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

Heterometallic perovskite-type metal-organic framework with an ammonium cation: structure, phonons, and optical response of $[NH_4]Na_{0.5}Cr_xAl_{0.5-x}(HCOO)_3$ (x=0, 0.025 and 1)

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Electronic Supplementary information

Fig. S1. The DSC trace for AmNaCr.

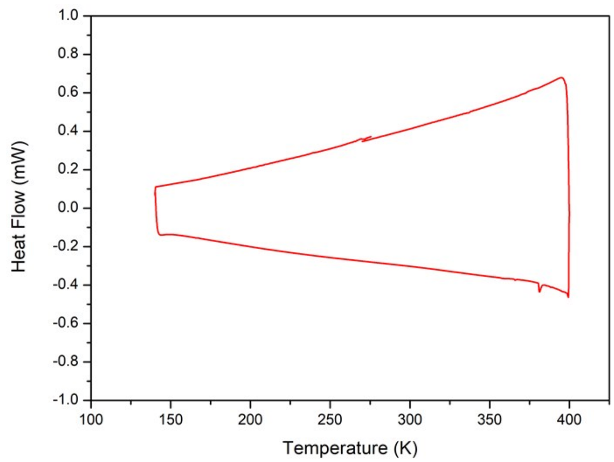


Fig. S2. The experimental XRD patterns of AmNaCr (red line) and AmNaAlCr (blue line) together with simulated one (black line) for AmNaCr basing on the crystal structure refinement.

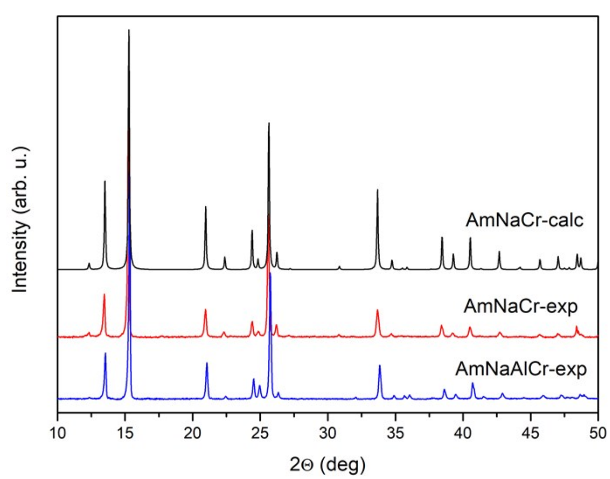


Fig. S3. X-ray diffraction experimental details for AmNaCr.

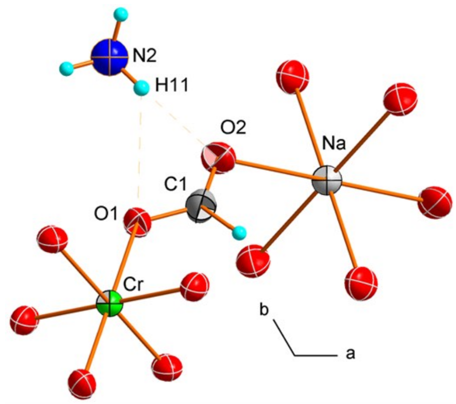
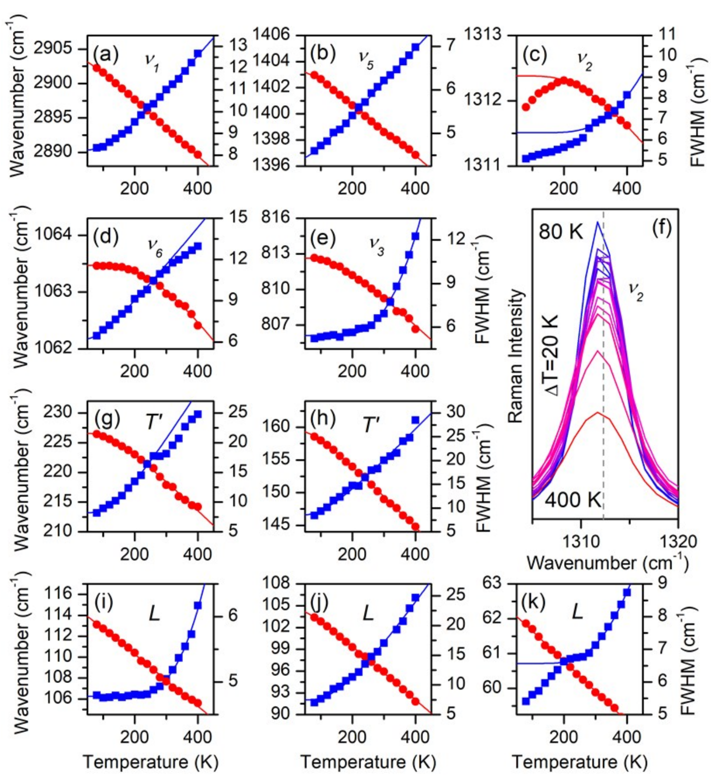


