

Supplementary Materials

Switchable dielectric constant, structural and vibrational studies of double perovskite organic-inorganic hybrids: (azetidinium)₂[KCr(CN)₆] and (azetidinium)₂[KFe(CN)₆]

Magdalena Rok^{†a}, Marcin Moskwa^a, Joanna Hetmańczyk^b, Łukasz Hetmańczyk^b, Grażyna Bator^a

^aFaculty of Chemistry, University of Wrocław, 14 F. Joliot – Curie, 50-383 Wrocław, Poland

^bFaculty of Chemistry, Jagiellonian University in Kraków, Gronostajowa 2, 30-387 Kraków, Poland

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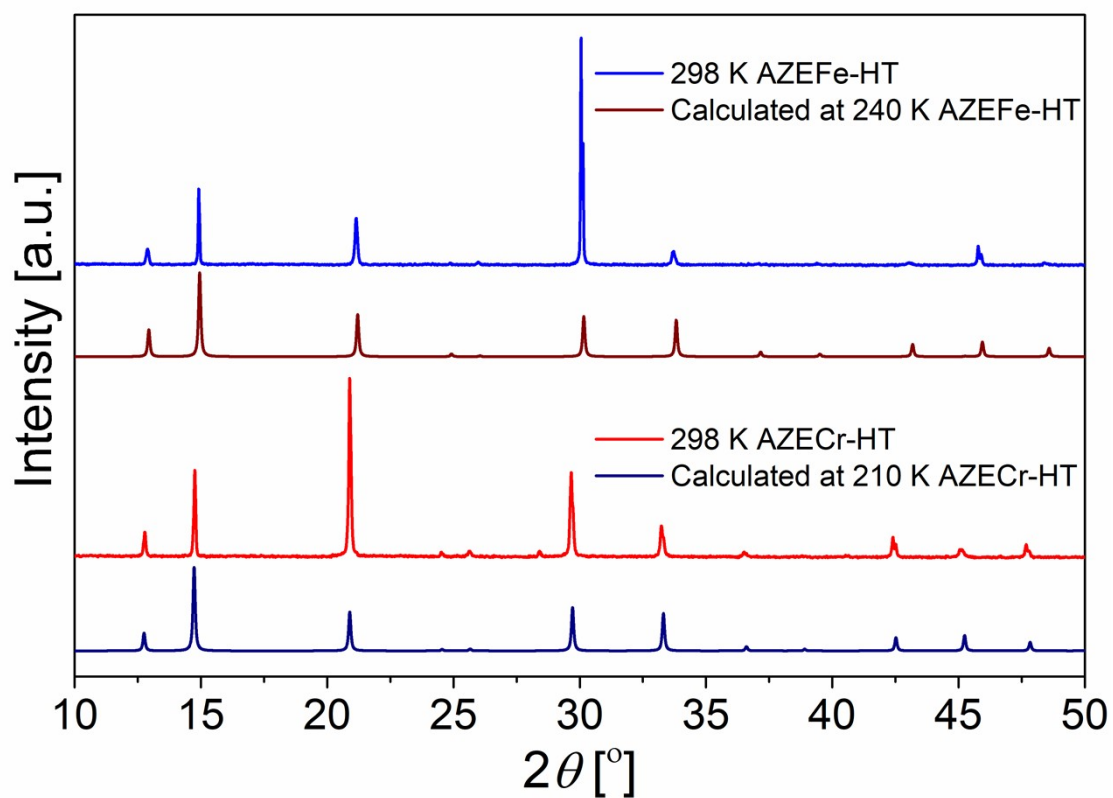
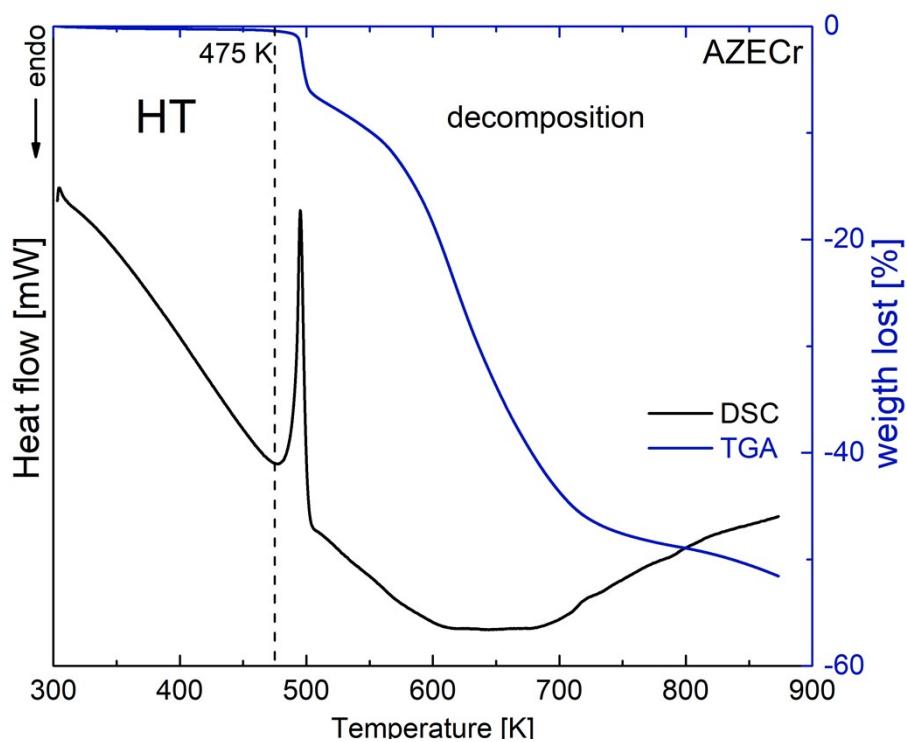


