Electronic Supplementary Material (ESI) for Dalton Transactions.

Novel bimetallic MOF phosphors with imidazolium cation: structure, phonons, high-pressure phase transitions and optical response

by M. Ptak *et al.*

Fig. S1. The DSC traces measured for ImNaCr (blue line) and ImNaAlCr (red line).

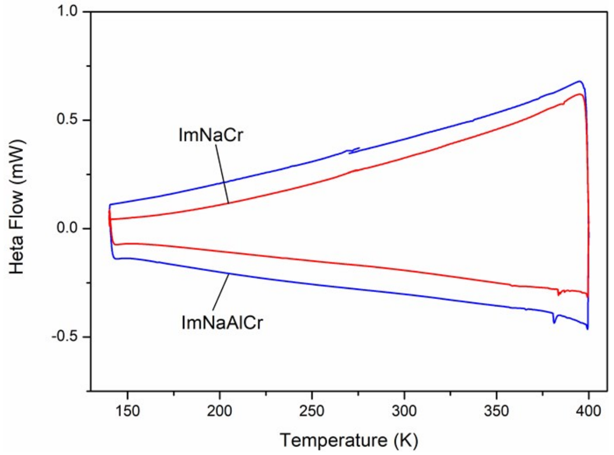


Fig. S2. The experimental XRD patterns of ImNaCr (blue line) and ImNaAlCr (red line) together with simulated ones (black lines) for ImNaCr and ImNaAl basing on the crystal structure refinement.

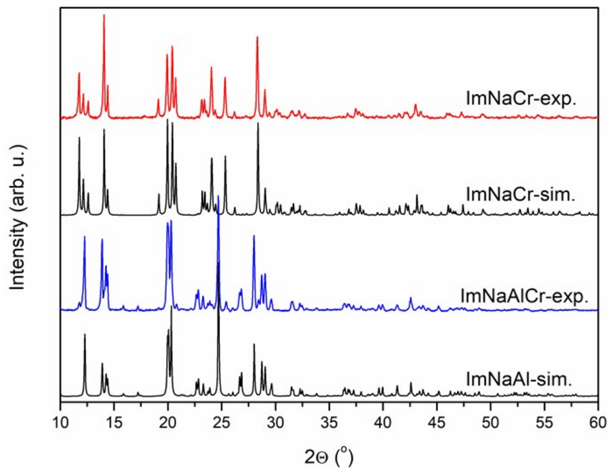
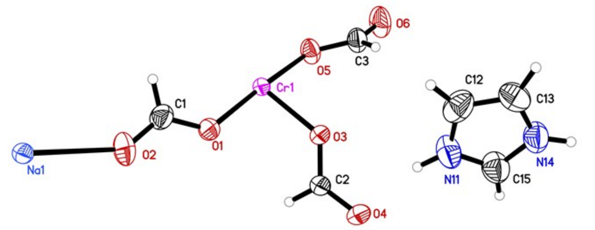


Fig. S3. The asymmetric part of unit cell for ImNaCr at (a) 293 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.

(a)



(b)

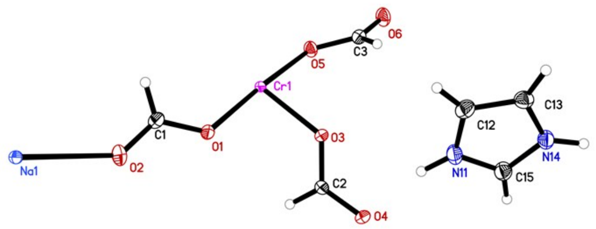
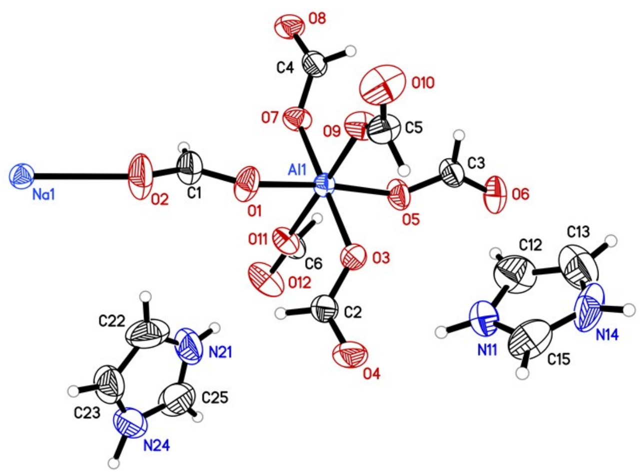
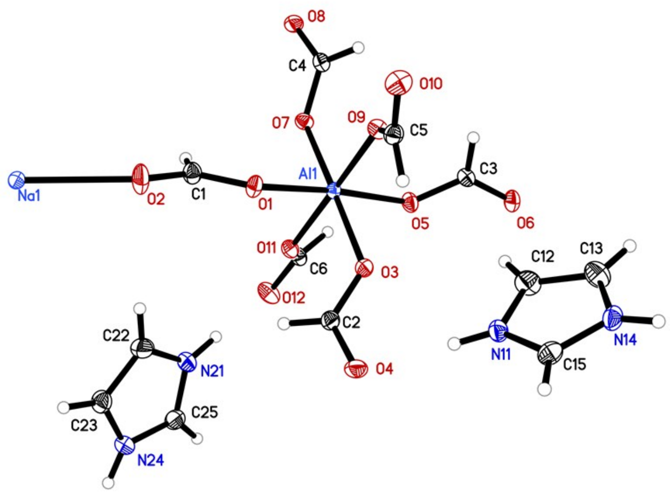


Fig. S4. The asymmetric part of unit cell for ImNaAl at (a) 293 K and (b) 100 K. Displacement ellipsoids are drawn at the 50% probability level.



