Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Three-Step Change in Uniaxial Negative Thermal Expansion by Switching Supramolecular Motion Modes in Ferromagnetically-Coupled Nickel Dithiolate Lattice

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§Experimental Section

General.

All reagents purchased were used without further purification. Elemental analyses were carried out by using a CHN analyzer (CE440, Exeter Analytical, Inc.) at Global Facility Center, Hokkaido University.

Synthesis.

Precursor of $(TBA^+)[Ni(dmit)_2]^-$ (TBA^+= tetra-*n*-butylammonium$^+$) was prepared using a procedure reported in the literature.[S1] A 42 % HBF_4 (602 mg, 2.88 mmol) was added to a solution of 2,2'-oxybis(ethylamine) (407 mg, 1.44 mmol) in CH_3CN (2 mL). The mixture solution was stirred at r.t. for 1 h. The solvent was removed under reduced pressure to obtain a white solid. The solid was recrystallized by $CHCl_3/CH_3OH$ to obtain a $((^+H_3N\text{-}C_2H_4)_2O)(BF_4^-)_2$. A solution of $(TBA^+)[Ni(dmit)_2]^-$ (20 mg, 0.04 mmol) in CH_3CN (20 mL) was added to a solution of [18]crown-6 (94 mg, 0.35 mmol) and $((^+H_3N\text{-}C_2H_4)_2O)(BF_4^-)_2$ (37 mg, 0.13 mmol) in CH_3CN (19 mL) and CH_3OH (1 mL). Crystal **1** was obtained by slow diffusion over a period of 4 days. Elemental analysis for crystal **1**: calcd. for $C_{40}H_{62}N_2Ni_2O_{13}S_{20}$: C: 31.25%, H: 4.06%, N: 1.82%, Found : C: 30.97%, H: 3.93%, N: 1.73%.

Crystal structure determination.

Temperature-dependent structural analysis of the single crystal **1** was performed using a Rigaku XtaLAB-Synergy diffractometer with a HyPix-6000 area detector and multilayer mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). A single

crystal was mounted on a MicroMountsTM tip (MiTeGen) with Paratone 8277 (Hampton Research). The temperature dependence was measured using the same crystal. For the reflection data, multi-scan absorption corrections were applied to the crystal. Data collection was performed and processed using the CrysAlisPRO interface (Oxford Diffraction, Agilent Technologies UK Ltd). The initial structure was solved using SHELXT,[S2] and structural refinement was performed using OLEX2 software.[S3] Anisotropic refinement was applied to all atoms, except for the hydrogen atoms. Cif files are deposited in Cambridge The Cambridge Crystallographic Data Centre (CCDC) with CCDC numbers 2384649, 2384650, 2384651, 2384652, 2384653, 2384654, 2384655, 2384656, 2384657, 2384658, 2384659, 2384660, 2384661, and 2384662 for crystal **1** at 113, 123, 133,143, 153, 163, 173, 183, 193, 213, 233, 253, 273, and 293 K, respectively. The CLTE was calculated using the *PASCal* web program based on the unit cell parameters at each temperature.[S4]

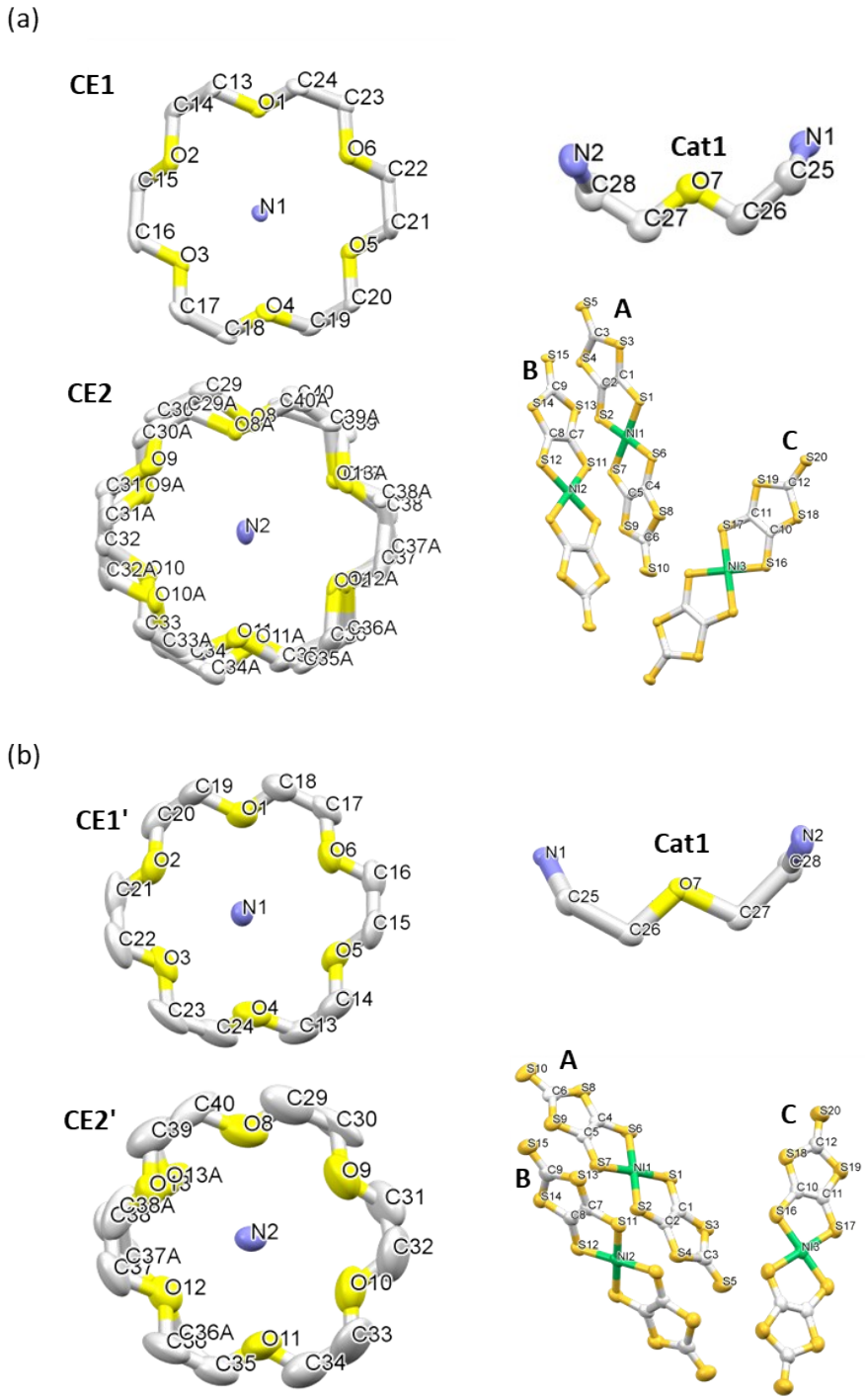
Physical Property Measurements.

