

Supplementary Materials

# Single-Ion Magnetism in a Three-Dimensional Thiocyanate-Bridged Dysprosium(III) Framework

Qingyun Wan <sup>1,2,\*</sup>, Mirosław Arczyński <sup>1,3,†</sup>, Masanori Wakizaka <sup>1,\*</sup>, Shraddha Gupta <sup>1</sup>, Nobuto Funakoshi <sup>1</sup> and Masahiro Yamashita <sup>1,4,\*</sup>

<sup>1</sup> Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki-Aza-Aoba, Aoba-Ku, Sendai 980-8578, Japan; mirosław.arczynski@uj.edu.pl (M.A.); gupta.shraddha07@gmail.com (S.G.); nobuto.funakoshi.e7@tohoku.ac.jp (N.F.)

<sup>2</sup> State Key Laboratory of Synthetic Chemistry, HKU-CAS Joint Laboratory on New Materials, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China

<sup>3</sup> Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland

<sup>4</sup> School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

\* Correspondence: qywan@connect.hku.hk (Q.W.); masanori.wakizaka.a7@tohoku.ac.jp (M.W.); yamasita@agnus.chem.tohoku.ac.jp (M.Y.); Tel.: +81-22-765-6544 (M.Y.)

† These authors contributed equally to this work.

**Table S1.** Crystal data and structure refinement for **1** at 120K. CCDC: 2249738.

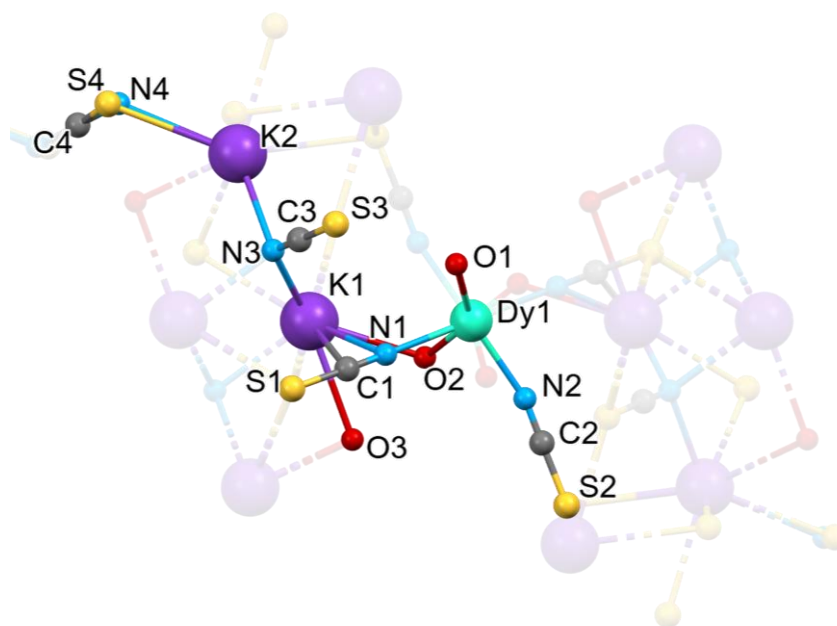
Identification code	a_120K
Empirical formula	C <sub>7</sub> DyN <sub>7</sub> O <sub>6</sub> S <sub>7</sub> H <sub>4</sub> K <sub>4</sub>
Formula weight	825.49
Temperature/K	120
Crystal system	monoclinic
Space group	I2/a
a/Å	20.0808(4)
b/Å	6.44050(10)
c/Å	22.2609(4)
α/°	90
β/°	107.379(2)
γ/°	90
Volume/Å <sup>3</sup>	2747.58(9)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.996
μ/mm <sup>-1</sup>	3.893
F(000)	1588.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.522 to 62.426
Index ranges	-27 ≤ h ≤ 28, -8 ≤ k ≤ 9, -32 ≤ l ≤ 31
Reflections collected	30592
Independent reflections	4045 [R <sub>int</sub> = 0.0447, R <sub>sigma</sub> = 0.0236]
Data/restraints/parameters	4045/4/162
Goodness-of-fit on F <sup>2</sup>	1.160
Final R indexes [I > 2σ (I)]	R <sub>1</sub> = 0.0187, wR <sub>2</sub> = 0.0410
Final R indexes [all data]	R <sub>1</sub> = 0.0241, wR <sub>2</sub> = 0.0487
Largest diff. peak/hole / e Å <sup>-3</sup>	1.43/-2.17