(a)

(b)



Tab. S1. Experimental data for ImNaCr and ImNaAl at 293 and 100 K.

	ImNaCr		ImNaAl	
Crystal data				
Chemical formula	$[(C_3H_5N_2)_2]NaCr(HCOO)_6$		$[(C_3H_5N_2)_2]NaAl(HCOO)_6$	
M_r	483.28		458.26	
Crystal system, space group	Monoclinic, $P2/n$		Monoclinic, $P2_1/n$	
Temperature (K)	293(1)	100.0(1)	293(1)	100.0(1)
a (Å) b (Å) c (Å)	9.2610(4) 8.5585(3) 12.2971(5)	9.3105(2) 8.4501(2) 12.2281(2)	12.2888(3) 12.4160(3) 12.7236(3)	12.1711(2) 12.3854(2) 12.6588(2)
β (°)	91.923(4)	92.147(2)	90.020(2)	90.455(2)
V (Å^3)	974.12(7)	961.37(3)	1941.34(8)	1908.18(5)
Z	2		4	
Radiation type	Mo $K\alpha$			
μ (mm^{-1})	0.68		0.20	
Crystal size (mm)	0.50 × 0.45 × 0.40		0.27 × 0.25 × 0.20	
Data collection				
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6337 1894 1643	6266 1885 1767	12994 3789 2616	12728 3724 3029
R_{int}	0.012	0.011	0.022	0.019
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617		0.617	
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.078, 1.06	0.020, 0.052, 1.07	0.038, 0.103, 1.01	0.025, 0.063, 0.95
No. of reflections	1894	1885	3789	3724
No. of parameters	143	143	283	283
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement			
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, -0.26	0.20, -0.29	0.34, -0.44	0.31, -0.22

Tab. S2. Selected HBs parameters for ImNaCr at 293 and 100 K.

D*–H···*A	***D*–H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*–H···*A* (°)**
293 K				
N11–H11···O3	0.87 (3)	2.56 (3)	3.250 (2)	136 (2)
N11–H11···O4	0.87 (3)	1.88 (3)	2.727 (2)	165 (2)
N14–H14···O5^{i}	0.89 (2)	2.53 (2)	3.0582 (19)	118.6 (16)
N14–H14···O6^{i}	0.89 (2)	1.99 (2)	2.877 (2)	173.3 (18)
C15–H15···O5^{i}	0.93	2.49	3.026 (2)	116.7
C13–H13···O1^{ii}	0.93	2.39	3.245 (2)	152.6
C15–H15···O5^{iii}	0.93	2.64	3.568 (2)	172.1

Symmetry code(s): (i) $x+1/2, -y+2, z-1/2$; (ii) $x+1, y, z$; (iii) $-x+1, -y+2, -z+1$.

100 K

N11–H11···O3	0.897 (18)	2.581 (17)	3.2661 (14)	133.7 (13)
N11–H11···O4	0.897 (18)	1.819 (18)	2.7050 (15)	169.0 (15)
N14–H14···O5^{i}	0.929 (15)	2.513 (14)	3.0153 (13)	114.1 (10)
N14–H14···O6^{i}	0.929 (15)	1.913 (15)	2.8359 (14)	171.6 (13)
C15–H15···O5^{i}	0.93	2.45	2.9695 (14)	115.5
C13–H13···O1^{ii}	0.93	2.38	3.2343 (14)	153.2
C13–H13···O2^{ii}	0.93	2.66	3.2487 (15)	122.0
C15–H15···O5^{iii}	0.93	2.60	3.5285 (14)	172.9

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

Tab. S3. Selected geometric parameters (Å, °) for ImNaCr at 293 K.

