Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Nitridochromate(IV) fluoride - $LiCa_8[CrN_3]_2N_2F$

Natalia Gloriozova[a], Yurii Prots[a], Mitja Krnel[a], Ulrich Burkhardt[a], Marcus Schmidt[a], Alim Ormeci[a], Franziska Jach[a,b,c], Peter Höhn*[a] and Yuri Grin[a]

[a]*Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany*

[b]*Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany*

[c]*Fraunhofer Institute for Integrated Systems and Device Technology IISB, Schottkystraße 10, 91058 Erlangen, Germany*

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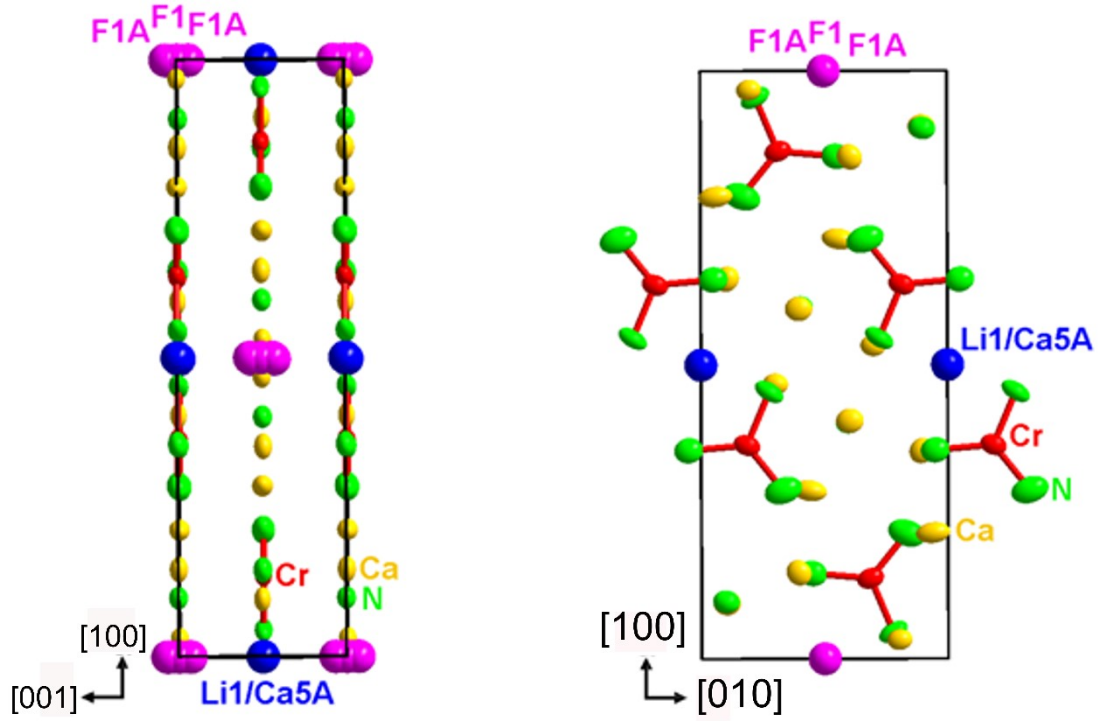


(a) (b)