Fig. S4. The temperature evolution of wavenumber (red circles, left scales) and FWHM (blue squares, right scales) of selected Raman bands corresponding to $HCOO^-$ ions: (a) ν_1 (symmetric CH stretching), (b) ν_5 (CH in plane bending), (c, f) ν_2 (symmetric stretching CO), (d) ν_6 (CH out of plane bending), (e) ν_3 (symmetric OCO bending), (g, h) translational and (i–k) librational modes.



Tab. S1. X-ray diffraction experimental details for AmNaCr.

Crystal data	
Chemical formula	$C_3H_7Cr_{0.50}NNa_{0.50}O_6$
M_r	190.59
Crystal system, space group	Trigonal, $R\bar{3}:H$
Temperature (K)	298
a, *c* (Å)	7.9386(5), 21.494(3)
V (Å^3)	1173.1(2)
Z	6
Radiation type	Mo*K*α
μ (mm^{-1})	0.82
Crystal size (mm)	0.18×0.15×0.09
Data collection	
Diffractometer	Xcalibur, Atlas
Absorption correction	Multi-scan *CrysAlis PRO*
T_{min}, T_{max}	0.855, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3383, 586, 444
R_{int}	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.655
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.092, 1.02
No. of reflections	586
No. of parameters	39
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.28, -0.30

Computer programs: *SHELXL2014*/7.

Tab. S2. Selected geometric parameters for AmNaCr (Å, º).

Cr–O1 × 6	1.9683(17)
Na–O2 × 6	2.4082(19)
O1–C1	1.255(3)
C1–O2	1.216(3)
C1–H1	0.9300
N2–H11	0.873(5)
N2–H21	0.871(5)

O–Cr–O$_{cis}$	88.74(7)–91.26 (7)
O–Cr–O$_{trans}$	180.0
O–Na–O$_{cis}$	86.70(7)–93.30 (7)
O–Na–O$_{trans}$	180.00(6)
O2–C1–O1	126.8(3)

Tab. S3. Selected Selected hydrogen-bond parameters for AmNaCr.

D–H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)
N2–H11···O2	0.873(5)	1.983(6)	2.852(2)	173.3(17)
N2–H21···O1^{i}	0.871(5)	2.592(5)	3.324(4)	142.19(9)
N2–H21···O1^{ii}	0.871(5)	2.592(5)	3.324(4)	142.19(9)
N2–H21···O1^{iii}	0.871(5)	2.592(5)	3.324(4)	142.19(9)

Symmetry code(s): (i) -*x*+1/3, -*y*+2/3, -*z*+5/3; (ii) *y*+1/3, -*x*+*y*+2/3, -*z*+5/3; (iii) *x*-*y*+1/3, *x*+2/3, -*z*+5/3.

Tab. S4. Factor group analysis for AmNaCr.[a]

Ion	Vibration	Free ion symmetry	Site symmetry	Factor group symmetry
$HCOO^-$		***C_{2v}***	***C_1***	***S_6***
	ν_1	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	ν_2	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	ν_3	$A_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	ν_4	$B_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	ν_5	$B_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	ν_6	$B_1^{(R,IR)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	T’	$A_1^{(R,IR)} + B_1^{(R,IR)} + B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)} + 3A_u^{(IR)} + 3E_g^{(R)} + 3E_u^{(IR)}$
	L	$A_2^{(R)} + B_1^{(R,IR)} + B_2^{(R,IR)}$	$3A^{(R,IR)}$	$3A_g^{(R)} + 3A_u^{(IR)} + 3E_g^{(R)} + 3E_u^{(IR)}$
NH_4^+		***T_d***	***C_3***	***S_6***
	ν_1	$A_1^{(R)}$	$A^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)}$
	ν_2	$E^{(R)}$	$E^{(R,IR)}$	$E_g^{(R)} + E_u^{(IR)}$
	ν_3	$F_2^{(R,IR)}$	$A^{(R,IR)} + E^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	ν_4	$F_2^{(R,IR)}$	$A^{(R,IR)} + E^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	T’	$F_2^{(R,IR)}$	$A^{(R,IR)} + E^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
	L	$F_1^{(-)}$	$A^{(R,IR)} + E^{(R,IR)}$	$A_g^{(R)} + A_u^{(IR)} + E_g^{(R)} + E_u^{(IR)}$
Cr^{3+}			***S_6***	***C_{2v}***
	T’		$A_u^{(IR)} + E_u^{(IR)}$	$A_u^{(IR)} + E_u^{(IR)}$
Na^+			***S_6***	***C_{2v}***
	T’		$A_u^{(IR)} + E_u^{(IR)}$	$A_u^{(IR)} + E_u^{(IR)}$