Cr1–O1^{i}	1.9512(10)	O2–C1	1.2045(19)
Cr1–O1	1.9512(10)	O3–C2	1.258(2)
Cr1–O3^{i}	1.9669(10)	O4–C2	1.216(2)
Cr1–O3	1.9669(10)	O4–Na1^{iii}	2.3833(12)
Cr1–O5^{i}	1.9760(10)	O5–C3	1.2567(18)
Cr1–O5	1.9760(10)	O6–C3	1.2151(18)
Na1–O4^{ii}	2.3833(12)	O6–Na1^{vii}	2.4098(12)
Na1–O4^{iii}	2.3833(12)	N11–C15	1.291(3)
Na1–O2^{iv}	2.3950(12)	N11–C12	1.367(3)
Na1–O2	2.3950(12)	N14–C15	1.281(2)
Na1–O6^{v}	2.4099(12)	N14–C13	1.360(3)
Na1–O6^{vi}	2.4099(12)	C12–C13	1.319(3)
O1–C1	1.2480(17)		
O1^{i}–Cr1–O1	95.60(7)	O4^{iii}–Na1–O6^{v}	95.37(5)
O1^{i}–Cr1–O3^{i}	89.97(4)	O2^{iv}–Na1–O6^{v}	82.45(5)
O1–Cr1–O3^{i}	90.83(4)	O2–Na1–O6^{v}	173.62(4)
O1^{i}–Cr1–O3	90.83(4)	O4^{ii}–Na1–O6^{vi}	95.37(5)
O1–Cr1–O3	89.97(4)	O4^{iii}–Na1–O6^{vi}	86.59(4)
O3^{i}–Cr1–O3	178.81(5)	O2^{iv}–Na1–O6^{vi}	173.62(4)
O1^{i}–Cr1–O5^{i}	174.90(4)	O2–Na1–O6^{vi}	82.45(5)
O1–Cr1–O5^{i}	89.43(5)	O6^{v}–Na1–O6^{vi}	99.08(7)
O3^{i}–Cr1–O5^{i}	89.16(4)	C1–O1–Cr1	130.41(10)
O3–Cr1–O5^{i}	89.97(4)	C1–O2–Na1	142.72(11)
O1^{i}–Cr1–O5	89.44(5)	C2–O3–Cr1	127.70(11)
O1–Cr1–O5	174.90(4)	C2–O4–Na1^{iii}	128.11(12)
O3^{i}–Cr1–O5	89.97(4)	C3–O5–Cr1	131.78(10)
O3–Cr1–O5	89.16(4)	C3–O6–Na1^{vii}	137.73(11)
O5^{i}–Cr1–O5	85.54(7)	C15–N11–C12	108.09(18)
O4^{ii}–Na1–O4^{iii}	176.99(6)	C15–N14–C13	108.91(16)
O4^{ii}–Na1–O2^{iv}	90.89(4)	O2–C1–O1	127.01(15)
O4^{iii}–Na1–O2^{iv}	87.11(4)	O4–C2–O3	124.89(17)
O4^{ii}–Na1–O2	87.11(4)	O6–C3–O5	124.13(14)
O4^{iii}–Na1–O2	90.89(4)	C13–C12–N11	106.82(17)
O2^{iv}–Na1–O2	96.71(7)	C12–C13–N14	106.54(16)
O4^{ii}–Na1–O6^{v}	86.59(4)	N14–C15–N11	109.62(19)
Na1–O2–C1–O1	−179.84(12)	C15–N11–C12–C13	−1.1(2)
Cr1–O1–C1–O2	165.49(13)	N11–C12–C13–N14	0.5(2)
Na1^{iii}–O4–C2–O3	175.31(10)	C15–N14–C13–C12	0.3(2)
Cr1–O3–C2–O4	179.28(11)	C13–N14–C15–N11	−1.0(3)
Na1^{vii}–O6–C3–O5	−139.08(14)	C12–N11–C15–N14	1.3(2)
Cr1–O5–C3–O6	176.14(12)		

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

Tab. S4. Selected geometric parameters (Å, °) for ImNaCr at 100 K.

Cr1–O1^{i}	1.9548(8)	O2–C1	1.2185(14)
Cr1–O1	1.9548(8)	O3–C2	1.2701(14)
Cr1–O3^{i}	1.9715(8)	O4–C2	1.2335(15)
Cr1–O3	1.9715(8)	O4–Na1^{iv}	2.3794(8)
Cr1–O5	1.9843(8)	O5–C3	1.2755(13)
Cr1–O5^{i}	1.9844(8)	O6–C3	1.2297(14)
Na1–O2^{ii}	2.3719(9)	O6–Na1^{vii}	2.4050(9)
Na1–O2	2.3719(9)	N11–C15	1.3212(16)
Na1–O4^{iii}	2.3794(8)	N11–C12	1.3766(16)
Na1–O4^{iv}	2.3794(8)	N14–C15	1.3233(16)
Na1–O6^{v}	2.4050(9)	N14–C13	1.3726(16)
Na1–O6^{vi}	2.4050(9)	C12–C13	1.3456(17)
O1–C1	1.2776(13)		
O1^{i}–Cr1–O1	95.57(5)	O2–Na1–O6^{v}	174.33(3)
O1^{i}–Cr1–O3^{i}	90.05(3)	O4^{iii}–Na1–O6^{v}	87.24(3)
O1–Cr1–O3^{i}	91.33(3)	O4^{iv}–Na1–O6^{v}	96.12(3)
O1^{i}–Cr1–O3	91.33(3)	O2^{ii}–Na1–O6^{vi}	174.32(3)
O1–Cr1–O3	90.05(3)	O2–Na1–O6^{vi}	81.26(3)
O3^{i}–Cr1–O3	177.95(4)	O4^{iii}–Na1–O6^{vi}	96.12(3)
O1^{i}–Cr1–O5	89.54(3)	O4^{iv}–Na1–O6^{vi}	87.24(3)
O1–Cr1–O5	174.71(3)	O6^{v}–Na1–O6^{vi}	99.90(4)
O3^{i}–Cr1–O5	90.05(3)	C1–O1–Cr1	128.88(7)
O3–Cr1–O5	88.44(3)	C1–O2–Na1	138.78(8)
O1^{i}–Cr1–O5^{i}	174.71(3)	C2–O3–Cr1	126.43(7)
O1–Cr1–O5^{i}	89.54(3)	C2–O4–Na1^{iv}	125.42(8)
O3^{i}–Cr1–O5^{i}	88.44(3)	C3–O5–Cr1	130.52(7)
O3–Cr1–O5^{i}	90.05(3)	C3–O6–Na1^{vii}	136.65(7)
O5–Cr1–O5^{i}	85.39(5)	C15–N11–C12	108.49(11)
O2^{ii}–Na1–O2	98.14(5)	C15–N14–C13	108.62(10)
O2^{ii}–Na1–O4^{iii}	89.48(3)	O2–C1–O1	125.32(10)
O2–Na1–O4^{iii}	87.12(3)	O4–C2–O3	123.66(11)
O2^{ii}–Na1–O4^{iv}	87.12(3)	O6–C3–O5	123.48(10)
O2–Na1–O4^{iv}	89.48(3)	C13–C12–N11	107.02(11)
O4^{iii}–Na1–O4^{iv}	174.81(5)	C12–C13–N14	107.04(11)
O2^{ii}–Na1–O6^{v}	81.26(3)	N11–C15–N14	108.84(11)
Na1–O2–C1–O1	176.94(8)	C15–N11–C12–C13	−0.33(14)
Cr1–O1–C1–O2	166.18(9)	N11–C12–C13–N14	0.57(14)
Na1^{iv}–O4–C2–O3	175.53(8)	C15–N14–C13–C12	−0.62(14)
Cr1–O3–C2–O4	177.12(8)	C12–N11–C15–N14	−0.06(14)
Na1^{vii}–O6–C3–O5	−136.36(9)	C13–N14–C15–N11	0.42(14)
Cr1–O5–C3–O6	176.68(8)		