Differential scanning calorimetry (DSC) measurements were carried out using a Q2000 differential scanning calorimeter (TA Instruments) in the temperature range from 180 to 300 K at a scanning rate of 5 K min^{-1} under a flow of N_2 gas (50 mL min^{-1}). Temperature- and frequency-dependence of dielectric constant was measured using an impedance analyzer 4294A (Agilent) with the four-probe AC impedance method at a frequency range of 10^3–10^4 Hz. The temperature was controlled using cryostats with temperature controller models 331 (Lake Shore Cryotronics Inc.). Electrical contacts were prepared using a silver paste (D-500,

Fujikura Kasei Co.,Ltd.) to attach the 25 μm ϕ gold wires to the single crystal. The temperature-dependent molar magnetic susceptibility (χ_m) for polycrystalline sample of **1** was measured using a Quantum Design MPMS-3 SQUID magnetometer. Prior to sample measurement, the magnetic susceptibility of the sample holder (aluminum film) was measured under identical conditions, then the susceptibility of the holder was subtracted from the gram susceptibility as the paramagnetic contribution. The diamagnetic component in the sample was subtracted based on Pascal's constant, -7.1674×10^{-4} cm^3 mol^{-1}.[S5] A magnetic field of 1 T was applied for all temperature-dependent measurements. Molecular weight of 1537.52 g mol^{-1} (the χ_m for two $[Ni(dmit)_2]^-$ molecules) was used for calculation of χ_m of crystal **1**.

Theoretical calculation

The extended Hückel molecular orbital method within the tight-binding approximation was applied to calculate the transfer integral (*t*) data between the $[Ni(dmit)_2]^-$ anions in crystal **1**. The lowest unoccupied molecular orbital of the $[Ni(dmit)_2]^-$ molecule was used as the basis function. According to the literature, semiempirical parameters for Slater-type atomic orbitals were obtained.[S6] The *t* values between each pair of molecules were assumed to be proportional to the overlap integral (*S*) according to the equation $t = -10S$ (eV).



§Figure S1. Crystallographically independent structures of crystal **1** at 113 K (a) and 213 K (b). The Ni, S, C, N, and O atoms are depicted in green, orange, gray, blue, and yellow, respectively. All molecules are depicted as ellipsoid models. Hydrogen atoms are omitted for clarity.

§Table S1. Distances and angles for N-H•••O hydrogen bonding.

	Contacted atoms					
	N1-H1B•••O1			N1-H1C•••O3		
T **/ K**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**
113	2.881(3)	2.019	157.700	2.911(4)	2.085	150.5
123	2.881(3)	2.017	158.070	2.91(4)	2.083	150.56
133	2.883(3)	2.018	158.260	2.912(4)	2.085	150.49
143	2.881(3)	2.023	156.730	2.909(4)	2.086	149.8
153	2.880(3)	2.023	156.550	2.91(4)	2.087	149.73
163	2.883(3)	2.028	155.910	2.912(4)	2.093	149.11
173	2.883(3)	2.035	154.500	2.913(4)	2.098	148.44
183	2.881(4)	2.029	155.280	2.913(4)	2.095	148.92
193	2.881(4)	2.039	153.230	2.916(4)	2.106	147.76
213	2.918(6)	2.111	148.730	2.888(5)	2.044	155.88
233	2.917(4)	2.122	146.840	2.885(4)	2.055	152.88
253	2.920(4)	2.130	145.910	2.887(4)	2.068	150.9
273	2.924(5)	2.144	145.910	2.892(5)	2.081	151.07
293	2.916(5)	2.138	145.760	2.898(5)	2.086	151.34

	Contacted atoms					
	N1-H1A•••O5			N2-H2C•••O8		
T **/ K**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**
113	2.917(4)	2.04	161.4	2.99(2)	2.15	154.8
123	2.918(4)	2.039	161.96	2.987(2)	2.143	153.68
133	2.92(4)	2.041	162.18	2.973(2)	2.136	152.52
143	2.914(4)	2.039	160.87	2.987(2)	2.146	153.32
153	2.914(4)	2.039	160.91	2.973(2)	2.13	153.73
163	2.917(4)	2.043	160.63	2.989(2)	2.152	152.54
173	2.917(4)	2.049	159.12	2.994(2)	2.18	148.58
183	2.917(4)	2.046	159.77	2.979(2)	2.158	149.53
193	2.917(4)	2.054	157.79	2.988(2)	2.187	146.5
213	2.919(5)	2.056	160.33	2.946(7)	2.178	142.96
233	2.927(4)	2.075	157.47	2.954(6)	2.19	142.26
253	2.927(4)	2.082	156.02	2.948(6)	2.207	139.3
273	2.932(5)	2.097	155.71	2.954(6)	2.211	140.68

293	2.925(5)	2.086	156.61	2.952(6)	2.216	139.73

	Contacted atoms					
	N2-H2A•••O10			N2-H2B•••O12		
T **/ K**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**
113	2.918(9)	2.112	147.1	2.88(2)	2.02	158.8
123	2.924(1)	2.122	146.32	2.888(2)	2.022	158.42
133	2.948(1)	2.151	145.67	2.824(2)	1.959	157.99
143	2.945(1)	2.147	145.88	2.884(2)	2.024	156.97
153	2.948(1)	2.15	146.04	2.893(2)	2.036	156.22
163	2.958(1)	2.165	145.14	2.886(3)	2.032	155.67
173	2.95(1)	2.177	142.42	2.929(2)	2.08	154.75
183	2.971(1)	2.189	143.62	2.924(3)	2.088	152.34
193	2.984(1)	2.215	141.82	2.89(2)	2.066	150.09
213	2.919(7)	2.097	151.31	2.881(5)	2.089	146.44
233	2.918(7)	2.103	150.12	2.891(5)	2.105	145.34
253	2.923(7)	2.13	146.59	2.895(5)	2.138	141.19
273	2.892(7)	2.081	151.07	2.889(5)	2.128	142.93
293	2.898(7)	2.086	151.34	2.90(5)	2.149	141.57