**Table S2.** Crystal data and structure refinement for **2** at 120K. CCDC: 2249739.

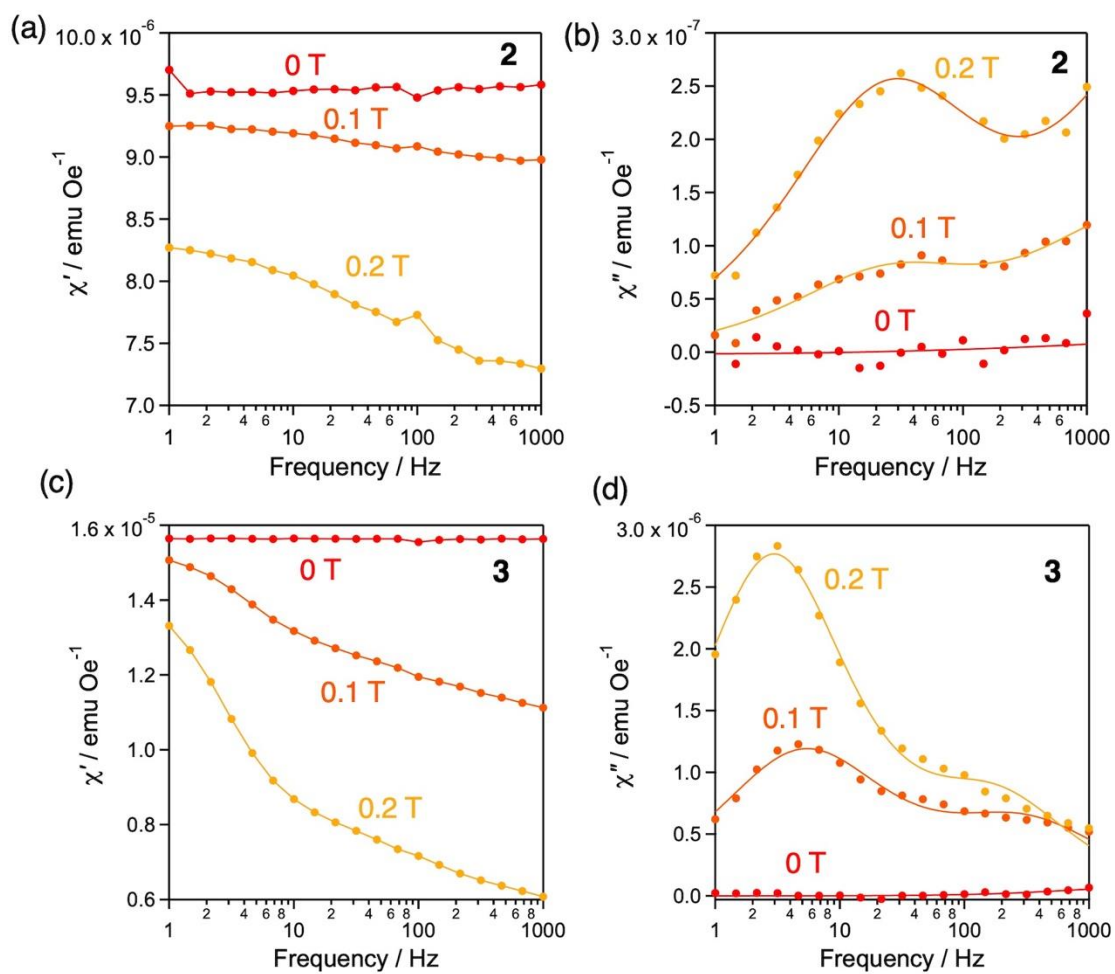
Identification code	a_120K
Empirical formula	C <sub>7</sub> TbN <sub>7</sub> O <sub>6</sub> S <sub>7</sub> H <sub>4</sub> K <sub>4</sub>
Formula weight	821.91
Temperature/K	120
Crystal system	monoclinic
Space group	I2/a
a/Å	20.0705(5)
b/Å	6.44920(10)
c/Å	22.2550(5)
α/°	90
β/°	107.304(3)
γ/°	90
Volume/Å <sup>3</sup>	2750.28(11)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.985
μ/mm <sup>-1</sup>	3.744
F(000)	1584.0
Crystal size/mm <sup>3</sup>	0.15 × 0.1 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.518 to 62.4
Index ranges	-28 ≤ h ≤ 29, -9 ≤ k ≤ 9, -32 ≤ l ≤ 28
Reflections collected	17985
Independent reflections	3942 [R <sub>int</sub> = 0.0679, R <sub>sigma</sub> = 0.0425]
Data/restraints/parameters	3942/4/162
Goodness-of-fit on F <sup>2</sup>	1.072
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0250, wR <sub>2</sub> = 0.0615
Final R indexes [all data]	R <sub>1</sub> = 0.0313, wR <sub>2</sub> = 0.0645
Largest diff. peak/hole / e Å <sup>-3</sup>	1.51/-2.29

