**ELECTRONIC SUPPLEMENTARY INFORMATION**

X-ray Crystallography. Single crystals of **2** were obtained with the procedure described in Ref. [1] and were protected with vacuum grease until measurement. The selected crystal was mounted with low temperature epoxy resin to a graphite fibre to enable conduction cooling inside a vacuum chamber. Further details on the experimental setup have been described elsewhere.[2]

The most intense peaks in the diffraction pattern fit a tetragonal body-centered lattice with unit cell vectors ($\mathbf{a}_I$, $\mathbf{b}_I$, $\mathbf{c}_I$) similar to those reported by Peng's group ($a_I = b_I \sim 10.8$ Å, $c_I \sim 26.2$ Å at room temperature).[3] Solution and refinement in space-group $I4/m$ indeed affords the heavily disordered structure published by these authors.[3] Full indexing requires a primitive tetragonal lattice ($\mathbf{a}_P$, $\mathbf{b}_P$, $\mathbf{c}_P$) with $a_P = b_P = a_I\sqrt{2} \sim 15.3$ Å, $c_I = c_P$, and $\mathbf{a}_P$ and $\mathbf{b}_P$ directed along the bisectors of $\mathbf{a}_I$ and $\mathbf{b}_I$. However, systematic absences (*hkl*: *h+l and k+l* odd) are impossible for a tetragonal space group. Furthermore, among *hk*0 reflections only those with even *h and k* are observed, while 00*l* is of course observed only for even *l*. Monoclinic