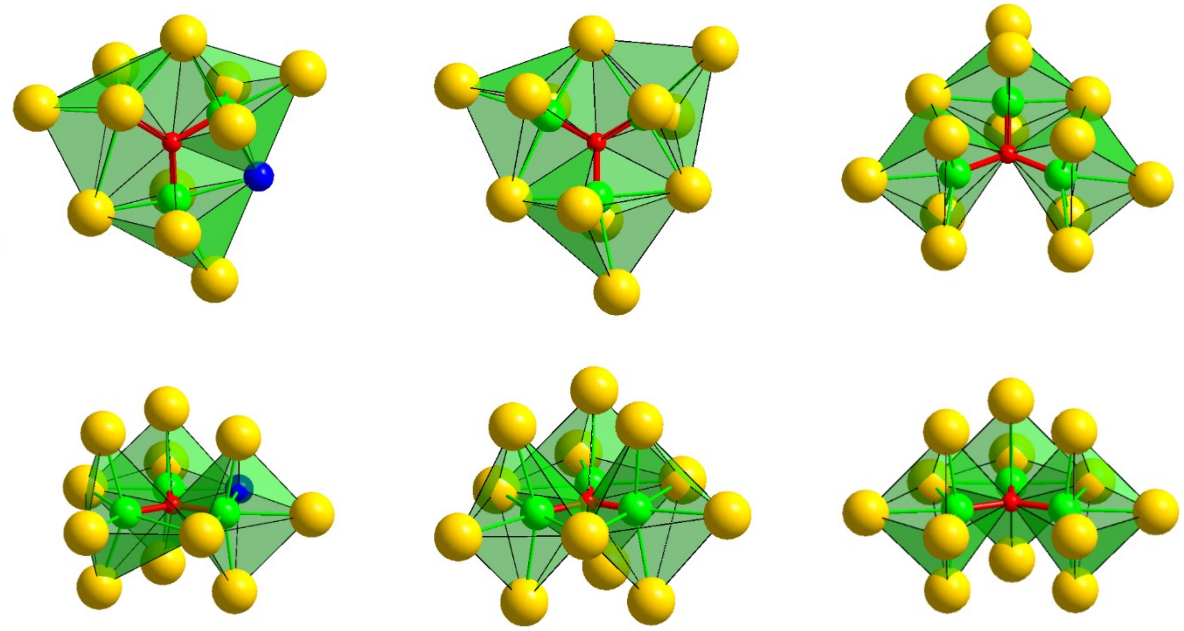
Figure S1. The projection of the crystal structure of $LiCa_8[CrN_3]_2N_2F$ along (a) [010] and (b) [001] direction. Anisotropic displacement parameters correspond to 98 % probability.

Table S1. Anisotropic displacement parameters (Å^2) of $LiCa_8[Cr^{IV}N_3]_2N_2F$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr1	0.0091(2)	0.0140(2)	0.0058(2)	0	0	-0.00199(16)
Ca1	0.0120(3)	0.0150(3)	0.0056(3)	0	0	0.0002(2)
Ca2	0.0088(3)	0.0126(3)	0.0065(3)	0	0	0.00049(19)
Ca3	0.0130(3)	0.0125(3)	0.0066(3)	0	0	-0.0011(2)
Ca4	0.0089(3)	0.0234(3)	0.0086(3)	0	0	0.0019(2)
N1	0.0098(10)	0.0160(13)	0.0066(12)	0	0	-0.0058(9)
N2	0.0128(12)	0.0170(13)	0.0073(12)	0	0	0.0010(9)
N3	0.0151(13)	0.0276(16)	0.0107(13)	0	0	0.0049(11)
N4	0.0101(11)	0.0144(12)	0.0072(11)	0	0	-0.0008(9)

Table S2. Selected interatomic distances in $LiCa_8[CrN_3]_2N_2F$.