[a]Key: (R), Raman active; (IR), infrared active; (–), inactive mode; T, translations; L, librations, ν_1–ν_6($HCOO^-$), characteristic vibrations of formate ions (see in paper); ν_1–ν_4(NH_4^+), characteristic vibrations of ammonium ions (see in paper).

Tab. S5. Room temperature IR and Raman (at 80 and 300 K) wavenumbers (cm^{-1}) measured for AmNaCr and AmNaAlCr compounds and proposed assignments.[a]

AmNaCr			AmNaAlCr		Assignment
Raman (80 K)	Raman (RT)	IR (RT)	Raman (RT)	IR (RT)	
		3561 w			$\nu_3(NH_4^+)$
		3433 w		3438 w	$\nu_3(NH_4^+)$
3299 vw	3277 vw	3285 w	3277 vw	3285 w	$\nu_3(NH_4^+)$
3193 vw				3188 w	$\nu_3(NH_4^+)$
3160 vw	3177 vw	3179 w		3163 w	$\nu_3(NH_4^+)$
3090 vw		3099 w		3119 w	$\nu_3(NH_4^+)$
3063 vw	3058 vw				$\nu_3(NH_4^+)$
3008 vw	3003 w		3019 w	3001 w	$\nu_1(NH_4^+)$
2986 vw	2987 sh	2982 m	2990sh		$\nu_1(NH_4^+)$
2964 vw	2968 sh				$\nu_1(NH_4^+)$
		2920 vw		2925 vw	$\nu_1(NH_4^+)$
2910 sh		2911 w	2897 vs		$\nu_1(NH_4^+)$
2902 m	2893 m	2893 w		2897 w	$\nu_1(HCOO^-)$
		2858 m	2847 w	2861 w	$\nu_1(HCOO^-)$
2846 m	2840 w	2847 m	2786 w		$\nu_1(NH_4^+)$
2787 w	2778 w	2770 vw		2787 vw	overtone
		2738 vw			overtone
		2622 vw		2663 sh	overtone
		2611 vw		2651 w	overtone
1706 vw	1701 vw	1709 w	1701 vw	1712 w	$\nu_2(NH_4^+)$
1650 m	1652 s	1643 sh	1668 w	1639 s	$\nu_4(HCOO^-)$
		1625 vs		1624 s	$\nu_4(HCOO^-)$
1589 vw	1587 vw	1603 vs	1594 w	1604 vs	$\nu_4(HCOO^-)$
1485 vw		1473 w	1478 vw	1476 vw	$\nu_4(NH_4^+)$
1460 w	1455 w	1443 w	1457 w	1445 w	$\nu_4(NH_4^+)$
	1398 s	1399 m			$\nu_5(HCOO^-)$
1403 s		1386 sh	1402 vs	1403 m	$\nu_5(HCOO^-)$
1349 sh	1344 vs				$\nu_5(HCOO^-)$
1342 vs			1359 vs		$\nu_5(HCOO^-)$
		1326 sh		1346 w	$\nu_2(HCOO^-)$
1312 m	1312 s	1311 vs	1323 s	1333 vs	$\nu_2(HCOO^-)$
		1285 m		1311 m	$\nu_2(HCOO^-)$
1063 w	1063 w	1063 vw	1068 w	1068 vw	$\nu_6(HCOO^-)$
813 w	810 w	815 m	805 w	823 m	$\nu_3(HCOO^-)$