**Table S3.** Crystal data and structure refinement for **3** at 120K. CCDC: 2249740.

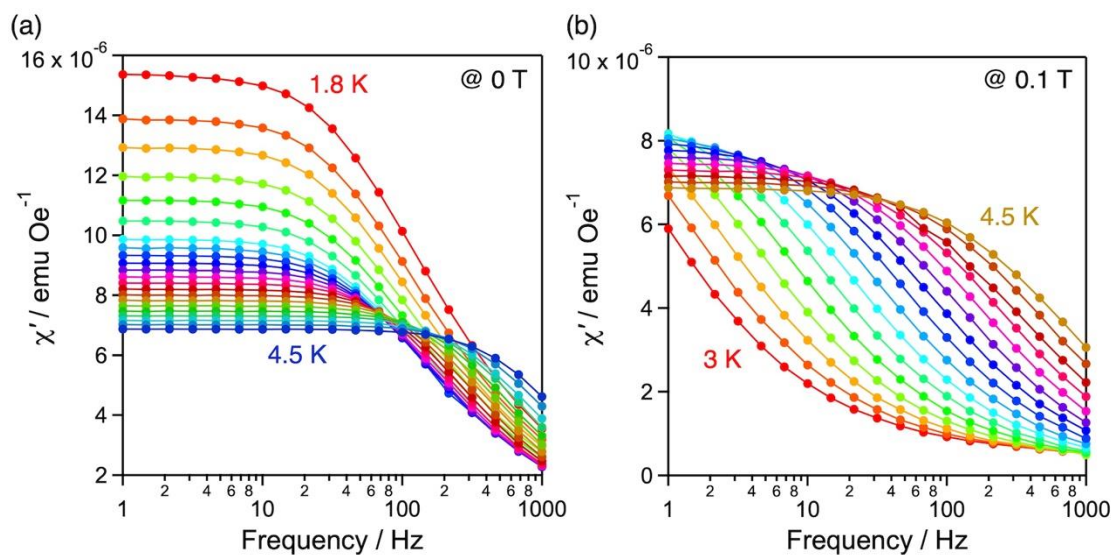
Identification code	a_120K
Empirical formula	C <sub>7</sub> GdK <sub>4</sub> N <sub>7</sub> O <sub>6</sub> S <sub>7</sub> H <sub>4</sub>
Formula weight	820.24
Temperature/K	120
Crystal system	monoclinic
Space group	I2/a
a/Å	20.0701(4)
b/Å	6.46040(10)
c/Å	22.2814(5)
α/°	90
β/°	107.245(2)
γ/°	90
Volume/Å <sup>3</sup>	2759.15(10)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.975
μ/mm <sup>-1</sup>	3.572
F(000)	1580.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.592 to 62.332
Index ranges	-26 ≤ h ≤ 27, -9 ≤ k ≤ 9, -32 ≤ l ≤ 31
Reflections collected	14860
Independent reflections	3825 [R <sub>int</sub> = 0.0187, R <sub>sigma</sub> = 0.0139]
Data/restraints/parameters	3825/4/163
Goodness-of-fit on F <sup>2</sup>	1.122
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0162, wR <sub>2</sub> = 0.0429
Final R indexes [all data]	R <sub>1</sub> = 0.0187, wR <sub>2</sub> = 0.0439
Largest diff. peak/hole / e Å <sup>-3</sup>	0.87/-0.79



