	104.76 (6)	O4—C2—K1^{xiv}	48.71 (13)
C1^{ix}—K1—C3^{xi}	90.59 (6)	O3—C2—K1^{xiv}	166.89 (18)
C1—K1—C3^{xi}	89.41 (6)	O4—C2—H2	117.3
C3^{x}—K1—C3^{xi}	180.0	O3—C2—H2	117.3
O2^{ix}—K1—C2^{xii}	99.43 (6)	K1^{xiv}—C2—H2	70.0
O2—K1—C2^{xii}	80.57 (6)	O6—C3—O5	125.1 (2)
O6^{x}—K1—C2^{xii}	74.83 (6)	O6—C3—K1^{xv}	47.01 (12)
O6^{xi}—K1—C2^{xii}	105.17 (6)	O5—C3—K1^{xv}	171.78 (18)
O4^{xii}—K1—C2^{xii}	19.79 (6)	O6—C3—H3	117.5
O4^{xiii}—K1—C2^{xii}	160.21 (6)	O5—C3—H3	117.5
C1^{ix}—K1—C2^{xii}	83.39 (6)	K1^{xv}—C3—H3	70.5
C1—K1—C2^{xii}	96.61 (6)	N1—C4—H4A	109.5
C3^{x}—K1—C2^{xii}	89.77 (6)	N1—C4—H4B	109.5
C3^{xi}—K1—C2^{xii}	90.23 (6)	H4A—C4—H4B	109.5
O2^{ix}—K1—C2^{xiii}	80.57 (6)	N1—C4—H4C	109.5

O2—K1—C2^{xiii}	99.43 (6)	H4A—C4—H4C	109.5
O6^{x}—K1—C2^{xiii}	105.17 (6)	H4B—C4—H4C	109.5
O6^{xi}—K1—C2^{xiii}	74.83 (6)		
O5^{vi}—Al1—O1—C1	27.5 (2)	K1—O2—C1—O1	177.7 (2)
O5—Al1—O1—C1	−152.5 (2)	Al1—O1—C1—O2	175.8 (2)
O3^{vi}—Al1—O1—C1	118.6 (2)	K1^{xiv}—O4—C2—O3	−165.1 (2)
O3—Al1—O1—C1	−61.4 (2)	Al1—O3—C2—O4	−174.6 (2)
O1—Al1—O5—C3	50.9 (2)	Al1—O3—C2—K1^{xiv}	126.7 (7)
O1^{vi}—Al1—O5—C3	−129.1 (2)	K1^{xv}—O6—C3—O5	−177.3 (2)
O3^{vi}—Al1—O5—C3	142.1 (2)	Al1—O5—C3—O6	177.31 (19)
O3—Al1—O5—C3	−37.9 (2)		

Symmetry code(s): (i) −*x*, −*y*+2, −*z*+1; (ii) *x*−1/2, −*y*+3/2, *z*−1/2; (iii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iv) −*x*+1, −*y*+2, −*z*+1; (v) *x*−1, *y*, *z*; (vi) −*x*+1, −*y*+1, −*z*+1; (vii) *x*+1, *y*, *z*; (viii) −*x*+1/2, *y*−1/2, −*z*+3/2; (ix) −*x*, −*y*, −*z*+1; (x) *x*−1/2, −*y*+1/2, *z*+1/2; (xi) −*x*+1/2, *y*−1/2, −*z*+1/2; (xii) *x*, *y*−1, *z*; (xiii) −*x*, −*y*+1, −*z*+1; (xiv) *x*, *y*+1, *z*; (xv) −*x*+1/2, *y*+1/2, −*z*+1/2.

The Al–O distances are in the range of 1.8888(16)–1.9011(16) Å, while the K–O change from 2.6812(18) to 2.7414(18) Å (1.885(4)–1.898(3) Å and 2.691(4)–2.748(4) Å for room-temperature structure, respectively). Taking into account the valence angles, the O–Al–O angles involving oxygen atoms *cis* to each other range from 88.80(7)° to 91.20(7), while those located *trans* amount to 180° (88.85(15)° to 91.28(15) and 180° for room temperature structure, respectively). The octahedral geometry in the KO_6 moiety is more distorted as the O–K–O angles involving oxygen atoms mutually *cis* range from 87.24(6)° to 92.76(6)°, while those located *trans* amount to 180° (87.55(14)° to 92.45(14) and 180° for room-temperature structure, respectively).