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

Tab. S5. Selected hydrogen bond parameters for ImNaAl at 293 and 100 K.

D*–H···*A	***D*–H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*–H···*A* (°)**
293 K				
N11–H11···O4	0.88 (2)	1.89 (2)	2.767 (2)	175 (2)
N14–H14···O8^{i}	0.82 (2)	2.07 (2)	2.845 (2)	157 (2)
N21–H21···O11	0.82 (2)	2.60 (2)	3.156 (3)	126 (2)
N21–H21···O12	0.82 (2)	1.97 (2)	2.789 (3)	173 (2)

N24–H24···O6ii	1.01 (2)	1.92 (2)	2.899 (3)	163.4 (18)
N24–H24···O10iii	1.01 (2)	2.67 (2)	3.177 (2)	111.2 (15)
C15–H15···O1iv	0.93	2.30	3.111 (3)	145.1
C23–H23···O9iii	0.93	2.52	3.364 (3)	151.0
C25–H25···O3ii	0.93	2.61	3.541 (3)	176.7
C25–H25···O5ii	0.93	2.58	3.167 (3)	121.3

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

100 K				
N11–H11···O3	0.848 (14)	2.652 (14)	3.1691 (13)	120.6 (11)
N11–H11···O4	0.848 (14)	1.921 (14)	2.7666 (13)	175.0 (13)
N14–H14···O8i	0.860 (14)	1.910 (14)	2.7576 (13)	168.2 (13)
N21–H21···O11	0.872 (13)	2.530 (13)	3.2095 (13)	135.4 (11)
N21–H21···O12	0.872 (13)	1.873 (13)	2.7293 (13)	166.7 (13)
N24–H24···O6ii	0.881 (13)	1.969 (13)	2.8181 (13)	161.6 (12)
N24–H24···O10iii	0.881 (13)	2.677 (13)	3.1470 (13)	114.5 (10)
C5–H5···O3	0.93	2.49	2.9485 (14)	111.0
C15–H15···O1iv	0.93	2.26	3.1149 (15)	152.0
C23–H23···O9iii	0.93	2.54	3.3794 (15)	150.6

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

Tab. S6. Selected geometric parameters (Å, °) for ImNaAl at 293 K.

Na1–O10i	2.3556(15)	O7–C4	1.260(2)
Na1–O2	2.3604(15)	O8–C4	1.219(2)
Na1–O4ii	2.3875(14)	O8–Na1ii	2.3963(13)
Na1–O12iii	2.3897(14)	O9–C5	1.262(2)
Na1–O8iv	2.3963(13)	O10–C5	1.188(2)
Na1–O6v	2.4357(14)	O10–Na1vii	2.3556(14)
Al1–O9	1.8730(13)	O11–C6	1.255(2)
Al1–O1	1.8785(13)	O12–C6	1.222(2)
Al1–O7	1.8848(12)	O12–Na1viii	2.3897(14)
Al1–O5	1.8941(13)	N11–C15	1.304(3)
Al1–O11	1.8984(12)	N11–C12	1.342(3)
Al1–O3	1.9057(12)	N14–C15	1.291(3)
O1–C1	1.250(2)	N14–C13	1.337(4)
O2–C1	1.204(2)	N21–C25	1.291(4)
O3–C2	1.262(2)	N21–C22	1.359(4)
O4–C2	1.223(2)	N24–C25	1.279(3)
O4–Na1iv	2.3875(14)	N24–C23	1.335(3)
O5–C3	1.241(2)	C12–C13	1.299(3)
O6–C3	1.214(2)	C22–C23	1.347(4)
O6–Na1vi	2.4357(14)		
O10i–Na1–O2	98.48(6)	O11–Al1–O3	89.31(5)
O10i–Na1–O4ii	87.54(6)	C1–O1–Al1	135.61(13)
O2–Na1–O4ii	97.61(6)	C1–O2–Na1	145.83(15)
O10i–Na1–O12iii	171.27(6)	C2–O3–Al1	131.73(12)
O2–Na1–O12iii	90.22(6)	C2–O4–Na1iv	133.90(13)
O4ii–Na1–O12iii	92.01(6)	C3–O5–Al1	137.04(13)
O10i–Na1–O8iv	89.08(6)	C3–O6–Na1vi	148.18(14)
O2–Na1–O8iv	80.04(5)	C4–O7–Al1	132.59(12)
O4ii–Na1–O8iv	175.57(6)	C4–O8–Na1ii	135.76(12)
O12iii–Na1–O8iv	91.76(5)	C5–O9—Al1	133.66(13)
O10i–Na1–O6v	82.12(6)	C5–O10–Na1vii	135.80(14)
O2–Na1–O6v	176.07(6)	C6–O11–Al1	130.53(12)
O4ii–Na1–O6v	86.29(5)	C6–O12–Na1viii	129.14(13)