Fig. S1. Powder X-ray diffraction pattern for **AZEFe** and **AZECr** at room-temperature and calculated ones based on phase I (high-temperature) single-crystal structures.

a)



b)

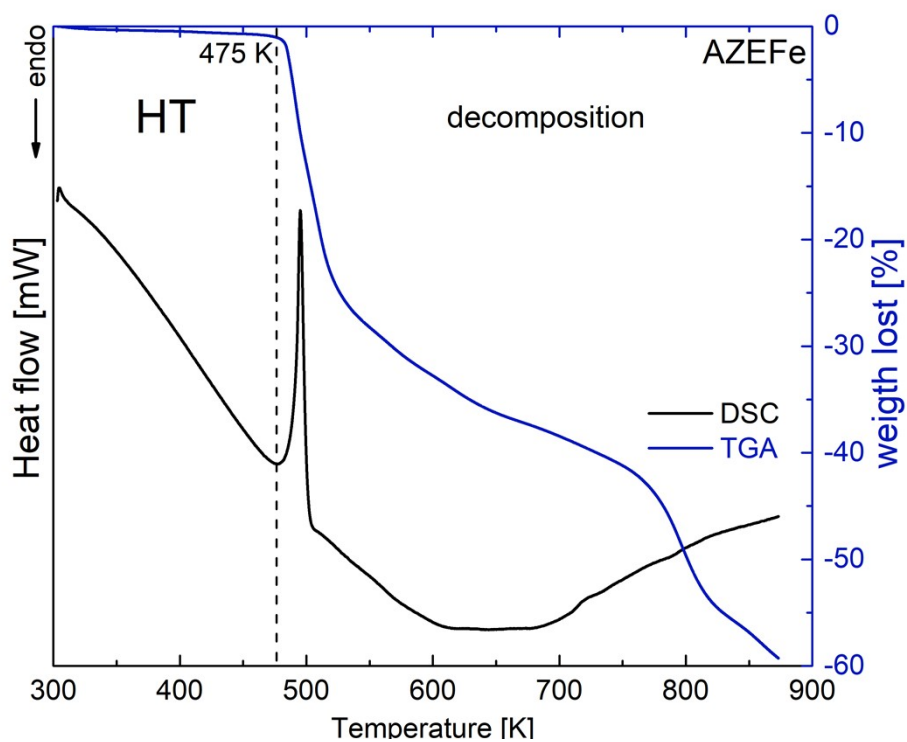


Fig. S2. The results of the simultaneous TGA/DSC analyses for a) **AZECr** (sample mass $m = 10.958$ mg, 5K/min.) and b) **AZEFe** (sample mass $m = 9.594$ mg, 5K/min.).