Tab. S6. Factor group analysis for MeANaCr. The number of equivalent formate ions should be tripled.[a]

Ion	Vibration	Free ion symmetry	Site symmetry	Factor group symmetry
		$\boldsymbol{C_{2v}}$ (*mm*2)	$\boldsymbol{C_1}$ (1)	$\boldsymbol{C_{2h}}$ (2/*m*)
$HCOO^-$	ν_1–ν_3	$3A_1$	3A	$3A_g+3A_u+3B_g+3B_u$
	ν_4–ν_6	$3B_1$	3A	$3A_g+3A_u+3B_g+3B_u$
	T'	$A_1+B_1+B_2$	3A	$3A_g+3A_u+3B_g+3B_u$
	L	$A_2+B_1+B_2$	3A	$3A_g+3A_u+3B_g+3B_u$
		$\boldsymbol{C_{3v}}$ (3*m*)	$\boldsymbol{C_1}$ (1)	$\boldsymbol{C_{2h}}$ (2/*m*)
MeA^+	ν_1–ν_5	$5A_1$	5A	$5A_g+5A_u+5B_g+5B_u$
	ν_6	A_2	A	$A_g+A_u+B_g+B_u$
	ν_7–ν_{12}	6E	12A	$12A_g+12A_u+12B_g+12B_u$
	T'	A_1+E	3A	$3A_g+3A_u+3B_g+3B_u$
	L	A_2+E	3A	$3A_g+3A_u+3B_g+3B_u$
Na^+			$\boldsymbol{C_i}(1)$	$\boldsymbol{C_{2h}}$ (2/*m*)
			$3A_u$	$3A_u+3B_u$
Cr^{3+}			$\boldsymbol{C_i}(1)$	$\boldsymbol{C_{2h}}$ (2/*m*)
			$3A_u$	$3A_u+3B_u$

Tab. S7. IR and Raman wavenumbers for studied MOF perovskites.[a]

MeANaCr		MeANaAlCr		MeNaAl		MeAKCr		MeAKAlCr		MeKAl		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3157 w		3167 w		3167 w		3174 w		3182 w		3182 w		$\nu(NH_3^+)$
	3039 w		3041 m		3040 m		3031 w		3032 w		3032 w	$\nu(NH_3^+)+\nu(CH_3)$
2995 m		3002 m		3004 m		2996 m		3002 m		3003 m		$\nu(CH_3)$
	2976 m		2978 s		2978 s		2973 m		2974 m		2974 m	$\nu(CH_3)$
						2920 sh		2916 sh		2916 sh		$\nu(CH_3)$
2901 sh		2902 sh		2902 sh		2900 m	2902 w	2901 m	2903 m	2902 m	2903 m	$\nu_1(HCOO^-)$
	2897 sh		2897 sh		2896 sh	2874 m	2873 sh	2878 m	2878 sh	2878 m	2878 sh	$\nu_1(HCOO^-)$
2882 m	2883 s	2888 m	2888 vs	2888 m	2888 vs	2861 m	2863 s	2865 m	2865 vs	2865 m	2865 vs	$\nu_1(HCOO^-)$
	2830 w		2825 w		2825 w		2824 w		2825 w		2825 w	$\nu(NH_3^+)$
2781 w		2785 w		2785 w		2786 w		2791 w		2791 w		o/cb
2758 sh	2757 w	2768 sh	2768 w	2769 sh	2767 w	2758 w	2758 w	2767 w	2767 w	2767 w	2768 w	o/cb
2614 w		2618 w		2619 w		2629 w		2631 w		2631 w		o/cb
2492 w		2498 w		2498 w		2507 w		2512 w		2512 w		o/cb