**Figure S1.** Asymmetric unit of 1 (2 and 3 are isostructural). ASU is in the foreground while extended structure is partly translucent bringing attention to the arrangement of Dy complex in relation to  $[K_4(SCN)_2]^{2+}$  layers. Purple atoms: K, yellow: S, grey: C, blue: N, red: O, cyan: Dy. H atoms were omitted for clarity.



**Figure S2.** The real part ( $\chi'$ ) and the imaginary part ( $\chi''$ ) of AC susceptibility of (a, b) **2** and (c, d) **3**, measured at 1.8 K under the magnetic field of 0, 0.1, 0.2 T. The curve lines for  $\chi''$  show a dual Debye model fit.



**Figure S3.** The real part of AC magnetic susceptibility ( $\chi'$ ) of **1** under the static magnetic field of 0 T and 0.1 T, respectively.

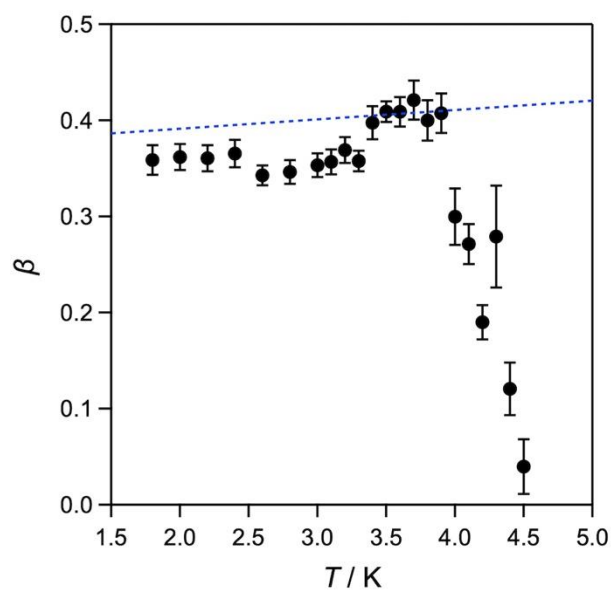
**Table S4.** AC susceptibility fitting data of the imaginary part of **1** at 0 T.