O12^{iii}–Na1–O6^{v}	89.15(5)	C15–N11–C12	107.7(2)
O8^{iv}–Na1–O6^{v}	96.10(5)	C15–N14–C13	109.1(2)
O9–Al1–O1	89.40(6)	C25–N21–C22	109.1(2)
O9–Al1–O7	90.72(6)	C25–N24–C23	110.7(2)
O1–Al1–O7	92.28(6)	O2–C1–O1	126.08 (19)
O9–Al1–O5	93.45(6)	O4–C2–O3	124.67(17)
O1–Al1–O5	174.17(6)	O6–C3–O5	126.46(19)
O7–Al1–O5	92.77(6)	O8–C4–O7	125.93(18)
O9–Al1–O11	177.85(6)	O10–C5–O9	128.30(19)
O1–Al1–O11	88.45(6)	O12–C6–O11	124.75(17)
O7–Al1–O11	89.39(6)	C13–C12–N11	108.1(2)
O5–Al1–O11	88.70(6)	C12–C13–N14	106.9(2)
O9–Al1–O3	90.62(6)	N14–C15–N11	108.3(2)
O1–Al1–O3	88.62(6)	C23–C22–N21	105.8(2)
O7–Al1–O3	178.40(6)	N24–C23–C22	106.0(2)
O5–Al1–O3	86.26(6)	N24–C25–N21	108.4(2)
O9–Al1–O1–C1	118.2(2)	Al1–O1–C1–O2	172.07(16)
O7–Al1–O1–C1	27.5(2)	Na1^{iv}–O4–C2–O3	−139.36(16)
O11–Al1–O1–C1	−61.8(2)	Al1–O3–C2–O4	−178.39(15)
O3–Al1–O1–C1	−151.14(19)	Na1^{vi}–O6–C3–O5	−175.38(15)
O9–Al1–O5–C3	−2.9(2)	Al1–O5–C3–O6	161.61(15)
O7–Al1–O5–C3	87.9(2)	Na1^{ii}–O8–C4–O7	168.98(13)
O11–Al1–O5–C3	177.3(2)	Al1–O7–C4–O8	−172.20(14)
O3–Al1–O5–C3	−93.3(2)	Na1^{vii}–O10–C5–O9	−179.94(14)
O9–Al1–O7–C4	21.13(17)	Al1–O9–C5–O10	−144.87(19)
O1–Al1–O7–C4	110.55(17)	Na1^{viii}–O12–C6–O11	165.47(14)
O5–Al1–O7–C4	−72.36(17)	Al1–O11–C6—O12	−179.99(15)
O11–Al1–O7–C4	−161.03(17)	C15–N11–C12–C13	0.6(3)
O1–Al1–O9–C5	71.02(18)	N11–C12–C13–N14	−0.9(3)
O7–Al1–O9–C5	163.30(18)	C15–N14–C13–C12	1.0(3)
O5–Al1–O9–C5	−103.89(18)	C13–N14–C15–N11	−0.6(3)
O3–Al1–O9–C5	−17.59(18)	C12–N11–C15–N14	0.0(3)
O1–Al1–O11–C6	145.05(17)	C25–N21–C22–C23	−0.4(3)
O7–Al1–O11–C6	52.75(17)	C25–N24–C23–C22	0.4(3)
O5–Al1–O11–C6	−40.03(17)	N21–C22–C23–N24	0.0(3)
O3–Al1–O11–C6	−126.30(17)	C23–N24–C25–N21	−0.7(3)
Na1–O2–C1–O1	−166.78(16)	C22–N21–C25–N24	0.7(3)

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

Tab. S7. Selected geometric parameters (Å, °) for ImNaAl at 100 K.