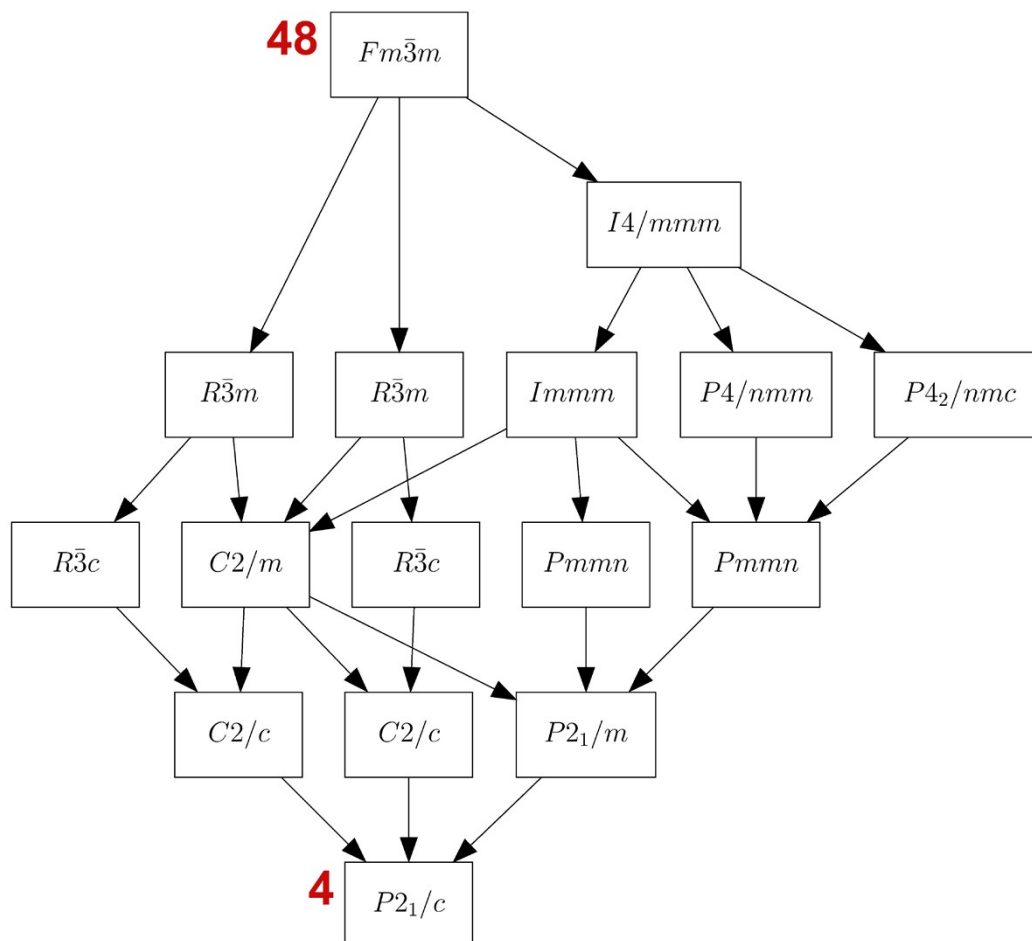


Fig. S3. The group-subgroup relation of the PT transition between HT and the LT phases of AZECr. The red numbers indicate total symmetry elements.