806 w	807 w	801 sh			$\nu_3(HCOO^-)$
		768 vw		763 vw	$\nu_3(HCOO^-)$
498 vw		475 vw		483 sh	$L(NH_4^+)$
		424 m		465 m	$T'(M^{3+})$
396 vw				424 m	$T'(M^{3+})$
350 w	345 m		342 w		$L(NH_4^+)$
319 vw					$L(NH_4^+)$
		284 w		323 w	$T'(M^{III})$
			312 w		$T'(NH_4^+)$
		258 vw			$T'(Na^+)$
250 vw			295 w		$T'(NH_4^+)$
243 w	235 w		236 w		$T'(NH_4^+)$
		226 w		232 w	$T'(Na^+)+T'(NH_4^+)$
226 w	218 m		221 m		$T'(HCOO^-)$
		206 w		206 w	$T'(HCOO^-)+T'(NH_4^+)$
204 w	196 m		194 m		$T'(HCOO^-)$
		190 sh		190 w	$T'(HCOO^-)+T'(NH_4^+)$
159 w	149 sh		151 m		$T'(HCOO^-)$
		144 w		144 w	$T'(HCOO^-)+T'(NH_4^+)$
134 w	132 m		136 m		$T'(HCOO^-)$
113 m	107 vs		109 vs		$L(HCOO^-)$
		103 vw		103 vw	$L(HCOO^-)$
103 m	96 vs		96 vs		$L(HCOO^-)$
76 vw		81 w		84 w	$L(HCOO^-)$
62 w	59 m		60 w		$L(HCOO^-)$

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν_1–$\nu_6(HCOO^-)$, characteristic vibrations of formate ions (see in paper); ν_1–$\nu_4(NH_4^+)$, characteristic vibrations of ammonium ions (see in paper); T', translations; L, librations.

Tab. S6. Room temperature IR and Raman (at 80 and 300 K) wavenumbers (cm^{-1}) measured for AmNaCr along with detailed assignments using DFT harmonic approximation.[a]

Calculated			Experimental			Assignment
Sym.	Raman	IR	Raman (80 K)	Raman (RT)	IR (RT)	
					3561 w	
					3433 w	
A_u		3375			3285 w	ν(NH)
A_g	3374		3299 vw	3277 vw		ν(NH)
			3193 vw			
			3160 vw	3177 vw	3179 w	
			3090 vw		3099 w	

			3063 vw	3058 vw		
			3008 vw	3003 w		
					2982 m	
					2920 vw	
			2986 vw	2987 sh		
			2964 vw	2968 sh		
			2910 sh			
					2911 w	
A_u		2938			2893 w	
E_u		2937			2858 m	$\nu_1(HCOO^-)$
E_g	2938		2902 vs	2893 vs		$\nu_1(HCOO^-)$
A_g	2937					$\nu_1(HCOO^-)$
					2847 m	$\nu_1(HCOO^-)$
A_g	2871		2846 m	2840 w		
E_g	2825		2787 w	2778 w		$\nu_3(NH_4^+)$
A_u		2876			2770 vw	$\nu_3(NH_4^+)$
E_u		2828			2738 vw	$\nu_1(NH_4^+)$
					2622 vw	$\nu_1(NH_4^+)$
					2611 vw	
E_u		1696			1709 w	
E_g	1686		1706 vw	1701 vw		$\nu_2(NH_4^+)$
A_g	1648		1650 m	1652 s		$\nu_2(NH_4^+)$
					1643 sh	$\nu_2(NH_4^+)+\nu_4(HCOO^-)$
E_u		1596			1625 vs	
A_u		1595			1603 vs	$\nu_2(NH_4^+)+\nu_4(HCOO^-)$
E_g	1589		1589 vw	1587 vw		$\nu_2(NH_4^+)+\nu_4(HCOO^-)$
A_g	1493		1485 vw			$\nu_2(NH_4^+)+\nu_4(HCOO^-)$
A_u		1492			1473 w	$\nu_4(NH_4^+)$
E_g	1441		1460 w	1455 w		$\nu_4(NH_4^+)$
E_u		1429			1443 w	$\nu_4(NH_4^+)$
E_g	1362		1403 s	1398 s		$\nu_4(NH_4^+)$
E_u		1358			1399 m	$\nu_5(HCOO^-)$
					1386 sh	$\nu_5(HCOO^-)$
A_u		1355			1326 sh	
A_g	1355		1349 sh	1344 vs		$\nu_5(HCOO^-)$
A_g	1326		1342 vs			$\nu_5(HCOO^-)$
A_u		1318			1311 vs	$\nu_2(HCOO^-)$
E_g	1307		1312 m	1312 s		$\nu_2(HCOO^-)$
E_u		1303			1285 m	$\nu_2(HCOO^-)$
A_u		1011			1063 vw	$\nu_2(HCOO^-)$
E_g	1010		1063 w	1063 w		$\nu_6(HCOO^-)$
E_u		1008				$\nu_6(HCOO^-)$
A_g	1007					$\nu_6(HCOO^-)$
A_u		790			815 m	$\nu_6(HCOO^-)$
A_g	784		813 w	810 w		$\nu_3(HCOO^-)+L(NH_4^+)+T'(M^{III})$
E_u		783			801 sh	$\nu_3(HCOO^-)+L(NH_4^+)$