T (K)	$\chi_T - \chi^S$ (emu/Oe)	$\tau$ (s)	$\alpha$	$\beta$	$\sigma \chi_T - \chi^S$ (emu/Oe)	$\sigma \tau$ (s)	$\sigma \alpha$	$\sigma \beta$
1.8	1.72E-05	0.003193	0.08272	0.35875	2.32E-07	0.000123	0.0096	0.0153
2	1.56E-05	0.003277	0.082641	0.36184	1.82E-07	0.000112	0.00854	0.0135
2.2	1.45E-05	0.003339	0.08067	0.3605	1.69E-07	0.000114	0.00862	0.0135
2.4	1.34E-05	0.003304	0.082774	0.36546	1.62E-07	0.000119	0.009	0.0143
2.6	1.28E-05	0.003438	0.075327	0.34269	1.26E-07	9.33E-05	0.00701	0.0104
2.8	1.20E-05	0.003324	0.071286	0.34621	1.37E-07	0.000105	0.00817	0.0123
3	1.12E-05	0.003049	0.067681	0.35329	1.25E-07	9.36E-05	0.00789	0.0123
3.1	1.08E-05	0.002905	0.058462	0.35675	1.27E-07	9.34E-05	0.00841	0.0131
3.2	1.04E-05	0.00263	0.05378	0.36911	1.22E-07	8.50E-05	0.00837	0.0136
3.3	1.03E-05	0.002435	0.045213	0.35772	1.02E-07	6.14E-05	0.00657	0.0106
3.4	9.71E-06	0.001996	0.055592	0.39751	1.35E-07	7.59E-05	0.00913	0.0172
3.5	9.41E-06	0.001714	0.04978	0.40913	7.91E-08	3.85E-05	0.00527	0.0106
3.6	9.25E-06	0.001475	0.045829	0.40894	1.18E-07	4.68E-05	0.00718	0.0154
3.7	9.01E-06	0.001222	0.043506	0.42106	1.52E-07	4.89E-05	0.00859	0.0204
3.8	9.17E-06	0.00104	0.041242	0.39991	1.84E-07	4.23E-05	0.00824	0.021
3.9	8.57E-06	0.00087	0 (fix)	0.41 (fix)	4.96E-08	1.28E-05	0	0
4	8.44E-06	0.000713	0 (fix)	0.41 (fix)	5.57E-08	1.18E-05	0	0
4.1	8.32E-06	0.000582	0 (fix)	0.41 (fix)	5.41E-08	9.26E-06	0	0
4.2	8.26E-06	0.000468	0 (fix)	0.41 (fix)	6.60E-08	8.84E-06	0	0
4.3	8.16E-06	0.00041	0 (fix)	0.41 (fix)	6.25E-08	7.20E-06	0	0
4.4	7.86E-06	0.000319	0 (fix)	0.41 (fix)	6.57E-08	5.66E-06	0	0
4.5	7.50E-06	0.000263	0 (fix)	0.42 (fix)	7.03E-08	4.88E-06	0	0