Na1–O10^{i}	2.3398(9)	O7–C4	1.2721(14)
Na1–O2	2.3456(9)	O8–C4	1.2345(14)
Na1–O12^{ii}	2.3794(9)	O8–Na1^{iv}	2.3864(9)
Na1–O8^{iii}	2.3864(9)	O9–C5	1.2813(13)
Na1–O4^{iv}	2.3931(9)	O10–C5	1.2151(14)
Na1–O6^{v}	2.4182(9)	O10–Na1^{vii}	2.3399(9)
Al1–O9	1.8717(8)	O11–C6	1.2659(14)
Al1–O1	1.8784(8)	O12–C6	1.2347(14)
Al1–O7	1.8911(8)	O12–Na1^{viii}	2.3793(9)
Al1–O11	1.8972(8)	N11–C15	1.3226(15)
Al1–O5	1.8997(8)	N11–C12	1.3661(16)
Al1–O3	1.9164(8)	N14–C15	1.3226(15)
O1–C1	1.2777(14)	N14–C13	1.3659(17)
O2–C1	1.2189(14)	N21–C25	1.3200(16)
O3–C2	1.2774(14)	N21–C22	1.3751(17)
O4–C2	1.2327(14)	N24–C25	1.3198(15)
O4–Na1^{iii}	2.3931(9)	N24–C23	1.3695(16)

O5–C3	1.2654(14)	C12–C13	1.3398(18)
O6–C3	1.2310(14)	C22–C23	1.3501(18)
O6–Na1^{vi}	2.4182(9)		
O10^{i}–Na1–O2	99.70(3)	O5–Al1–O3	86.27(3)
O10^{i}–Na1–O12^{ii}	169.82(3)	C1–O1–Al1	132.30(8)
O2–Na1–O12^{ii}	89.59(3)	C1–O2–Na1	141.97(9)
O10^{i}–Na1–O8^{iii}	86.23(3)	C2–O3–Al1	130.16(8)
O2–Na1–O8^{iii}	79.45(3)	C2–O4–Na1^{iii}	131.29(8)
O12^{ii}–Na1–O8^{iii}	91.43(3)	C3–O5–Al1	133.98(8)
O10^{i}–Na1–O4^{iv}	89.57(3)	C3–O6–Na1^{vi}	146.86(8)
O2–Na1–O4^{iv}	99.18(3)	C4–O7–Al1	131.90(8)
O12^{ii}–Na1–O4^{iv}	93.07(3)	C4–O8–Na1^{iv}	133.79(8)
O8^{iii}–Na1–O4^{iv}	175.29(3)	C5–O9–Al1	129.35(8)
O10^{i}–Na1–O6^{v}	81.74(3)	C5–O10–Na1^{vii}	130.33(8)
O2–Na1–O6^{v}	176.22(3)	C6–O11–Al1	129.98(7)
O12^{ii}–Na1–O6^{v}	88.73(3)	C6–O12–Na1^{viii}	125.96(8)
O8^{iii}–Na1–O6^{v}	97.21(3)	C15–N11–C12	108.65(11)
O4^{iv}–Na1–O6^{v}	84.29(3)	C15–N14–C13	108.91(11)
O9–Al1–O1	89.15(4)	C25–N21–C22	108.87(10)
O9–Al1–O7	91.73(4)	C25–N24–C23	109.49(11)
O1–Al1–O7	92.16(3)	O2–C1–O1	124.69(11)
O9–Al1–O11	178.39(4)	O4–C2–O3	123.84(11)
O1–Al1–O11	89.32(4)	O6–C3–O5	124.90(11)
O7–Al1–O11	88.81(4)	O8–C4–O7	124.68(11)
O9–Al1–O5	92.63(4)	O10–C5–O9	125.64(11)
O1–Al1–O5	174.77(4)	O12–C6–O11	123.74(11)
O7–Al1–O5	92.71(4)	C13–C12–N11	107.30(11)
O11–Al1–O5	88.85(4)	C12–C13–N14	106.91(11)
O9–Al1–O3	91.03(4)	N14–C15–N11	108.23(11)
O1–Al1–O3	88.78(3)	C23–C22–N21	106.95(11)
O7–Al1–O3	177.09(4)	C22–C23–N24	106.44(11)
O11–Al1–O3	88.45(4)	N24–C25–N21	108.24(11)
O9–Al1–O1–C1	127.16(10)	Al1–O1–C1–O2	171.95(9)
O7–Al1–O1–C1	35.46(11)	Na1^{iii}–O4–C2–O3	−133.92(10)
O11–Al1–O1–C1	−53.33(10)	Al1–O3–C2–O4	−173.71(8)
O3–Al1–O1–C1	−141.79(10)	Na1^{vi}–O6–C3–O5	−170.37(9)
O9–Al1–O5–C3	−4.59(11)	Al1–O5–C3–O6	161.84(9)
O7–Al1–O5–C3	87.27(11)	Na1^{iv}–O8–C4–O7	170.88(7)
O11–Al1–O5–C3	176.02(11)	Al1–O7–C4–O8	−171.90(8)
O3–Al1–O5–C3	−95.45(11)	Na1^{vii}–O10–C5–O9	−175.55(8)
O9–Al1–O7–C4	15.92(10)	Al1–O9–C5–O10	−149.53(10)
O1–Al1–O7–C4	105.13(10)	Na1^{viii}–O12–C6–O11	164.02(8)
O11–Al1–O7–C4	−165.59(10)	Al1–O11–C6–O12	179.75(8)
O5–Al1–O7–C4	−76.80(10)	C15–N11–C12–C13	0.00(15)
O1–Al1–O9–C5	60.69(10)	N11–C12–C13–N14	−0.19(15)
O7–Al1–O9–C5	152.82(10)	C15–N14–C13–C12	0.31(15)
O5–Al1–O9–C5	−114.39(10)	C13–N14–C15–N11	−0.31(14)
O3–Al1–O9–C5	−28.08(10)	C12–N11–C15–N14	0.19(14)
O1–Al1–O11–C6	150.78(10)	C25–N21–C22–C23	−0.56(14)
O7–Al1–O11–C6	58.61(10)	N21–C22–C23–N24	0.59(14)
O5–Al1–O11–C6	−34.12(10)	C25–N24–C23–C22	−0.44(15)
O3–Al1–O11–C6	−120.42(10)	C23–N24–C25–N21	0.09(15)
Na1–O2–C1–O1	−167.97(8)	C22–N21–C25–N24	0.29(14)