space-group $A2/a$ (*z* unique axis) pseudo-merohedrally twinned by 90° rotation along *z* gives exactly such systematic absences. Due to twinning, reflection *hkl* overlaps with *k−hl* and this adds intensity to the reflections of the prime component with *k+l* = odd, unless *h+l* is also odd. An *a*-type glide plane combined with an *A* lattice requires *h and k* to be even in observable *hk*0 reflections. Since twinning overlaps *hk*0 with *k−h*0, this condition remains valid also for the twinned sample. An obvious relabelling of unit cell axes to have *y* as the unique axis leads to space group $C2/c$, which was used for the final integration of data collection frames.
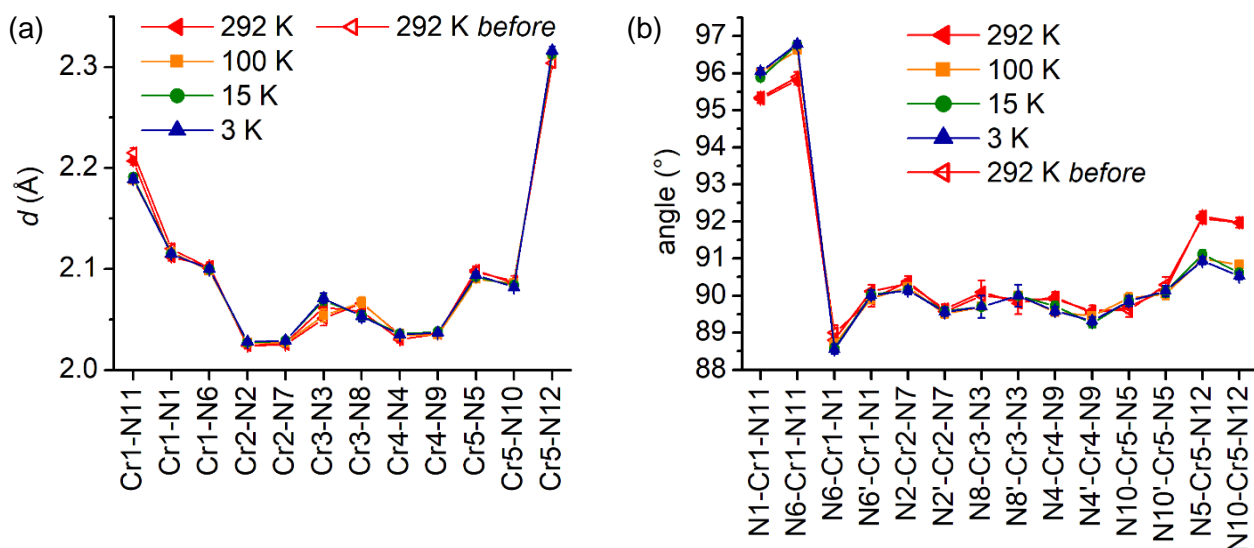
Fig. S1 (a) Cr-N distances and (b) *cis* N-Cr-N angles in **2** at different temperatures.
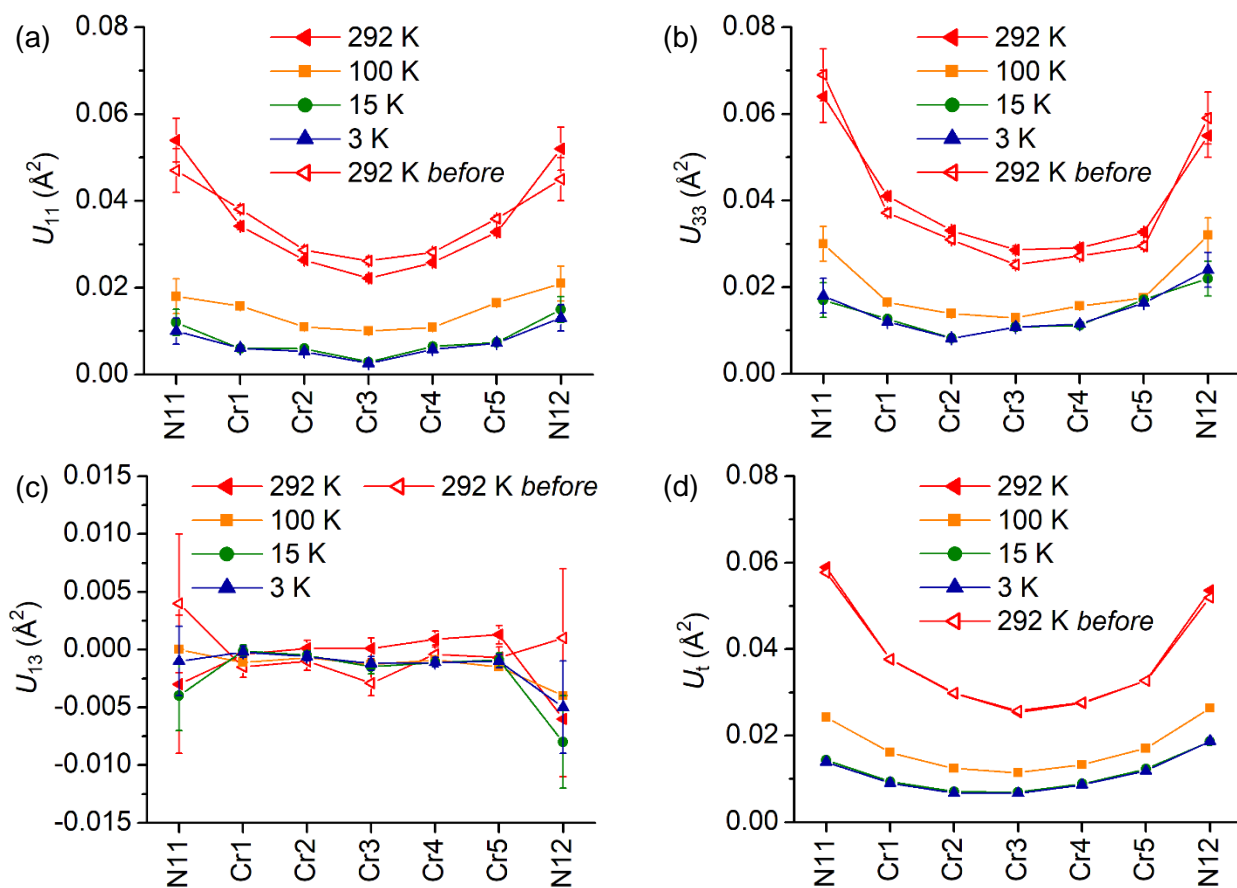
Fig. S2 (a) U_{11}, (b) U_{33}, (c) U_{13}, and (d) U_t values for metal atoms, N11, and N12 in **2** at different temperatures. U_t was obtained by averaging the principal mean-square atomic displacements orthogonal to *y*. Notice that $U_{12} = U_{23} = 0$ by symmetry.
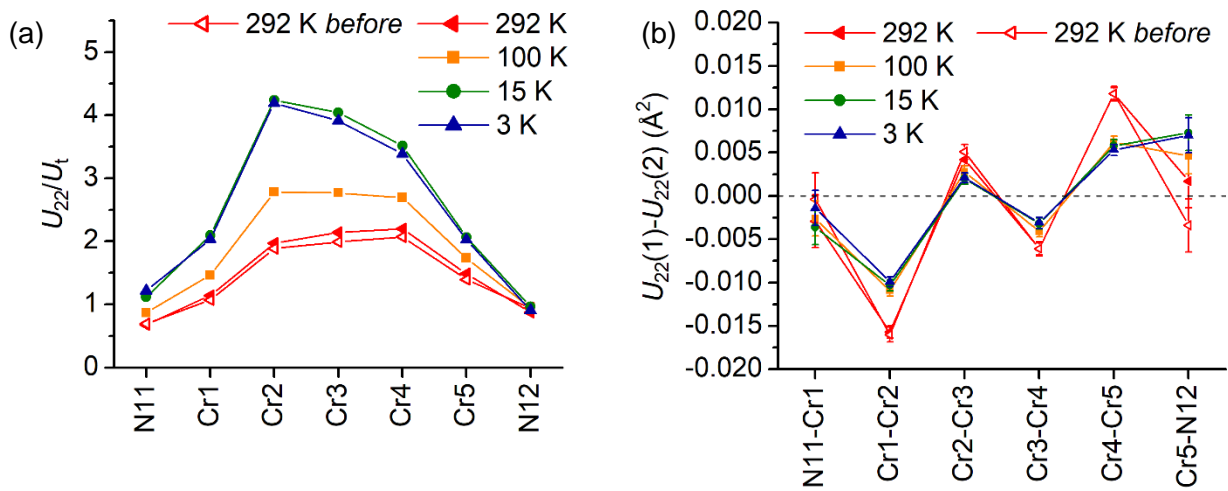
Fig. S3 (a) Prolateness of displacement ellipsoids and (b) difference between U_{22} values of neighbouring atoms in **2** at different temperatures.