	Contacted atoms					
	N2-H2C•••O8A			N2-H2A•••O10A		
T **/ K**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**
113	2.74(2)	1.86	160.5	2.94(1)	2.06	163
123	2.761(2)	1.89	159.56	2.929(1)	2.048	162.49
133	2.767(2)	1.9	158.45	2.915(1)	2.036	161.83
143	2.742(2)	1.876	158.38	2.905(1)	2.027	161.8
153	2.756(2)	1.888	158.71	2.90(2)	2.021	161.9
163	2.741(2)	1.878	157.65	2.889(2)	2.017	160.21
173	2.728(2)	1.877	154.72	2.895(2)	2.027	158.94
183	2.75(3)	1.896	155.22	2.866(2)	1.994	159.84
193	2.743(3)	1.903	152.66	2.868(2)	2.005	157.59

	Contacted atoms		
	N2-H2B•••O12A		
T **/ K**	**N•••O distance(Å)**	**H•••O distance(Å)**	**N-H•••O angle(°)**
113	2.95(2)	2.07	159.9
123	2.945(2)	2.077	159.16
133	3.008(2)	2.146	157.75
143	2.95(2)	2.079	159.75
153	2.93(4)	2.052	161.68
163	2.946(3)	2.071	161.01
173	2.894(3)	2.039	156.04
183	2.885(4)	2.01	161.03
193	2.929(4)	2.064	158.51

§Table S2. Distances and angles for C-H•••O interactions between crown ethers at 113 and 143 K.

Contacted units	**list of atoms**	**C•••O distance**	**H•••O distance**	**C-H•••O angle**
113 K				
CE1•••CE1	C16-H16B•••O1	3.570(5)	2.666	152.04
CE1•••CE1	C17-H17A•••O5	3.628(6)	2.796	142.04
CE2A•••CE2A	[a] C40A-H40D•••O9A	3.66(2)	2.794	146
CE2B•••CE2B	C40A-H40D•••O9A	3.61(1)	2.743	146.7
CE2A•••CE2A	C29A-H29A•••O13A	3.61(1)	2.764	143.6
143 K				
CE1•••CE1	[a] C16-H16B•••O1	3.576(5)	2.672	152
CE2A•••CE2A	C30-H30B•••O12	3.89(3)	2.987	145
CE2A•••CE2A	C39-H39A•••O10	3.66(2)	2.805	152
CE2B•••CE2B	C40A-H40D•••O9A	3.61(1)	2.734	147.9
CE2B•••CE2B	C29A-H29C•••O13A	3.62(1)	2.775	143.2

[a] C-H•••O interactions in a complementary manner.

§Table S3. Distance between sulfur•••sulfur atoms less than the sum of the van der Waals radii of two sulfur between two [Ni(dmit)$_2$] anions.

	Contacted units				
	A•••A		**A•••B**	**A•••C**	**B•••C**
	Distance between contacted atoms / Å				
***T* / K**	S7•••S9	S7•••S7	S3•••S14	S1•••S18	S12•••S18
113	3.45(1)	3.43(1)	3.637(1)	3.563(2)	3.573(2)
123	3.452(2)	3.435(1)	3.638(2)	3.568(2)	3.575(2)
133	3.457(2)	3.441(1)	3.639(2)	3.575(2)	3.577(2)
143	3.455(2)	3.444(1)	3.636(2)	3.576(2)	3.572(2)
153	3.459(2)	3.449(1)	3.638(2)	3.583(2)	3.574(2)
163	3.462(2)	3.454(1)	3.638(2)	3.59(2)	3.574(2)
173	3.468(2)	3.46(1)	3.642(2)	3.599(2)	3.575(2)
183	3.469(2)	3.466(1)	3.644(2)	3.609(2)	3.575(2)
193	3.475(2)	3.473(1)	3.645(2)	3.621(2)	3.576(2)
	Distance between contacted atoms / Å				
	S6•••S8	S6•••S6	S6•••S13	S5•••S14	S14•••S19
213	3.489(2)	3.491(2)	3.637(2)	3.835(2)	3.581(2)
233	3.50(2)	3.503(1)	3.651(2)	3.837(2)	3.58(2)
253	3.507(2)	3.517(1)	3.662(2)	3.838(2)	3.579(2)
273	3.508(2)	3.523(1)	3.67(2)	3.844(2)	3.579(2)
293	3.52(2)	3.538(1)	3.679(2)	3.849(2)	3.586(2)

§Table S4. Distances and angles for C-H•••S interactions between cation and anion **C**.

	Contacted atoms C27-H27A•••S19		
T **/ K**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**
113	3.735(5)	2.852	148.96
123	3.74(5)	2.858	148.8
133	3.742(5)	2.857	149.18
143	3.74(5)	2.853	149.39
153	3.743(5)	2.854	149.71
163	3.749(5)	2.862	149.47
173	3.753(5)	2.863	149.92
183	3.755(5)	2.865	149.98
193	3.764(5)	2.871	150.32
	Contacted atoms C27-H27B•••S16		
	C•••S distance(Å)	**H•••S distance(Å)**	**C-H•••S angle(°)**
213	3.781(5)	2.897	150.45
233	3.798(5)	2.91	151.13
253	3.804(5)	2.914	151.48
273	3.82(5)	2.938	151.83
293	3.831(5)	2.945	152.32

§Table S5. Distances and angles for C-H•••C interactions between cation and anion **C**.