atoms			*d*, Å	atoms			*d*, Å
Cr1	–N3	×1	1.728(3)	Ca4	–N4	×1	2.353(3)
	–N1	×1	1.730(3)		–N2	×1	2.470(3)
	–N2	×1	1.735(3)		–N3	×2	2.5933(10)
Cr1	–Ca5A	×1	2.7535(5)		–N3	×1	3.152(3)
	–Ca1	×1	3.1511(9)	N1	–Ca5A	×1	2.181(3)
	–Ca4	×1	3.1791(8)	N1	–Li1	×1	2.181(3)
	–Ca2	×2	3.1948(5)	N2	–Li1	×1	2.571(3)
	–Ca3	×2	3.2666(6)	F1	–F1A	×1	0.33(2)
	–Ca4	×1	3.3796(6)	F1	–Li1	×2	2.4716(2)
Cr1	–Li1	×1	2.7535(5)	F1	–Ca5A	×1	2.4716(2)
Ca1	–N4	×2	2.4721(2)	F1A	–F1A	×1	0.67(5)
	–N1	×1	2.549(3)	F1	–Ca5A	×1	2.14(2)
	–N1	×1	2.623(3)	F1A	–Li1	×1	2.14(2)
	–N2	×1	2.689(3)				
	–N3	×1	2.870(3)				
Ca1	–Li1	×1	3.3574(7)				
Ca1	–Ca3	×2	3.3915(6)				
	–Ca2	×2	3.4022(6)				
Ca2	–F1	×1	2.2911(6)				
	–F1A	×2	2.315(3)				
Ca2	–N4	×1	2.384(3)				
	–N4	×1	2.468(3)				
	–N1	×2	2.4904(4)				
Ca2	–Ca2	×1	3.1080(12)				
	–Ca4	×1	3.3391(9)				
Ca2	–Li1	×1	3.3702(5)				
Ca3	–N4	×1	2.325(3)				
	–N3	×1	2.496(3)				
	–N2	×2	2.5040(5)				
Ca3	–F1	×1	2.6789(6)				
	–F1A	×2	2.700(3)				



(a) (b) (c)

Figure S2. Coordination of $[CrN_3]^{x-}$ units in (a) $LiCa_8[CrN_3]_2N_2F$, (b) $Sr_3[CrN_3]$, and (c) $Ca_3[CrN_3]$, viewed perpendicular (top), and along (bottom) trigonal planar units. Red spheres: Cr; green spheres: N; blue spheres: Li; yellow spheres: alkaline-earth metals.