Table S1 Crystal data and refinement parameters for **2** at different temperatures.

formula	$C_{62}H_{44}Cr_5N_{22}S_2$				
M (g mol^{-1})	1421.31				
T (K)	292[a]	100	15	3	292[b]
crystal system	monoclinic				
space group	$C2/c$ (No. 15)				
a (Å)	15.2547(4)	15.1037(4)	15.0601(4)	15.0605(4)	15.2426(3)
b (Å)	26.2195(8)	26.1632(8)	26.1633(7)	26.1672(7)	26.2039(7)
c (Å)	15.2032(4)	15.0198(4)	14.9768(4)	14.9728(4)	15.2056(3)
α (°)	90.000				
β (°)	90.0121(16)	90.0189(16)	90.0266(16)	90.023(2)	90.0060(10)
γ (°)	90.000				
V (Å^3)	6080.8(3)	5935.2(3)	5901.2(3)	5900.6(3)	6073.4(2)
Z	4				
ρ_{calcd} (g cm^{-3})	1.553	1.591	1.600	1.600	1.554
crystal size (mm^3)	0.38×0.25×0.25				
λ (Å)	0.71073				
μ (mm^{-1})	0.996	1.020	1.026	1.026	0.997
θ_{max} (°)	26.382	26.364	26.377	26.376	26.368
refls. coll./indep.	5214/5214	5092/5092	5069/5069	5064/5064	5213/5213
params./restrs.	417/466				
$R1$	0.0704	0.0426	0.0420	0.0413	0.0564
$wR2$	0.1585	0.1008	0.1023	0.1005	0.1159
$R1$ [$I > 2\sigma(I)$]	0.0506	0.0335	0.0349	0.0343	0.0360
$wR2$ [$I > 2\sigma(I)$]	0.1344	0.0921	0.0961	0.0942	0.0985
GOF	1.061	1.042	1.051	1.050	1.016
res. max/min (eÅ^{-3})	0.706/−1.047	0.789/−1.158	0.795/−1.064	0.754/−1.042	0.299/−0.833

[a]Before cooling down. [b]After cooling down.