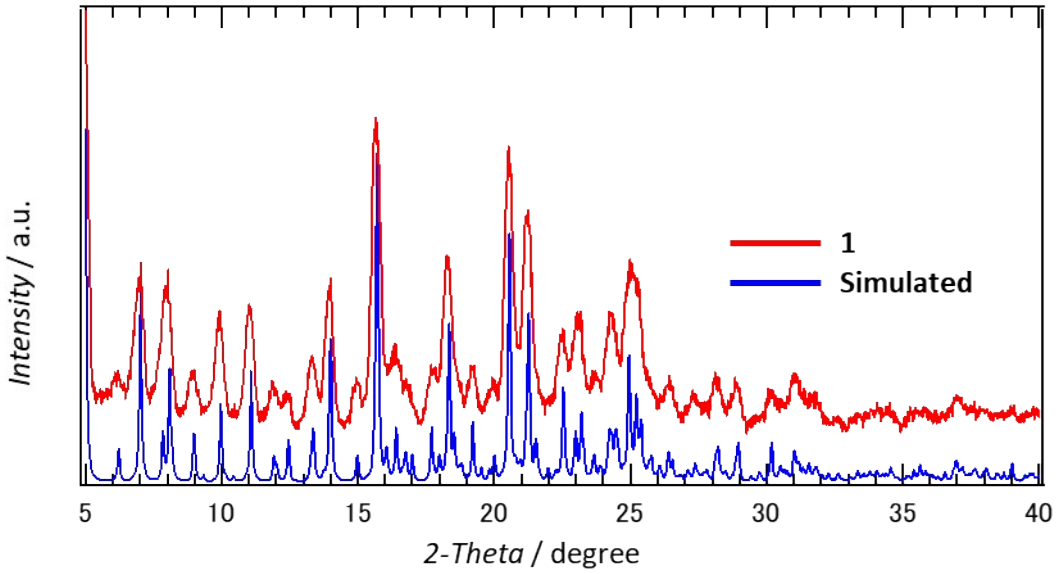
	Contacted atoms C27-H27A•••C11		
T **/ K**	**C•••C distance(Å)**	**H•••C distance(Å)**	**C-H•••C angle(°)**
113	3.765(6)	2.82	159.84
123	3.765(6)	2.821	159.81
133	3.764(6)	2.819	159.69
143	3.759(6)	2.816	159.42
153	3.757(6)	2.814	159.35
163	3.758(6)	2.814	159.45
173	3.759(6)	2.817	159.19
183	3.754(6)	2.811	159.41
193	3.757(6)	2.815	159.13
	Contacted atoms C27-H27B•••C10		
	C•••C distance(Å)	**H•••C distance(Å)**	**C-H•••C angle(°)**
213	3.754(6)	2.818	159.8
233	3.76(6)	2.823	160.09
253	3.752(6)	2.818	159.51
273	3.761(6)	2.836	159.86
293	3.766(6)	2.836	160.78

§Table S6. Distances and angles for C-H•••S interactions between **CE1** and anion **A**.

	Contacted atoms					
	C18-H18B•••S2			C20-H20A•••S10		
T **/ K**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**
113	3.849(4)	2.966	149.08	3.749(5)	2.853	150.8
123	3.851(4)	2.97	148.92	3.75(5)	2.852	151.1
133	3.858(4)	2.974	149.28	3.747(5)	2.85	151.01
143	3.852(4)	2.971	148.85	3.738(5)	2.843	150.64
153	3.855(4)	2.974	148.83	3.737(5)	2.841	150.67
163	3.859(5)	2.981	148.33	3.737(5)	2.843	150.5
173	3.865(5)	2.985	148.62	3.731(5)	2.84	150.11
183	3.864(5)	2.984	148.63	3.728(5)	2.837	150.11
193	3.864(5)	2.982	148.95	3.728(5)	2.836	150.18
	Contacted atoms					
	C23-H23A•••S4			C21-H21B•••S10		
	C•••S distance(Å)	**H•••S distance(Å)**	**C-H•••S angle(°)**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**
213	3.869(6)	2.994	149.29	3.718(7)	2.842	149.2
233	3.872(6)	2.996	149.49	3.718(6)	2.845	148.87
253	3.883(7)	3.006	149.54	3.711(6)	2.842	148.35
273	3.882(7)	3.011	150.09	3.706(6)	2.857	146.68
293	3.888(7)	3.018	149.82	3.706(6)	2.857	146.64

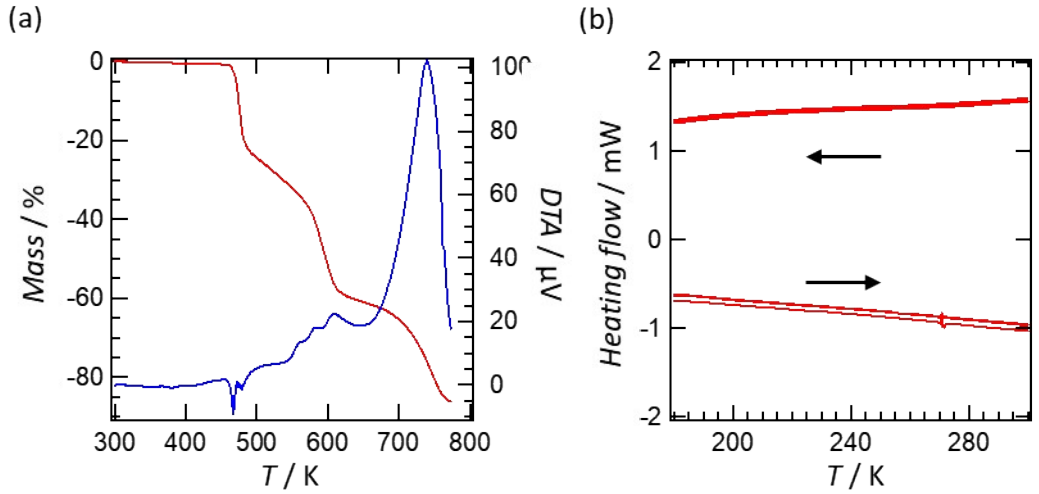
§Table S7. Distances and angles for C-H•••S interactions between **CE2** and anion **A**.