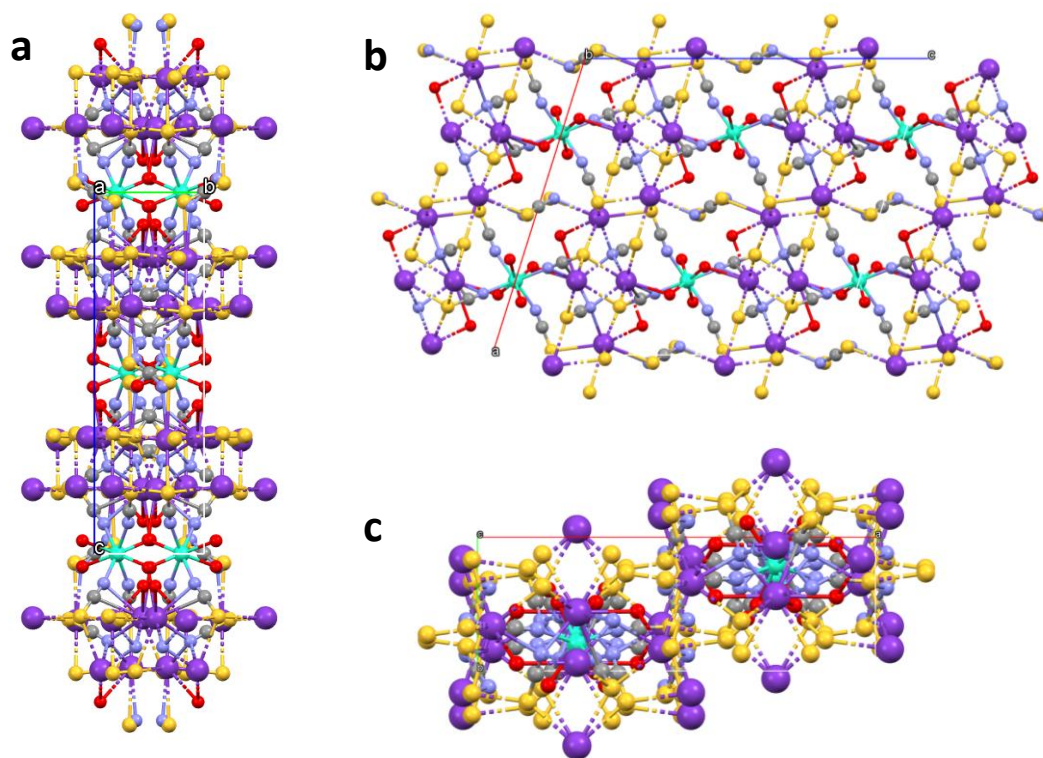


**Table S5.** AC susceptibility fitting data of the imaginary part of **1** at 0.1 T.

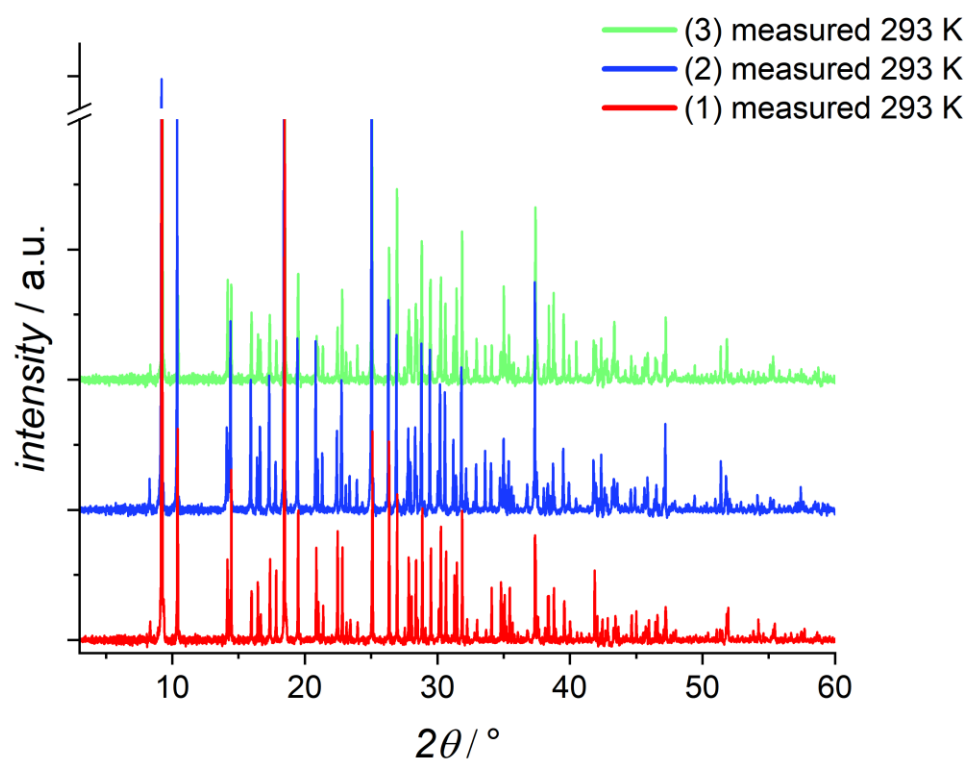
T (K)	$\chi^T - \chi^S$ (emu/Oe)	$\tau$ (s)	$\alpha$	$\beta$	$\sigma \chi^T - \chi^S$ (emu/Oe)	$\sigma \tau$ (s)
3	1.17E-05	0.19969	0.43599	3.23E-07	0.0161	0.0091
3.1	1.07E-05	0.1001	0.42012	2.28E-07	0.0059	0.00953
3.2	1.00E-05	0.053154	0.4066	9.28E-08	0.00126	0.00517
3.3	9.55E-06	0.029784	0.39475	9.32E-08	0.000692	0.00625
3.4	9.11E-06	0.017332	0.37859	8.27E-08	3.55E-04	0.00629
3.5	8.76E-06	0.010387	0.36469	8.72E-08	2.28E-04	0.00716
3.6	8.47E-06	0.006507	0.35228	8.92E-08	1.50E-04	0.00771
3.7	8.21E-06	0.004166	0.34181	9.48E-08	1.04E-04	0.00853
3.8	8.02E-06	0.002693	0.33593	1.10E-07	7.88E-05	0.0101
3.9	7.77E-06	0.001816	0.32369	1.09E-07	5.33E-05	0.0104
4	7.59E-06	0.001234	0.31755	1.18E-07	3.98E-05	0.0114
4.1	7.40E-06	0.000856	0.31196	1.19E-07	2.85E-05	0.0116
4.2	7.23E-06	0.000597	0.30361	1.22E-07	2.10E-05	0.0117
4.3	6.95E-06	0.000474	0.28091	1.53E-07	2.11E-05	0.0149
4.4	6.77E-06	0.000321	0.28556	1.11E-07	1.12E-05	0.00986
4.5	6.61E-06	0.000235	0.27876	1.19E-07	9.11E-06	0.00958