Table S2 Cr-N distances (Å) in **2** at different temperatures (K).

T	Cr1-N11[a]	Cr1-N1	Cr1-N6	Cr2-N2	Cr2-N7	Cr3-N3	Cr3-N8	Cr4-N4	Cr4-N9	Cr5-N5	Cr5-N10	Cr5-N12[a]
292[b]	2.215(5)	2.120(5)	2.101(5)	2.024(3)	2.025(3)	2.051(7)	2.066(6)	2.035(3)	2.036(3)	2.097(5)	2.088(5)	2.304(5)
3	2.189(4)	2.115(3)	2.100(3)	2.028(2)	2.029(2)	2.071(5)	2.053(5)	2.035(2)	2.037(2)	2.094(3)	2.082(3)	2.316(4)
15	2.191(4)	2.115(3)	2.100(3)	2.027(2)	2.029(2)	2.069(5)	2.054(5)	2.036(2)	2.038(2)	2.092(3)	2.084(3)	2.313(4)
100	2.188(4)	2.117(3)	2.098(3)	2.027(2)	2.027(2)	2.054(6)	2.067(5)	2.034(2)	2.035(2)	2.090(3)	2.086(3)	2.312(4)
292[c]	2.207(4)	2.112(4)	2.103(4)	2.024(3)	2.027(3)	2.062(6)	2.058(6)	2.030(3)	2.036(3)	2.099(4)	2.086(4)	2.304(4)

[a]Nitrogen donor of isothiocyanato ligand. [b]Before cooling down. [c]After cooling down.

Table S3 Deviation (Å) of Cr atoms from the mean plane through their equatorial N donors in **2** at different temperatures (K).[a]

T	Cr1	Cr2	Cr3	Cr4	Cr5
292[b]	−0.2067(21)	0.0412(20)	−0.0634(21)	0.1363(20)	0.0741(21)
3	−0.2352(16)	0.1031(16)	−0.1102(17)	0.1986(16)	0.0267(16)
15	−0.2321(16)	0.0978(16)	−0.1054(17)	0.1936(16)	0.0317(16)
100	−0.2318(16)	0.0961(16)	−0.1052(17)	0.1900(16)	0.0333(16)
292[c]	−0.2043(18)	0.0429(17)	−0.0627(19)	0.1356(17)	0.0753(18)

[a]A positive deviation is a displacement along the Cr1-Cr5 vector. [b]Before cooling down.
[c]After cooling down.

Table S4 Mean-square displacement amplitudes (Å^2) in **2** at different temperatures (K).[a]

T	$U_{11}(\text{N11}^b)$	$U_{11}(\text{Cr1})$	$U_{11}(\text{Cr2})$	$U_{11}(\text{Cr3})$	$U_{11}(\text{Cr4})$	$U_{11}(\text{Cr5})$	$U_{11}(\text{N12}^b)$
292[c]	0.047(5)	0.0381(9)	0.0287(8)	0.0262(9)	0.0282(7)	0.0359(8)	0.045(5)
3	0.010(3)	0.0061(5)	0.0053(4)	0.0026(6)	0.0058(4)	0.0073(5)	0.013(3)
15	0.012(3)	0.0060(5)	0.0060(4)	0.0029(6)	0.0065(5)	0.0074(5)	0.015(3)
100	0.018(4)	0.0158(6)	0.0110(5)	0.0100(7)	0.0109(5)	0.0165(6)	0.021(4)
292[d]	0.054(5)	0.0342(8)	0.0264(7)	0.0222(8)	0.0258(7)	0.0328(8)	0.052(5)