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

Tab. S8. Factor group analysis for ImNaCr and ImNaAl/ImNaAlCr (in parenthesis). The number of nonequivalent $HCOO^-$ ions is three (six) for ImNaCr (ImNaAl/ImNaAlCr) and, therefore, the total number of vibrational modes for this ion is three (six) times larger than presented by the correlation diagram. The asymmetric part of unit cell for ImNaAl/ImNaAlCr contains two Im^+ cations, therefore, the number of vibrational modes for this ion must be multiplied by two.

Ion	Vibration	Free ion symmetry	Site symmetry	Factor group symmetry
		$\boldsymbol{C_{2v}}$	$\boldsymbol{C_1}$	$\boldsymbol{C_{2h}}$
$HCOO^-$	ν_1	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν_2	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν_3	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν_4	$B_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν_5	$B_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν_6	$B_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	T’	$A_1^{(R,IR)}+B_1^{(R,IR)}+B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$
	L	$A_2^{(R)}+B_1^{(R,IR)}+B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$
		$\boldsymbol{C_{2v}}$	$\boldsymbol{C_1}$	$\boldsymbol{C_{2h}}$
Im^+	ν(NH)	$A_1^{(R,IR)}+B_2^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	ν(C’H)	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν(CH)	$A_1^{(R,IR)}+B_2^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	ν(CC)	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ν_s(CN)	$A_1^{(R,IR)}+B_2^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	ν_{as}(CN)	$A_1^{(R,IR)}+B_2^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	δ(NH)	$A_1^{(R,IR)}+B_1^{(R,IR)}+B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$
	δ(CH)	$A_1^{(R,IR)}+B_2^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	δ(C’H)	$B_2^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$
	ω(NH)	$A_2^{(R,IR)}+B_1^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	ω(CH)	$A_2^{(R,IR)}+B_1^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	γ(ring)	$A_1^{(R,IR)}+B_2^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	τ(ring)	$A_2^{(R,IR)}+B_1^{(R,IR)}$	$2A^{(R,IR)}$	$2A_g^{(R)}+2A_u^{(IR)}+2B_g^{(R)}+2B_u^{(IR)}$
	T’	$A_1^{(R,IR)}+B_1^{(R,IR)}+B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$
	L	$A_2^{(R,IR)}+B_1^{(R,IR)}+B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$
			$\boldsymbol{C_2}$ ($\boldsymbol{C_1}$)	$\boldsymbol{C_{2h}}$
Cr^{3+}/Al^{3+}	T’		$A^{(R,IR)}+2B^{(R,IR)}$ ($3A^{(R,IR)}$)	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$ ($3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$)
Na^+	T’		$A^{(R,IR)}+2B^{(R,IR)}$ ($3A^{(R,IR)}$)	$A_g^{(R)}+A_u^{(IR)}+B_g^{(R)}+B_u^{(IR)}$ ($3A_g^{(R)}+3A_u^{(IR)}+3B_g^{(R)}+3B_u^{(IR)}$)

Tab. S9. The observed Raman and IR wavenumbers (cm^{-1}) for studied compounds together with proposed assignments.