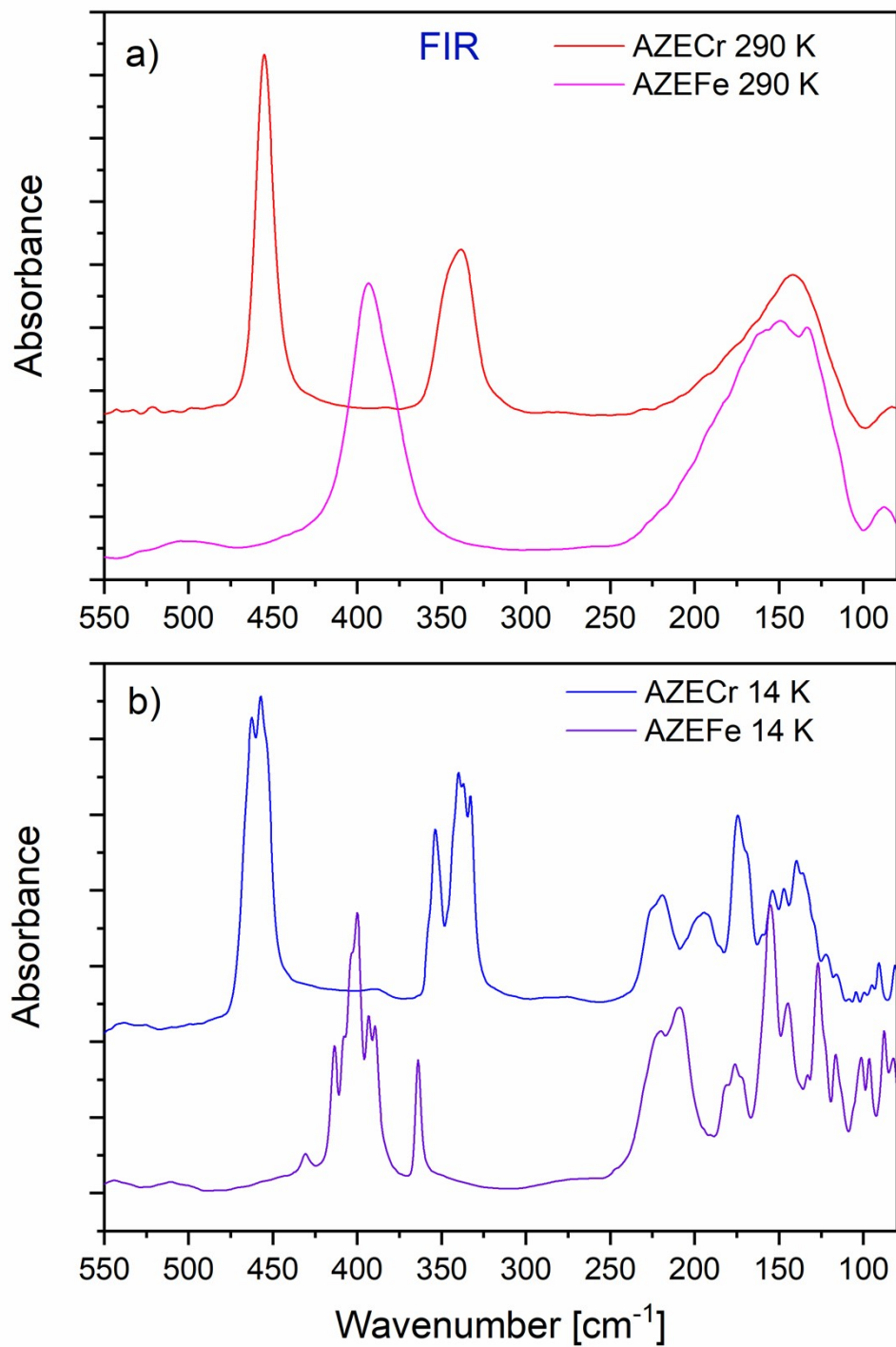


Fig. S4. Experimental Far Infrared spectra (FT-FIR) for **AZECr** and **AZEFe** at two extreme temperatures in the wavenumber range between 550 and 80 cm⁻¹.