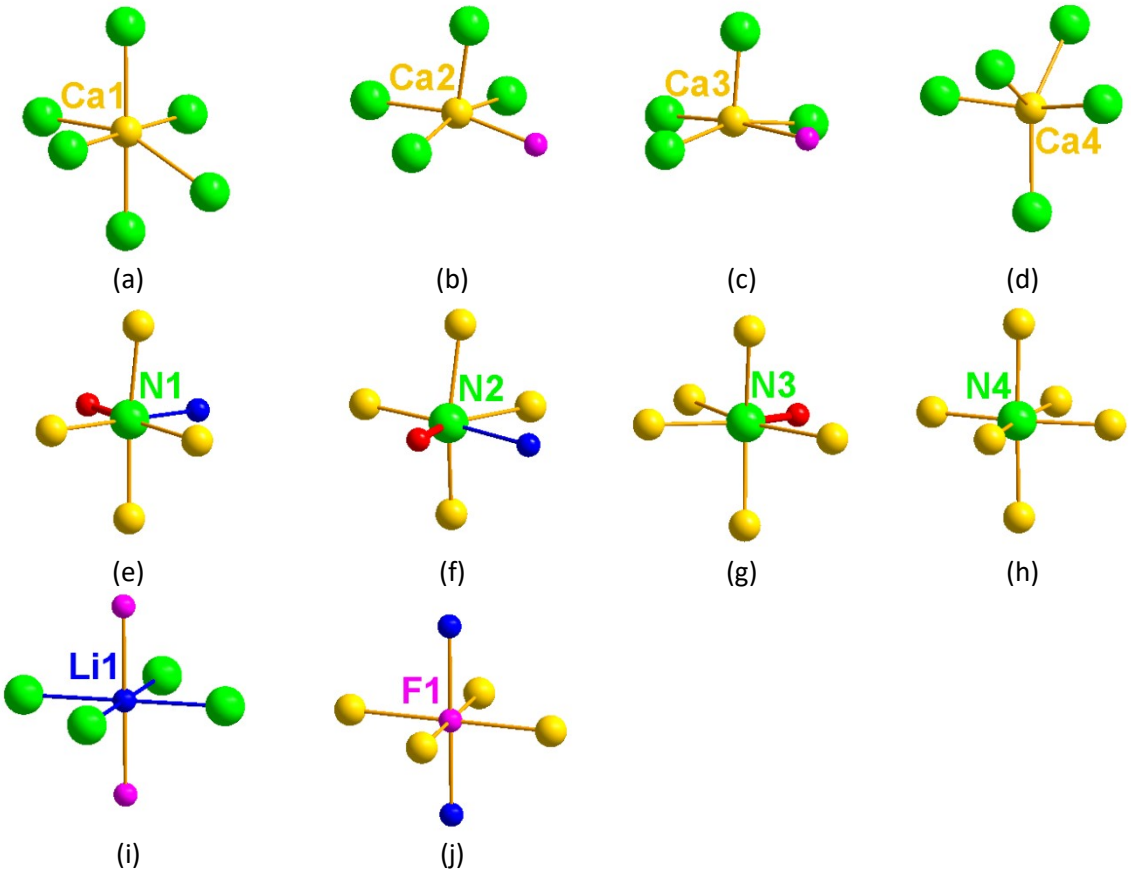


Figure S3. Atomic coordination in the ideal structure of $LiCa_8[Cr^{IV}N_3]_2N_2F$ structure. Red spheres: Cr; green spheres: N; blue spheres: Li; yellow spheres: Ca; purple spheres: F.

Table S3. Expected internal vibrational modes for $[CrN_3]^{5-}$ anion within $LiCa_8[CrN_3]_2N_2F$ crystal structure according to molecular site group analysis.

molecular vibration	molecular point group	molecular selection rules	site symmetry	factor group	solid-state selection rules	number of expected bands	
	D_{3h}		C_s	D_{2h}		IR	Raman
$\upsilon_s(CrN_3)$	A_1'	R	A'	A_g	R		
				B_{1g}	R		
				B_{2u}	IR		
				B_{3u}	IR		
$\upsilon_{as}(CrN_3)$	E'	IR, R	$2\,A'$	$2\,A_g$	2 R	6	6
				$2\,B_{1g}$	2 R		
				$2\,B_{2u}$	2 IR		
				$2\,B_{3u}$	2 IR		
δ(NCrN)	E'	IR, R	$2\,A'$	$2\,A_g$	2 R		
				$2\,B_{1g}$	2 R	4	4
				$2\,B_{2u}$	2 IR		
				$2\,B_{3u}$	2 IR		
γ(NCrN)	A_2''	IR	A''	A_u	-		
				B_{1u}	IR		
				B_{2g}	R	1	2
				B_{3g}	R		