ImiNaCr		**ImiNaAlCr**		**ImiNaAl**		**Assignment**
IR	**Raman**	**IR**	**Raman**	**IR**	**Raman**	
	3179 sh		3187 sh		3185 sh	ν(CH)
3159 m	3164 w	3168 m	3167 w	3167 w	3166 w	ν(CH)
3147 sh	3149 w	3152 sh	3152 w	3153 w	3152 w	ν(CH)
3096 w		3100 w		3101 w		ν(NH)
3049 vw	3048 vw	3049 vw	3040 vw	3050 vw	3042 vw	ν(NH)
2996 w	2987 w	2994 w	2986 w	2987 w	2987 w	ν(NH)
2965 w	2967 w	2963 w		2963 w		ν(NH)
2886 w	2889 w	2895 w	2898 sh	2896 w	2897 sh	$\nu_1(HCOO^-)$
			2888 m		2887 m	$\nu_1(HCOO^-)$
2872 sh	2870 sh		2870 m		2869 m	$\nu_1(HCOO^-)$
2854 m	2856 m	2857 m	2853 s	2858 m	2853 s	$\nu_1(HCOO^-)$
2762 w		2764 w		2765 w		ν(NH)/ot/cb
2736 w	2732 w	2749 w	2746 w	2748 w	2747 w	ν(NH)/ot/cb
			2707 w		2709 w	ν(NH)/ot/cb
2668 w		2668 w		2670 w		ν(NH)/ot/cb
2637 w		2640 w		2640 w		ν(NH)/ot/cb
2586 w		2590 w		2592 w		ν(NH)/ot/cb
2542 vw		2543 vw		2545 vw		ν(NH)/ot/cb
2506 vw		2507 vw		2508 vw		ν(NH)/ot/cb
1675 m	1677 m	1687 m	1690 m	1688 m	1690 m	$\nu_4(HCOO^-)$
1630 vs		1640 vs	1626 vw	1641 vs	1629 vw	$\nu_4(HCOO^-)$
1610 vs	1607 vw	1624 vs		1624 vs		$\nu_4(HCOO^-)$
			1598 w		1598 w	$\nu_4(HCOO^-)$
1583 s		1586 s	1584 w	1587 s	1585 w	$\nu_4(HCOO^-)$
	1532 vw		1529 vw		1530 vw	ν(ring)
1457 vw	1457 m	1460 vw	1460 m	1460 vw	1460 m	δ(NH)+ν(ring)
		1435 vw	1437 m	1435 vw	1437 m	δ(NH)+ν(ring)
1382 w	1381 s	1388 sh	1389 m	1389 sh	1388 m	$\nu_5(HCOO^-)$
1374 m	1373 vs	1383 m	1380 vs	1383 m	1380 vs	$\nu_5(HCOO^-)$
	1342 m		1355 m		1355 m	$\nu_5(HCOO^-)$
1330 m		1342 m	1340 w	1342 m		$\nu_2(HCOO^-)$
1322 sh	1322 w				1337 w	$\nu_2(HCOO^-)$
1311 m	1308 w	1324 m	1317 w	1325 m	1316 w	$\nu_2(HCOO^-)$
1301 m		1311 m		1311 m		$\nu_2(HCOO^-)$
1294 m	1297 w					$\nu_2(HCOO^-)$
	1277 vw		1274 vw		1273 vw	δ(CH)
	1270 vw					δ(CH)
	1257 vw		1253 vw		1253 vw	δ(CH)
	1251 vw					δ(CH)
1220 w	1222 m	1223 w	1223 m	1223 w	1224 m	δ(CH)
	1213 sh		1204 m		1205 m	δ(CH)+δ(ring)
1186 w	1187 w	1189 w	1188 m	1189 m	1189 m	δ(CH)+δ(ring)
			1179 m		1179 m	δ(CH)+δ(ring)
1130 vw	1129 w	1130 vw	1129 w	1131 vw	1130 w	δ(CH)+δ(ring)
1122 sh			1119 vw		1120 vw	δ(CH)+δ(ring)
1106 w		1106 vw		1106 vw		δ(CH)+δ(ring)
1101 sh	1102 m		1101 m		1102 m	δ(CH)+δ(ring)
1091 sh	1096 sh		1093 m		1092 m	δ(CH)+δ(ring)
			1063 w		1063 w	$\nu_6(HCOO^-)$
1049 w	1054 w	1050 w	1053 w	1050 w	1052 w	$\nu_6(HCOO^-)$
988 w		991 w		993 w		γ(NH)
907 w	908 w	907 w	910 w	907 w	909 w	δ(ring)
	902 sh		902 w		902 sh	δ(ring)

	878 vw		879 vw		881 vw	δ(ring)
			861 vw		861 vw	δ(ring)
853 sh		855 sh		855 w		γ(NH)
840 w		846 w		845 w		γ(NH)
816 s	811 sh	820 s	818 sh	820 s	817 sh	ν_3($HCOO^-$)
	802 w		806 sh		805 sh	ν_3($HCOO^-$)
794 w		797 w	798 w	797 w	798 w	ν_3($HCOO^-$)
766 sh		768 sh	769 vw	767 sh	769 vw	δ(ring)
762 w		763 w		763 w		δ(ring)
638 w	637 vw	639 w	635 vw	639 w	636 vw	τ(ring)
635 w		636 w		636 w		τ(ring)
625 vw	628 w	626 vw	627 w	626 vw	628 w	τ(ring)
418 s		461 s		460 s		T'(M^{3+})
		423 w				T'(M^{3+})
	348 w		349 w		348 w	L($HCOO^-$)+T'($HCOO^-$)
		318 vw	305 w	316 vw	309 w	L($HCOO^-$)+T'($HCOO^-$)
				302 vw		L($HCOO^-$)+T'($HCOO^-$)
280 w		299 vw	287 w		290 w	L($HCOO^-$)+T'($HCOO^-$)
230 w		245 sh		240 sh		L($HCOO^-$)+T'($HCOO^-$)+T'(Na^+)
211 m			222 sh		224 sh	L($HCOO^-$)+T'($HCOO^-$)+T'(Na^+)
187 m	186 s	191 m	194 sh	192 sh	194 vs	L($HCOO^-$)+T'($HCOO^-$)
			176 sh		176 sh	L($HCOO^-$)
	134 sh		142 vs	137 sh	140 vs	L($HCOO^-$)
118 w	121 vs	119 vw	122 vs		124 vs	L($HCOO^-$)
	109 sh		110 vs		110 vs	L($HCOO^-$)
	91 sh		93 sh		94 sh	L($HCOO^-$)
75 vw		81 vw		82 vw		L($HCOO^-$)