	Contacted atoms					
	C32-H32B•••S10			C35-H35B•••S6		
T **/ K**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**
113	3.71(2)	2.983	131.11	3.687(2)	2.81	148.05
123	3.709(2)	2.98	131.32	3.683(2)	2.804	148.29
133	3.711(2)	2.99	130.53	3.694(2)	2.808	149.17
143	3.704(2)	2.984	130.54	3.677(2)	2.792	149.06
153	3.691(2)	2.952	132.21	3.665(2)	2.795	146.89
163	3.699(2)	2.967	131.63	3.665(3)	2.796	146.76
173	3.696(2)	2.961	131.88	3.659(3)	2.764	150.62
183	3.707(2)	2.988	130.41	3.665(3)	2.784	148.56
193	3.702(2)	2.964	132.16	3.674(3)	2.767	152.41
	Contacted atoms					
	C40-H40B•••S10			C36-H36B•••S3		
	C•••S distance(Å)	**H•••S distance(Å)**	**C-H•••S angle(°)**	**C•••S distance(Å)**	**H•••S distance(Å)**	**C-H•••S angle(°)**
213	3.72(8)	2.929	138.54	3.348(1)	2.676	126.09
233	3.738(8)	2.95	138.24	3.349(1)	2.656	127.93
253	3.738(7)	2.944	138.83	3.364(1)	2.692	126.19
273	3.754(8)	2.976	138.21	3.359(1)	2.689	126.67
293	3.762(8)	2.97	139.62	3.369(2)	2.684	128

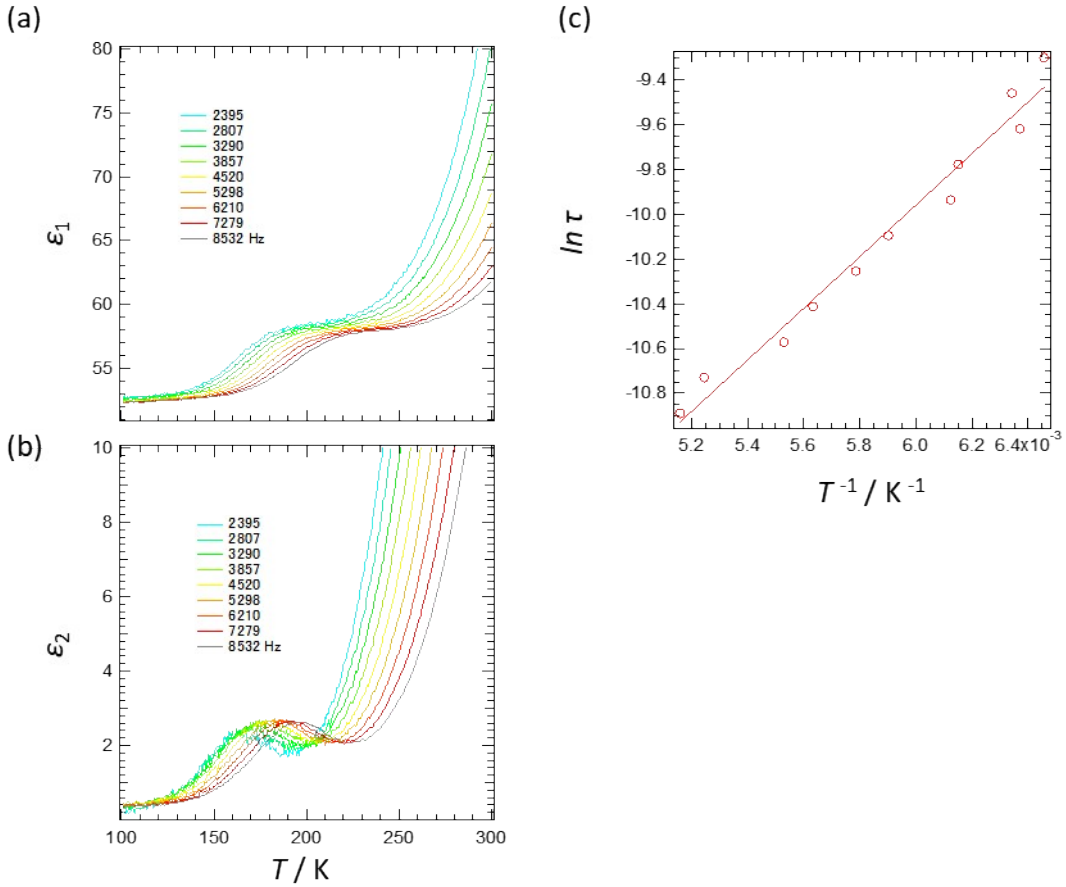


§Figure S2. Powder X-ray diffraction (PXRD) pattern of crystal **1** measured at room temperature. Simulated patterns were compared with the experimental ones to confirm purity of the sample.