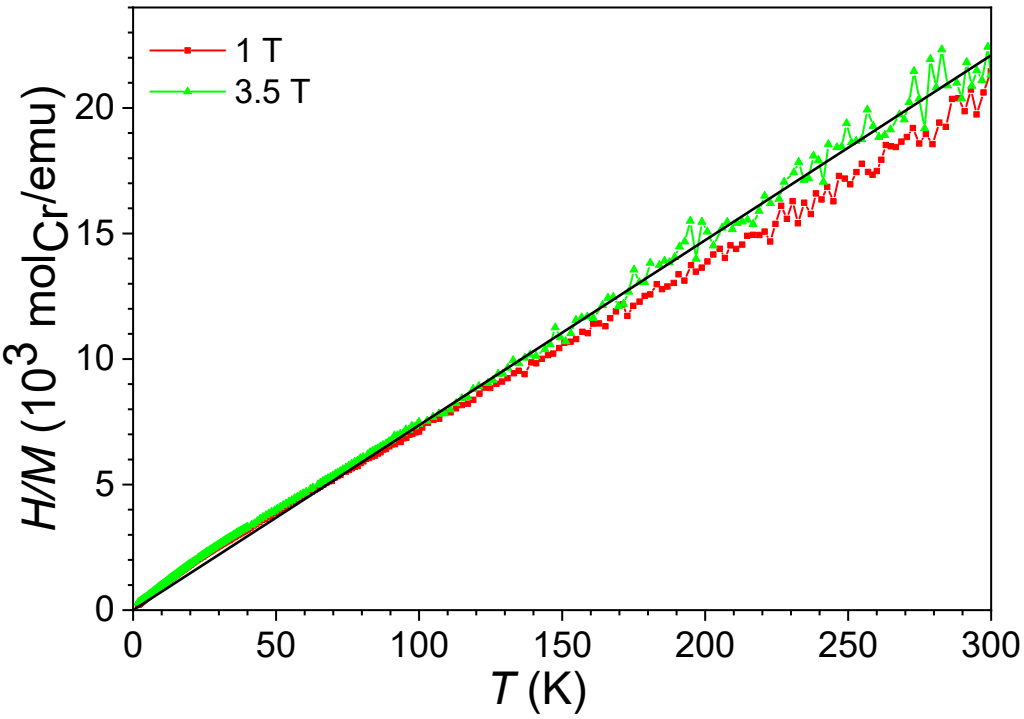


Figure S4. Inverse susceptibility vs. temperature fitted with Curie equation (black line) of $LiCa_8[CrN_3]_2N_2F$.

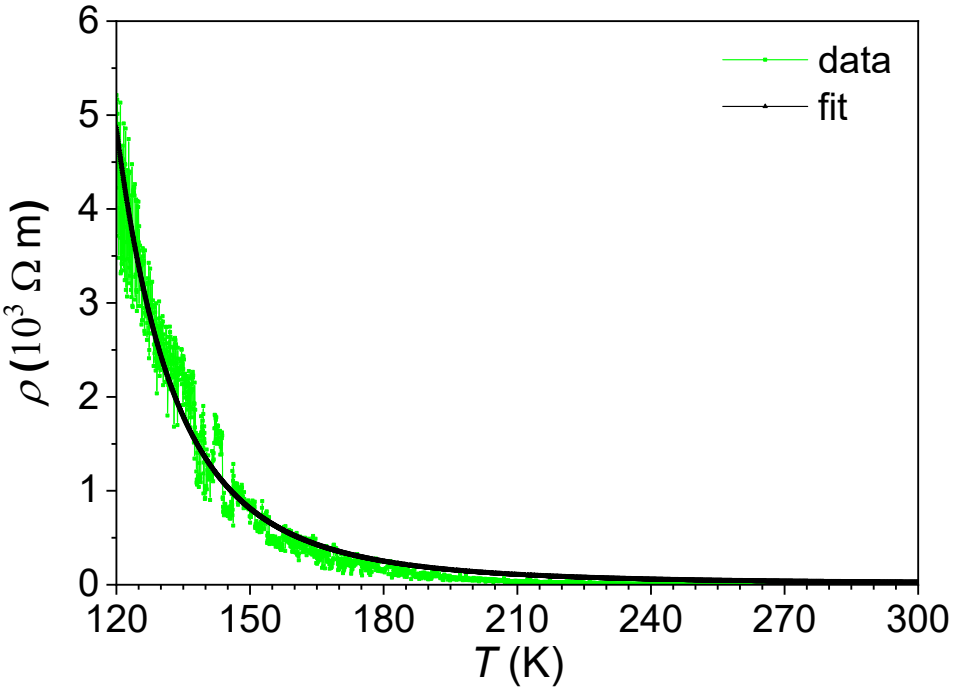


Figure S5. Electrical resistivity of $LiCa_8[CrN_3]_2N_2F$ in the temperature range 120 K to 300 K**.**

Table S4. Synthesis of $LiCa_8[CrN_3]_2N_2F$.