E_g	774		806 w	807 w		$\nu_3(HCOO^-)+T'(M^{III})$
A_u		628			768 vw	$\nu_3(HCOO^-)+L(NH_4^+)$
A_g	626		498 vw			$L(NH_4^+)$
E_u		488			475 vw	$L(NH_4^+)$
E_g	481		396 vw			$L(NH_4^+)$
A_u		422			424 m	$L(NH_4^+)$
E_u		420				$L(NH_4^+)+L(HCOO^-)+T'(Cr^{3+})$
A_g	336		350 w	345 m		$L(NH_4^+)+L(HCOO^-)+T'(Cr^{3+})$
E_g	319		319 vw			$L(NH_4^+)+L(HCOO^-)$
E_u		286			284 w	$L(NH_4^+)+L(HCOO^-)$
A_u		281				$T'(NH_4^+)+L(HCOO^-)+T'(Cr^{3+})+T'(Na^+)$
E_g	268					$T'(NH_4^+)+L(HCOO^-)+T'(Cr^{3+})$
A_u		261			258 vw	$T'(NH_4^+)+L(HCOO^-)$
A_g	256		250 vw			$T'(NH_4^+)+T'(HCOO^-)+T'(Na^+)$
E_u		254				$T'(NH_4^+)+L(HCOO^-)$
A_u		234			226 w	$T'(NH_4^+)+T'(HCOO^-)+T'(Na^+)$
A_g	228		243 w	235 w		$T'(NH_4^+)+T'(HCOO^-)+T'(Na^+)$
E_g	225		226 w	218 m		$T'(NH_4^+)+T'(HCOO^-)$
E_u		217				$T'(NH_4^+)+T'(HCOO^-)$
A_g	204		204 w			$T'(NH_4^+)+L(HCOO^-)+T'(Na^+)$
E_u		197			206 w	$T'(NH_4^+)+T'(HCOO^-)$
A_u		195			190 sh	$T'(NH_4^+)+L(HCOO^-)+T'(Na^+)$
A_g	168			196 m		$T'(NH_4^+)+T'(HCOO^-)+T'(Na^+)$
A_u		160				$T'(NH_4^+)+T'(HCOO^-)$
E_g	159		159 w	149 sh		$T'(NH_4^+)+T'(HCOO^-)+T'(Na^+)$
E_u		149			144 w	$L(NH_4^+)+T'(HCOO^-)$
E_g	126		134 w	132 m		$L(NH_4^+)+T'(HCOO^-)+T'(Cr^{3+})+T'(Na^+)$
A_u		120				$T'(NH_4^+)+T'(HCOO^-)$
A_g	115		113 m	107 vs		$T'(NH_4^+)+L(HCOO^-)$
E_u		107			103 vw	$T'(NH_4^+)+L(HCOO^-)$
E_g	104		103 m	96 vs		$L(HCOO^-)+T'(Cr^{3+})+T'(Na^+)$
A_g	92		76 vw			$T'(NH_4^+)+L(HCOO^-)$
A_u		82			81 w	$L(NH_4^+)+L(HCOO^-)$
E_u		79				$L(NH_4^+)+L(HCOO^-)+T'(Cr^{3+})+T'(Na^+)$
E_g	40		62 w	59 m		$L(NH_4^+)+L(HCOO^-)+T'(Cr^{3+})+T'(Na^+)$
						$T'(NH_4^+)+L(HCOO^-)$

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν_1–$\nu_6(HCOO^-)$, characteristic vibrations of formate ions (see in paper); ν_1–$\nu_4(NH_4^+)$, characteristic vibrations of ammonium ions (see in paper); T', translations; L, librations.