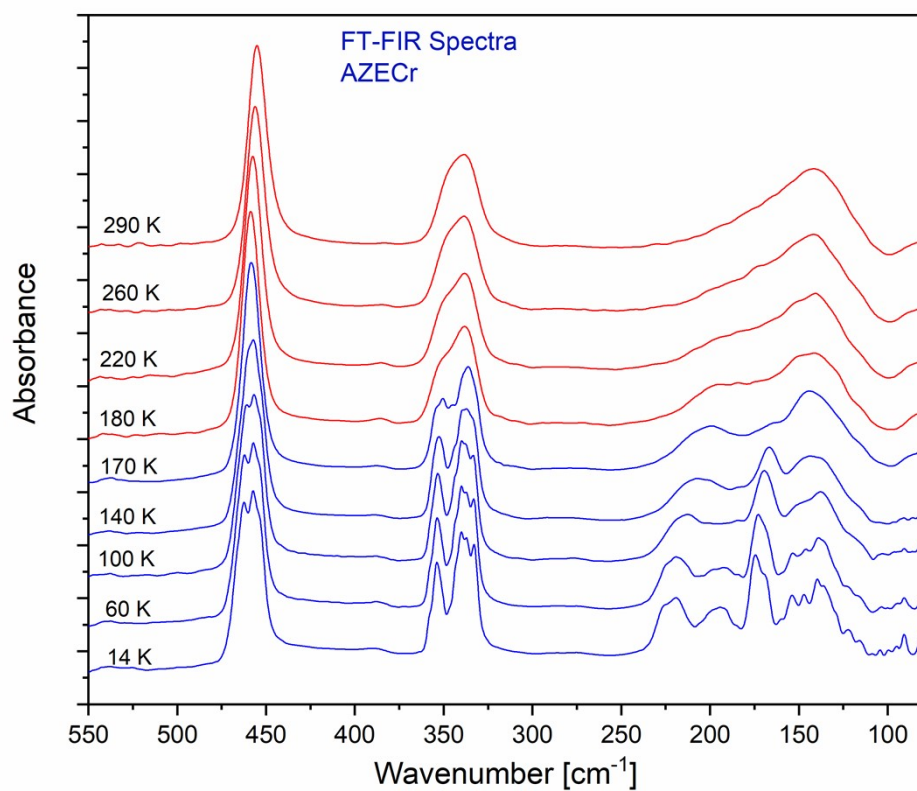


Fig. S5. FT-FIR spectra in the wavenumber range of 550–80 cm⁻¹ at different temperatures (during cooling of the **AZECr** sample). The spectra in the high and low temperature phases were marked in red and blue colours, respectively.