	1659 m		1671 m		1671 m		1659 m		1672 w		1673 w	$\nu_4(HCOO^-)+\delta_{as}(NH_3^+)$
1647 s	1654 sh	1655 s	1654 vw	1659 s	1654 vw	1650 s		1655 s		1655		$\nu_4(HCOO^-)+\delta_{as}(NH_3^+)$
1616 s		1629 s		1631 s		1630 s		1628 s		1628 s		$\nu_4(HCOO^-)+\delta_{as}(NH_3^+)$
1597 vs		1611 vs		1610 vs		1609 vs		1612 vs		1612 vs		$\nu_4(HCOO^-)+\delta_{as}(NH_3^+)$
1592 sh		1596 sh		1597 sh		1599 sh		1599 sh		1599 sh		$\nu_4(HCOO^-)+\delta_{as}(NH_3^+)$
	1585 vw		1591 w		1590 w		1587 vw		1594 vw		1594 vw	$\nu_4(HCOO^-)$
1515 w		1515 w		1515 w		1521 w		1526 w		1526 w		$\delta_s(NH_3^+)$
1466 w	1467 w	1467 w	1468 w	1467 w	1467 w	1467 w	1467 w	1467 w	1467 w	1467 w	1468 w	$\delta_s(NH_3^+)+\delta_{as}(CH_3)$
1460 w	1459 w	1460 w	1460 w	1460 w	1460 w	1461 w	1461 w	1462 w	1461 w	1462 w	1461 w	$\delta_{as}(CH_3)$
1422 vw	1421 vw	1423 w	1422 vw	1423 vw	1422 vw	1423 vw	1422 vw	1424 vw	1422 vw	1424 vw	1423 vw	$\delta_s(CH_3)$
1389 w	1388 vs	1394 m	1392 vs	1394 m	1392 vs	1391 m	1390 vs	1395 m	1394 s	1395 m	1394 s	$\nu_5(HCOO^-)$
1385 sh	1384 sh	1387 sh	1388 sh	1388 sh	1388 sh	1385 sh	1386 sh	1389 sh	1390 sh	1390 sh	1390 sh	$\nu_5(HCOO^-)$
	1342 s		1356 vs		1356 vs		1345 s		1360 vs		1360 vs	$\nu_5(HCOO^-)$
1321 vs		1344 vs		1345 vs		1326 vs		1346 vs		1346 vs		$\nu_2(HCOO^-)$
	1316 m		1328 m		1328 m							$\nu_2(HCOO^-)$
1305 s	1309 m	1329 s	1323 m	1330 s	1322 m	1315 s	1322 s	1336 s	1334 m	1336 s	1334 m	$\nu_2(HCOO^-)$
1296 sh		1323 sh		1325 sh		1307 sh		1323 sh		1323 sh		$\nu_2(HCOO^-)$
1225 sh		1225 sh		1226 sh		1224 sh		1225 sh		1225 sh		$\rho(CH_3)$
	1066 w		1070 w		1071 w		1065 w		1068 w		1070 w	$\nu_6(HCOO^-)$
	1061 w		1065 w		1066 w		1068 w		1062 w		1063 w	$\nu_6(HCOO^-)$
1004 w	1004 w	1005 w	1004 m	1005 w	1004 m	1004 w	1004 m	1005 w	1004 m	1004 w	1004 m	$\nu(CN)$
987 w		990 w		990 w		990 w		992 w		992 w		$\nu(CN)$
969 w		973 w		973 w		981 sh		985 sh		985 w		$\nu(CN)$
927 w		928 w		928 w		928 w		929 w		928 w		$\rho(NH_3^+)$
827 sh		834 sh		834 sh		824 sh		832 sh		832 sh		$\nu_3(HCOO^-)$
821 sh		825 m		825 m		819 sh		822 m		822 m		$\nu_3(HCOO^-)$
817 m						815 m						$\nu_3(HCOO^-)$
	808 vw		810 w		811 w		806 vw		808 w		808 w	$\nu_3(HCOO^-)$
	802 vw		805 w		805 w		799 vw		803 w		803 w	$\nu_3(HCOO^-)$
						430 sh		461 sh		461 sh		$T'(M^{3+})+T(HCOO^-)$
426 m		478 sh		481 sh		407 m		450 m		452 m		$T'(M^{3+})+\nu_t+T(HCOO^-)$
411 sh	348 w	457 m	343 w	449 m	342 w		346 w	413 w	341 w		340 w	$T(HCOO^-)$
			310 w		310 w			316 w	307 w	316 w	308 w	$T(HCOO^-)$
282 m		321 w	289 w	320 w	289 w	276 m			289 w		289 w	$T'(M^{3+})+T(HCOO^-)$
245 m	239 w	251 m	238 w		235 w	238 m	241 w	246 m	248 w	247 m	250 w	$T(HCOO^-)$
				250 m			230 w		229 w		228 w	$T(HCOO^-)+T'(M^+)$
224 m	206 sh	228 m		224 m				201 m		202 m		$T(HCOO^-)+T'(M^+)$
						197 m	211 w					$L(HCOO^-)+T'(M^+)$
184 m		196 m		196 m		173 m		176 m		176 m		$L(HCOO^-)+T'(MeA^+)+L(MeA^+)+T'(M^+)$
	168 s	182 m	166 vs	182 m	166 vs	153 sh	165 s	154 sh	162 vs	155 sh	162 vs	$L(HCOO^-)+T'(MeA^+)+L(MeA^+)+T'(M^+)$
167 m	122 s	164 m	124 m	165 m	124 m		132 m		139 m		139 m	$L(HCOO^-)+T'(MeA^+)+L(MeA^+)$
	103 m		106 w		106 w		116 m		116 m		117 m	$L(HCOO^-)+T'(MeA^+)+L(MeA^+)$
102 w		108 w		105 w								$L(HCOO^-)+T'(MeA^+)+L(MeA^+)$
						86 w		90 w		88 w		$L(HCOO^-)+T'(MeA^+)+L(MeA^+)$