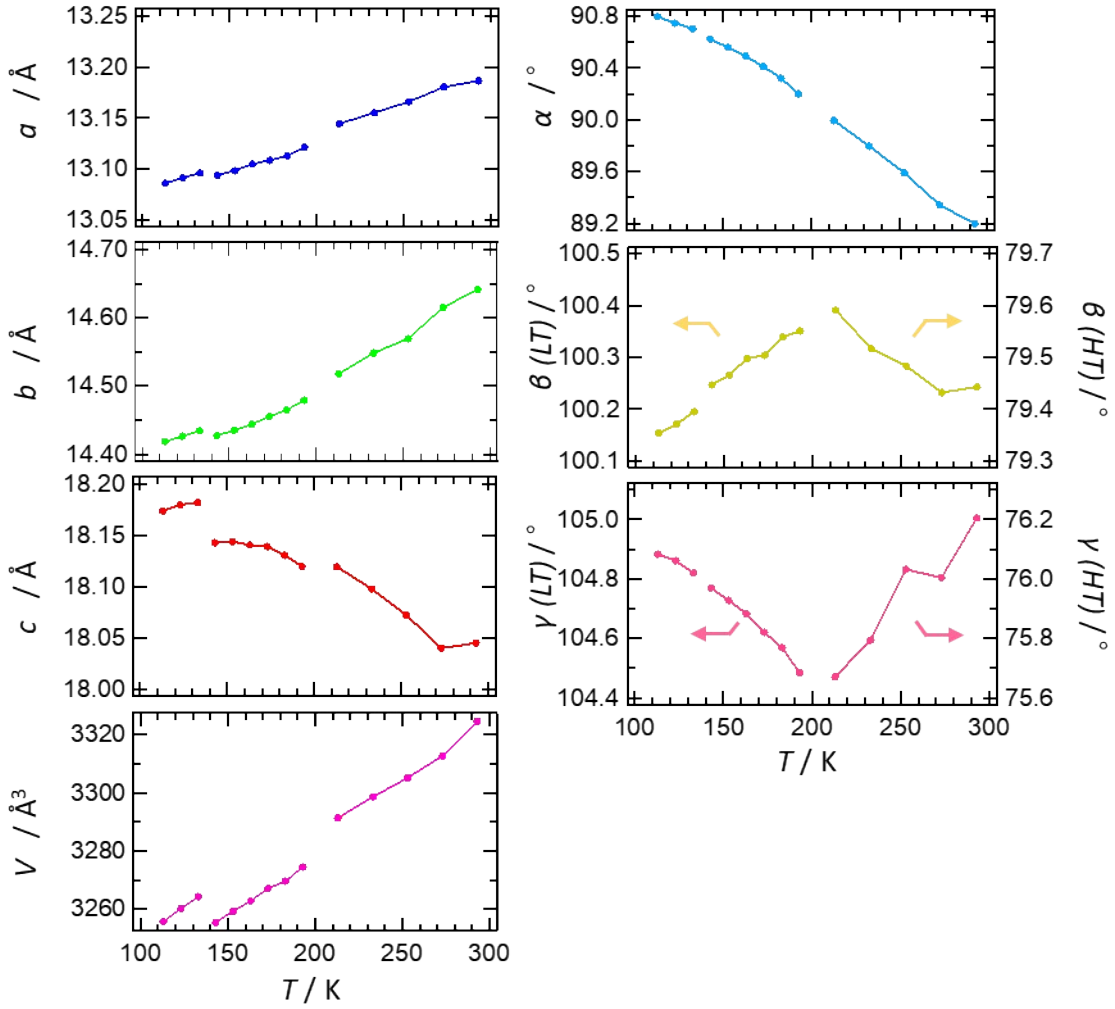
PXRD pattern are measured with a Rigaku RINT2113 in the 2θ region of 5-40°. The measurements were performed with CuK_{α} radiation (λ = 1.5418 Å) at scanning rate of 1.2°•min^{-1} under an applied electric voltage and current of 40 KV and 40 mA, respectively.



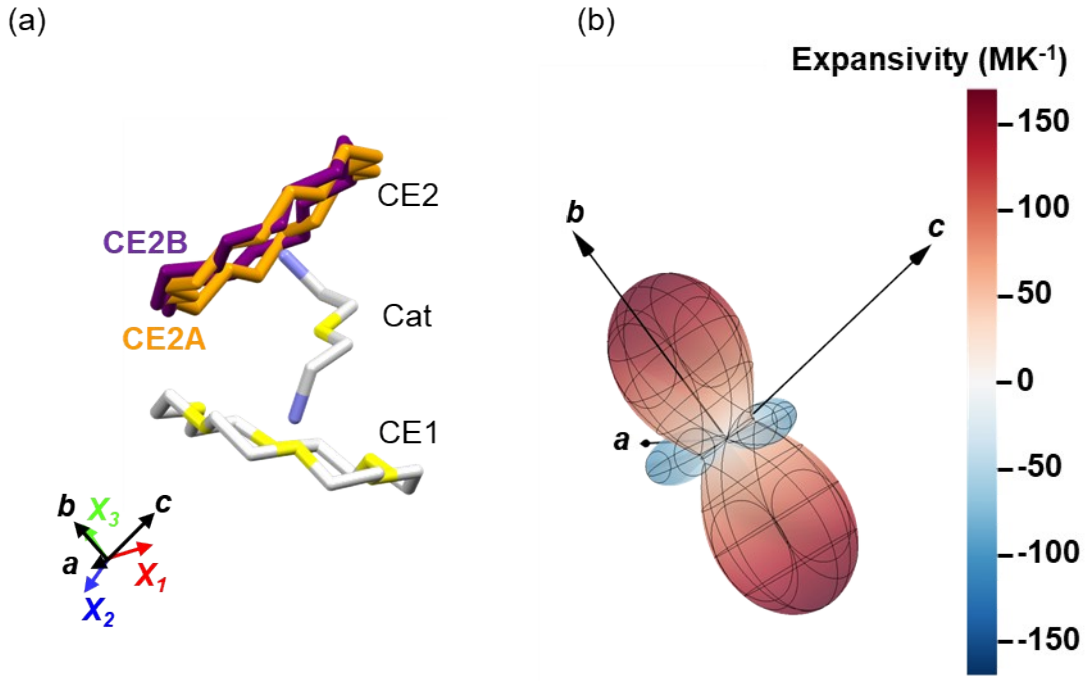
§Figure S3. (a) TG-DTA measurement for crystal **1**. (b) DSC from 180 to 300 K. Thermogravimetric-differential thermal analysis (TG-DTA) was conducted using a *Rigaku* Thermo Plus TG8120 with 10 K/min heating rate under nitrogen gas flow.



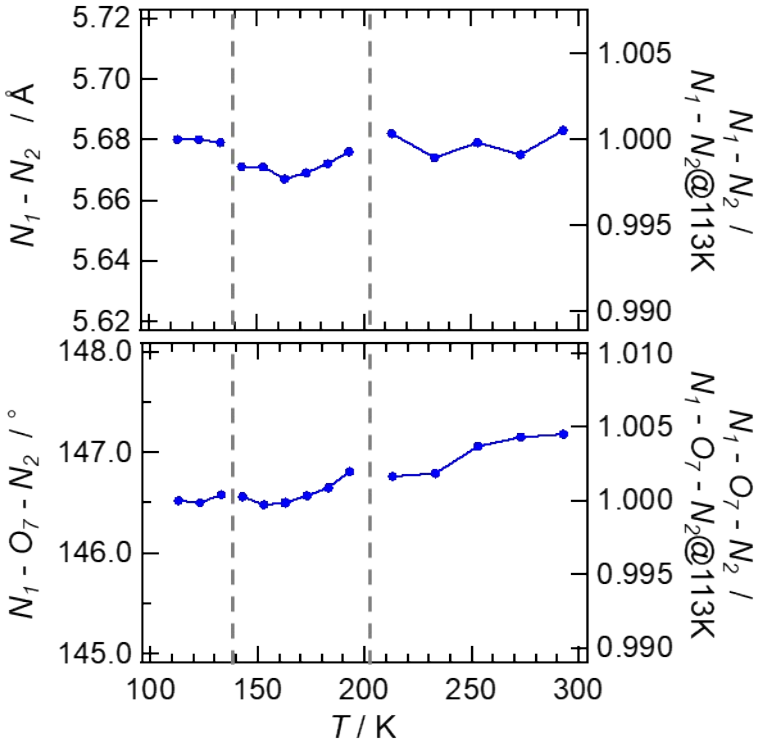
§Figure S4. (a) The real part and (b) imaginary part of the dielectric constant and (c) Arrhenius plot for dielectric relaxation.