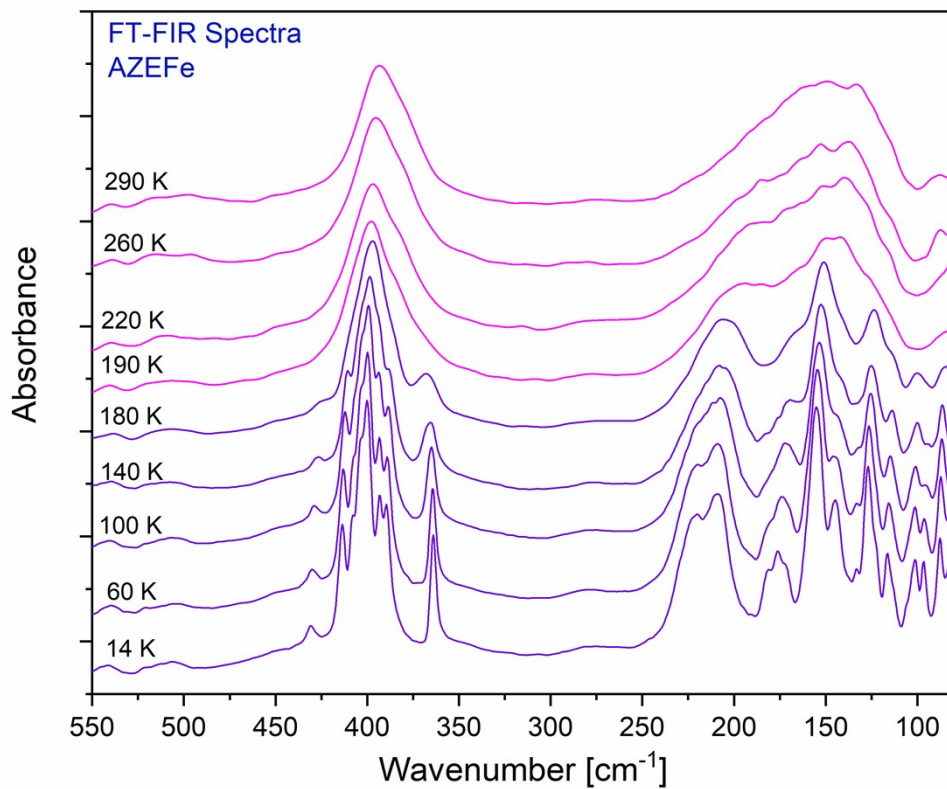


Fig. S6. FT-FIR spectra in the wavenumber range of 550–80 cm^{-1} at different temperatures (during cooling of the **AZEFe** sample). The spectra in the high and low temperature phases were marked in magenta and violet colours, respectively.

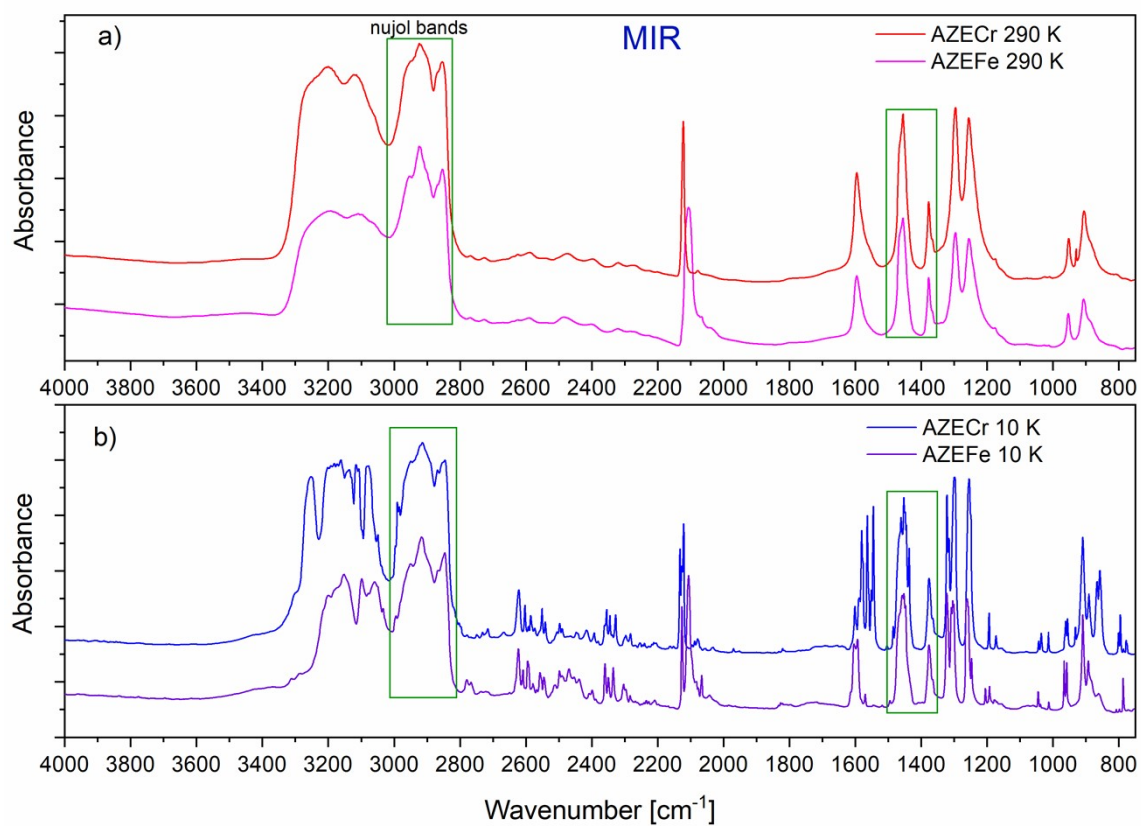


Fig. S7. Experimental Middle Infrared spectra (FT-MIR) for **AZECr** and **AZEFe** at two extreme temperatures in the wavenumber range between 4000 and 750 cm⁻¹.

Table S1. Crystal data and brief information about structure refinement results for **AZECr-HT**, **AZECr-LT**, and **AZFe-HT** at 210 K, 120, and 240 K, respectively.