T	$U_{22}(\text{N11}^b)$	$U_{22}(\text{Cr1})$	$U_{22}(\text{Cr2})$	$U_{22}(\text{Cr3})$	$U_{22}(\text{Cr4})$	$U_{22}(\text{Cr5})$	$U_{22}(\text{N12}^b)$
292[c]	0.040(3)	0.0404(6)	0.0564(6)	0.0513(6)	0.0574(6)	0.0456(6)	0.049(3)
3	0.017(2)	0.0184(4)	0.0283(4)	0.0262(4)	0.0293(5)	0.0240(4)	0.017(2)
15	0.016(2)	0.0196(4)	0.0299(5)	0.0279(4)	0.0311(5)	0.0253(5)	0.018(2)
100	0.021(2)	0.0236(4)	0.0345(5)	0.0317(4)	0.0358(5)	0.0296(5)	0.025(2)
292[d]	0.040(3)	0.0429(5)	0.0586(5)	0.0544(5)	0.0605(5)	0.0487(5)	0.047(3)

T	$U_{33}(\text{N11}^b)$	$U_{33}(\text{Cr1})$	$U_{33}(\text{Cr2})$	$U_{33}(\text{Cr3})$	$U_{33}(\text{Cr4})$	$U_{33}(\text{Cr5})$	$U_{33}(\text{N12}^b)$
292[c]	0.069(6)	0.0372(9)	0.0310(8)	0.0252(9)	0.0272(7)	0.0295(8)	0.059(6)
3	0.018(4)	0.0120(6)	0.0082(5)	0.0108(7)	0.0115(5)	0.0164(6)	0.024(4)
15	0.017(4)	0.0127(6)	0.0082(5)	0.0108(7)	0.0112(5)	0.0171(6)	0.022(4)
100	0.030(4)	0.0165(6)	0.0139(5)	0.0129(7)	0.0157(5)	0.0175(6)	0.032(4)
292[d]	0.064(6)	0.0410(9)	0.0331(7)	0.0286(9)	0.0291(7)	0.0327(8)	0.055(5)

T	$U_{13}(\text{N11}^b)$	$U_{13}(\text{Cr1})$	$U_{13}(\text{Cr2})$	$U_{13}(\text{Cr3})$	$U_{13}(\text{Cr4})$	$U_{13}(\text{Cr5})$	$U_{13}(\text{N12}^b)$
292[c]	0.004(6)	–0.0015(9)	–0.0010(8)	–0.0029(11)	–0.0004(8)	–0.0007(9)	0.001(6)
3	–0.001(3)	–0.0002(5)	–0.0006(4)	–0.0012(6)	–0.0011(4)	–0.0010(6)	–0.005(4)
15	–0.004(3)	–0.0001(5)	–0.0005(4)	–0.0015(6)	–0.0011(4)	–0.0009(6)	–0.008(4)
100	0.000(4)	–0.0011(6)	–0.0007(4)	–0.0013(6)	–0.0009(4)	–0.0015(6)	–0.004(4)
292[d]	–0.003(6)	–0.0004(8)	0.0001(7)	0.0001(9)	0.0009(7)	0.0013(8)	–0.006(5)

T	$U_{t}(\text{N11}^b)$	$U_{t}(\text{Cr1})$	$U_{t}(\text{Cr2})$	$U_{t}(\text{Cr3})$	$U_{t}(\text{Cr4})$	$U_{t}(\text{Cr5})$	$U_{t}(\text{N12}^b)$
292[c]	0.0577	0.0377	0.0299	0.02575	0.0277	0.0327	0.05195
3	0.01395	0.00905	0.00675	0.0067	0.00865	0.01185	0.01875
15	0.01435	0.00935	0.00705	0.0069	0.00885	0.01225	0.01865
100	0.0242	0.0161	0.0124	0.01145	0.0133	0.01705	0.02635
292[d]	0.05895	0.0376	0.02975	0.0254	0.0275	0.03275	0.0536

[a]By symmetry, $U_{12} = U_{23} = 0$ and U_{22} is a principal component of the U-tensor. [b]Nitrogen donor of isothiocyanato ligand. [c]Before cooling down. [d]After cooling down.

References

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