[a]Key: vs, very strong s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

Based on the DFT results, the stretching vibrations of the NH_3^+ and CH_3 groups, depending on the halogen ion, are expected in the 3035–3224 cm^{-1} and 2853–3094 cm^{-1} ranges,[2] respectively. Thus, we assigned the broader bands with the highest wavenumbers to the $\nu(NH_3^+)$ modes and narrower bands to the $\nu(CH_3)$ modes. In real systems these bands are overlapped due to the H-bonding causing downshifts of the $\nu(NH_3^+)$ modes, therefore, we do not divide them into symmetric and antisymmetric ones. The assignment is more precise in the case of bending modes. The $\delta_{as}(NH_3^+)$ and $\delta_s(NH_3^+)$ modes are observed in the 1597–1672 cm^{-1} and 1466–1526 cm^{-1} ranges, respectively, depending on the metal ions. The former ones are coupled to the ν_4 modes of formate ions. The $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ modes do not overlap each other and are observed at about 1459–1468 cm^{-1} and 1421–1424 cm^{-1}, respectively. As expected, they are less sensitive to the substitution of metal ions since they are not involved in creation of HBs. The values are in very good agreement with DFT data predicting the $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ modes in the 1451–1462 cm^{-1} and 1419–1421 cm^{-1} ranges, respectively.[2] The rocking $\rho(NH_3^+)$ and $\rho(CH_3)$ modes were found as weak bands at about 928 cm^{-1} and 1225 cm^{-1}, respectively. A few bands in the 969–1004 cm^{-1} range were assigned to the stretching vibrations of the CN bond, $\nu(CN)$. The torsional mode ν_t that have A_2 symmetry and is silent for the free $CH_3NH_3^+$ molecule becomes active in the C_{2h} symmetry (Tab. S6). Previous DFT calculations estimated its energy to about 402 cm^{-1}.[3] Our studies show that it can be found at about 407 cm^{-1} and 450 cm^{-1} for analogues with Cr^{3+} and Al^{3+} ions, respectively, and is coupled to lattice modes.

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