	AZECr-HT	AZECr-LT	AZFe-HT
Crystal data			
Chemical formula	[C ₃ H ₈ N] ₂ [KCr(CN) ₆]		[C ₃ H ₈ N] ₂ [KFe(CN) ₆]
M_r	363.43		367.28
Crystal system, space group	Cubic, $Fm\bar{3}m$	Monoclinic, $P2_1/c$	Cubic, $Fm\bar{3}m$
Temperature (K)	210(2)	120(2)	240(2)
a, b, c (Å)	12.018(2), 12.018(2), 12.018(2)	14.120(3), 8.627(3), 14.871(2)	11.843(2), 11.843(2), 11.843(2)
β (°)	90.00	110.70(2)	90.00
V (Å ³)	1736(2)	1694(2)	1661(2)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.91		1.17
Crystal size (mm)	0.49 × 0.37 × 0.25	0.49 × 0.37 × 0.25	0.34 × 0.30 × 0.21
Data collection			
Diffractionmeter	KUMA KM4 with Sapphire CCD detector	KUMA KM4 with Sapphire CCD detector	Xcalibur, Ruby, Gemini ultra
Absorption correction	Multi-scan	Multi-scan	Analytical
T_{\min}, T_{\max}	0.790, 1.000	0.439, 1.000	0.714, 0.773
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3179, 149, 140	3114, 3114, 2192	1197, 143, 139
R_{int}	0.042	Dataset merged	0.019
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.676	0.606	0.681
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.098, 1.14	0.082, 0.249, 1.08	0.039, 0.096, 1.24
No. of reflections	149	3114	143
No. of parameters	19	204	19
No. of restraints	0	0	6
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.38, -0.32	1.68, -0.60	0.32, -0.72

Table S2. Hydrogen-bond geometry [\AA , $^\circ$] for **AZECr** at 120 K (**AZECr-LT**).

$D-H\cdots A$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1A—H1A1 \cdots N2 ⁱ	2.31	3.138(8)	151
N1A—H1A2 \cdots N4	2.20	3.000(8)	147
N1B—H1B1 \cdots N3	2.11	2.946(8)	152
N1B—H1B2 \cdots N5 ⁱⁱ	2.19	3.087(8)	169

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y+1, -z+1$.

Table S3. Selected bond lengths and the shortest Cr \cdots K distances (\AA) for **AZECr-LT** at 120 K.

Cr2 ⁱ \cdots K1 ⁱⁱ	5.8720(9)
Cr2 \cdots K1 ⁱⁱⁱ	5.9239(13)
Cr2 \cdots K1 ⁱ	5.9396(13)
Cr1 \cdots K1	5.9971(13)
Cr2 ⁱⁱ \cdots K1	6.0126(13)
Cr2 \cdots K1	6.0549(9)

Symmetry codes: (i) $x, y+1, z$; (ii) $x, -y+3/2, z+1/2$; (iii) $x, -y+1/2, z+1/2$.

Table S4. Comparison of the band positions in the infrared (FT-FIR, FT-MIR) spectra at the 290 K for **AZECr** and **AZEFc** compounds (vs-very strong, s-strong, m-medium, br-broad, sh-shoulder, w-weak, vw-very weak).

IR wavenumbers at 290 K [cm^{-1}]		Tentative assignments
AZECr	AZEFc	
3204 vs	3197 vs	ν_{as} (N–H) stretching
3119 vs	3104 vs	ν_{s} (N–H) stretching
2122 s	2106 s	ν (C–N) stretching
1595 s	1597 s	δ (NH ₂) bending
1297 s	1297 s	ω (CH ₂) wagging
1255 s	1255 s	ρ (CH ₂) rocking + ω (NH ₂) wagging
953 m	953 m	ν (C–C ring) stretching
929 w		ν (C–C ring) stretching
906 m	907 m	ν (C–C ring) stretching + ρ (NH ₂) rocking
455 m	505 vw, br	ν (M–C) stretching
339 m	393 m	δ (M–C–N) bending
141 m, br	161, 149, 133 m, br	δ (C–M–C) bending + ν_{L} (lattice)