§Figure S5. Temperature dependence of unit cell dimensions and volume for crystal **1** over which the same crystal was studied. (HT : High Themperature phase, LT : Low Temperature phase)



§Figure S6. The structure of supramolecular cations. Indicatrix plots for structural data of **1**. PASCal indicatrix Plotter was used to plot the data. The software was obtained from the web site: https://www.pascalapp.co.uk/



§Figure S7. Temperature dependence of the intramolecular N1•••N2 interatomic distance and N1•••O7•••N2 angles (left axis) and compared with each value at 113 K (right axis) for crystal **1**.

§Table S8. Crystal data, data collection, and reduction parameters for crystal **1**.

Crystal	**1**		
Temperature / K	113	123	133
Crystal Dimensions / mm³	0.1×0.5×0.7		
Chemical formula	$C_{40}H_{62}N_2Ni_2O_{13}S_{20}$		
Formula weight	1537.53		
Crystal system	*Triclinic*		
Space group	$P\bar{1}$		
a / Å	13.0860(3)	13.0913(3)	13.0962(3)
b / Å	14.4188(3)	14.4264(3)	14.4347(3)
c / Å	18.1738(4)	18.1799(4)	18.1822(5)
α / deg	90.798(2)	90.747(2)	90.702(2)
β / deg	100.154(2)	100.171(2)	100.195(2)
γ / deg	104.883(2)	104.861(2)	104.820(2)
V / Å³	3255.84(13)	3260.32(13)	3264.37(14)
Z	2		
D_{calc} / g·cm^{-3}	1.568	1.566	1.564
μ(Mo K$_\alpha$) / cm^{-1}	1.274	1.272	1.271
$2\theta_{max}$ / *deg*	61.792	61.882	61.828
Reflections measured	43040	43134	43163
Independent reflections	16286	16308	16316
Reflections used	16286	16308	16316
R_1 [a]	0.0508	0.0523	0.0523
R_w (F^2) [a]	0.1193	0.1223	0.1223
GOF	1.016	1.019	1.023
CCDC No.	2384649	2384650	2384651

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

Crystal	**1**		
Temperature / K	143	153	163
Crystal Dimensions / mm³	0.1×0.5×0.7		
Chemical formula	$C_{40}H_{62}N_2Ni_2O_{13}S_{20}$		
Formula weight	1537.53		
Crystal system	*Triclinic*		
Space group	$P\bar{1}$		
a / Å	13.0939(3)	13.0985(4)	13.1048 (4)
b / Å	14.4272(4)	14.4353(3)	14.4438(3)
c / Å	18.1428(4)	18.1439(5)	18.1407(5)
α / deg	90.624(2)	90.560(2)	90.492(2)
β / deg	100.247(2)	100.266(2)	100.298(2)
γ / deg	104.770(2)	104.728(2)	104.682(2)
V / Å³	3255.51(13)	3259.35(15)	3262.86(15)
Z	2		
D_{calc} / g·cm^{-3}	1.568	1.567	1.565
μ(Mo K$_\alpha$) / cm^{-1}	1.274	1.273	1.271
$2\theta_{max}$ / *deg*	61.870	61.842	61.836
Reflections measured	43224	43335	43468
Independent reflections	16302	16329	16348
Reflections used	16302	16329	16348
R_1 [a]	0.0524	0.0532	0.0540
$R_w(F^2)$ [a]	0.1199	0.1232	0.1235
GOF	1.011	1.032	1.028
CCDC No.	2384652	2384653	2384654

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

Crystal	**1**		
Temperature / K	173	183	193
Crystal Dimensions / mm³	0.1×0.5×0.7		
Chemical formula	$C_{40}H_{62}N_2Ni_2O_{13}S_{20}$		
Formula weight	1537.53		
Crystal system	*Triclinic*		
Space group	$P\bar{1}$		
a / Å	13.1087(4)	13.1130(4)	13.1212 (4)
b / Å	14.4553(3)	14.4648(3)	14.4791(3)
c / Å	18.1391(5)	18.1307(5)	18.1199(5)
α / deg	90.412(2)	90.322(2)	90.200(2)
β / deg	100.304(2)	100.339(2)	100.351(2)
γ / deg	104.620(2)	104.569(2)	104.484(2)
V / Å³	3267.30(15)	3269.70(15)	3274.58(15)
Z	2		
D_{calc} / g·cm^{-3}	1.563	1.562	1.559
μ(Mo K$_\alpha$) / cm^{-1}	1.270	1.269	1.267
$2\theta_{max}$ / *deg*	61.896	61.864	61.730
Reflections measured	43610	43704	43961
Independent reflections	16391	16409	16431
Reflections used	16391	16409	16431
R_1 [a]	0.0544	0.0551	0.0553
$R_w(F^2)$ [a]	0.1259	0.1263	0.1281
GOF	1.029	1.029	1.027
CCDC No.	2384655	2384656	2384657