sample	starting materials / molar ratio						obtained phases
	Ca_2N	Ca_3N_2	Cr	CaF_2	Li_3N	Li	
1	1	0.6	0.9	0.5	1.5	22	$LiCa_8[CrN_3]_2N_2F$, Li_3N
2	-	1	1.3	0.9	1.8	12	$LiCa_8[CrN_3]_2N_2F$, $Ca_6[Cr_2N_6]F$,[1] Li_3N

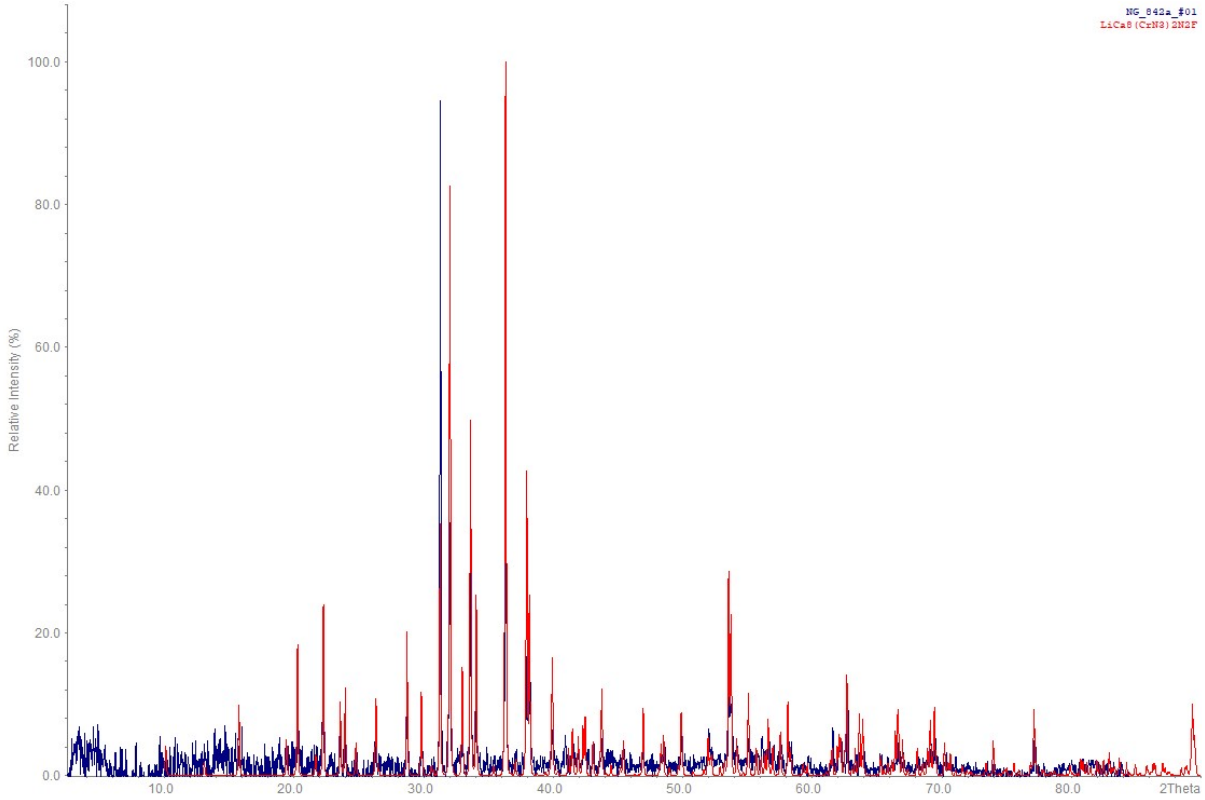


Figure S6. PXRD of ground crystals of $LiCa_8[CrN_3]_2N_2F$ (in blue) and theoretical pattern calculated from single crystal data (in red).

References

1. N. Gloriozova, P. Höhn, unpublished work.