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

Crystal	**1**		
Temperature / K	213	233	253
Crystal Dimensions / mm³	0.2×0.5×0.8		
Chemical formula	$C_{40}H_{62}N_2Ni_2O_{13}S_{20}$		
Formula weight	1537.53		
Crystal system	*Triclinic*		
Space group	$P\bar{1}$		
a / Å	13.1444(3)	13.1552(4)	13.1660(5)
b / Å	14.5178(5)	14.5482(6)	14.5697(6)
c / Å	18.1193(5)	18.0978(7)	18.0721(7)
α / deg	89.995(2)	89.797(3)	89.590(3)
β / deg	79.591(2)	79.517(3)	79.483(3)
γ / deg	75.671(2)	75.794(3)	76.032(3)
V / Å³	3291.35(17)	3298.60(2)	3305.20(2)
Z	2		
D_{calc} / g·cm^{-3}	1.551	1.548	1.545
μ(Mo K$_\alpha$) / cm^{-1}	1.260	1.258	1.255
$2\theta_{max}$ / *deg*	52.746	52.744	52.744
Reflections measured	37421	38461	38905
Independent reflections	13452	13499	13529
Reflections used	13452	13499	13529
R_1 [a]	0.0551	0.0521	0.0514
$R_w(F^2)$ [a]	0.1367	0.1286	0.1276
GOF	1.037	1.044	1.034
CCDC No.	2384658	2384659	2384660

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

Crystal	**1**	
Temperature / K	273	293
Crystal Dimensions / mm³ /mm³	0.2×0.5×0.8	
Chemical formula	$C_{40}H_{62}N_2Ni_2O_{13}S_{20}$	
Formula weight	1537.53	
Crystal system	*Triclinic*	
Space group	$P\bar{1}$	
a / Å	13.1803(5)	13.1866(5)
b / Å	14.6150(7)	14.6416(5)
c / Å	18.0399(7)	18.0448(7)
α / deg	89.343(3)	89.198(3)
β / deg	79.432(3)	79.443(3)
γ / deg	76.004(4)	76.205(3)
V / Å³	3312.70(2)	3324.60(2)
Z	2	
D_{calc} / g·cm^{-3}	1.541	1.536
μ(Mo K_α) / cm^{-1}	1.252	1.248
$2\theta_{max}$ / *deg*	52.738	52.744
Reflections measured	39008	39226
Independent reflections	13558	13618
Reflections used	13558	13618
R_1 [a]	0.0528	0.0516
$R_w(F^2)$ [a]	0.1338	0.1297
GOF	1.045	1.038
CCDC No.	2384661	2384662

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

§Table S9. output file of *PASCal* calculation for crystal **1** between 113 to 133 K.

Output			Direction		
Axes	α (M K^{-1})	σα (M K^{-1})	*a*	*b*	*c*
X_1	− 18.1210	1.8946	0.4630	− 0.600	0.6525
X_2	47.7425	0.2011	0.9470	0.1151	− 0.300
X_3	101.3108	0.5615	0.4420	0.7936	0.4181
V	130.9734	1.5332			

% Change in length						
T (K)	X_1 (%)	X_2 (%)	X_3 (%)	X_1,calc (%)	X_2,calc (%)	X_3,calc (%)
113	0	0	0	0.0027	0.0003	− 0.0008
123	− 0.0101	0.0486	0.0989	− 0.0154	0.048	0.1005
133	− 0.0362	0.0955	0.2026	− 0.0336	0.0958	0.2018

Volume		
T (K)	*V* (Å^3)	*V*lin (Å^3)
113	3255.843	3255.914
123	3260.319	3260.178
133	3264.372	3264.442

§Table S10. output file of *PASCal* calculation for crystal **1** between 143 to 193 K.

Output Axes	α (M K^{-1})	σ α (M K^{-1})	Direction *a*	*b*	*C*
X_1	− 74.1330	6.5341	0.4402	− 0.5167	0.7343
X_2	37.1844	0.6950	0.9111	− 0.1653	− 0.3776
X_3	152.3713	8.3966	0.5755	0.7713	0.2717
V	114.7932	2.6595			

% Change in length						
T / K	X_1	X_2	X_3	X_1, calc	X_2, calc	X_3, calc
143	0	0	0	0.0282	0.0035	− 0.0315
153	− 0.0413	0.0391	0.1201	− 0.0459	0.0407	0.1208
163	− 0.1050	0.0889	0.2418	− 0.1200	0.0779	0.2732
173	− 0.1597	0.1123	0.4101	− 0.1942	0.1150	0.4256
183	− 0.2595	0.1485	0.5483	− 0.2683	0.1522	0.5780
193	− 0.3771	0.1900	0.7761	− 0.3424	0.1894	0.7303

Volume		
T / K	*V* / Å^3	*V*lin / Å^3
143	3255.515	3255.541
153	3259.353	3259.278
163	3262.857	3263.016
173	3267.303	3266.753
183	3269.696	3270.490
193	3274.580	3274.227

§Table S11. output file of *PASCal* calculation for crystal **1** between 213 to 293 K.

Output Axes	α (M K^{-1})	σ α (M K^{-1})	Direction *a*	*b*	*c*
X_1	− 104.9990	8.6499	− 0.3869	− 0.4653	0.7961
X_2	35.4035	2.6705	0.8997	0.2809	0.3342
X_3	193.7307	1.6950	− 0.6070	0.7617	0.2267
V	122.3889	7.3061			

% Change in length						
T / K	X_1	X_2	X_3	X_1, calc	X_2, calc	X_3, calc
213	0	0	0	− 0.0282	0.0013	− 0.0043
233	− 0.2243	0.0836	0.3619	− 0.2382	0.0721	0.3831
253	− 0.4879	0.1079	0.8051	− 0.4482	0.1430	0.7706
273	− 0.7329	0.2547	1.1353	− 0.6582	0.2138	1.1580
293	− 0.7957	0.2685	1.5506	− 0.8682	0.2846	1.5455

Volume		
T / K	*V* / Å^3	*V*lin / Å^3
213	3291.352	3290.371
233	3298.603	3298.427
253	3305.177	3306.484
273	3312.698	3314.540
293	3324.587	3322.597

§Reference

S1. G. Steimecke, H.-J. Sieler, R. Kirmse and E. Hoyer, *Phosphorus and Sulfur and the Related Elements*, 1979, **7**, 49–55.

S2. G. M. Sheldrick, *Acta Cryst A*, 2015, **71**, 3–8.

S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. a. K. Howard and H. Puschmann, *J Appl Cryst*, 2009, **42**, 339–341.

S4. M. J. Cliffe and A. L. Goodwin, *J Appl Cryst,* 2012, **45**, 1321–1329.

S5. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.

S6. T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito and H. Inokuchi, *Bulletin of the Chemical Society of Japan*, 1984, **57**, 627–633.