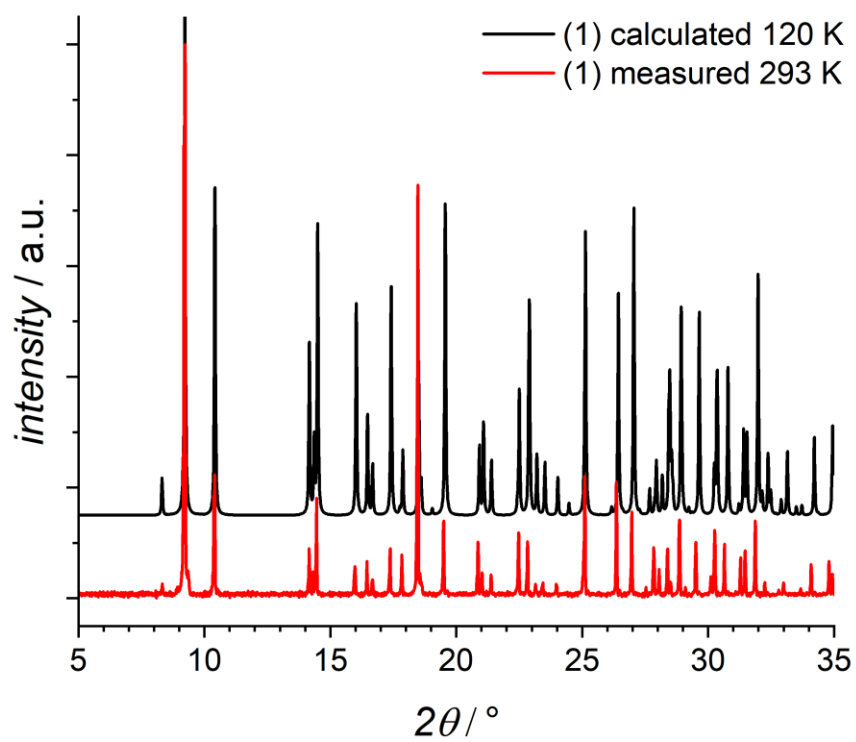
**Figure S4.** Plots of temperature dependence of  $b$  of **1** at 0 T fitted by using equations 2 and 3 in the manuscript.



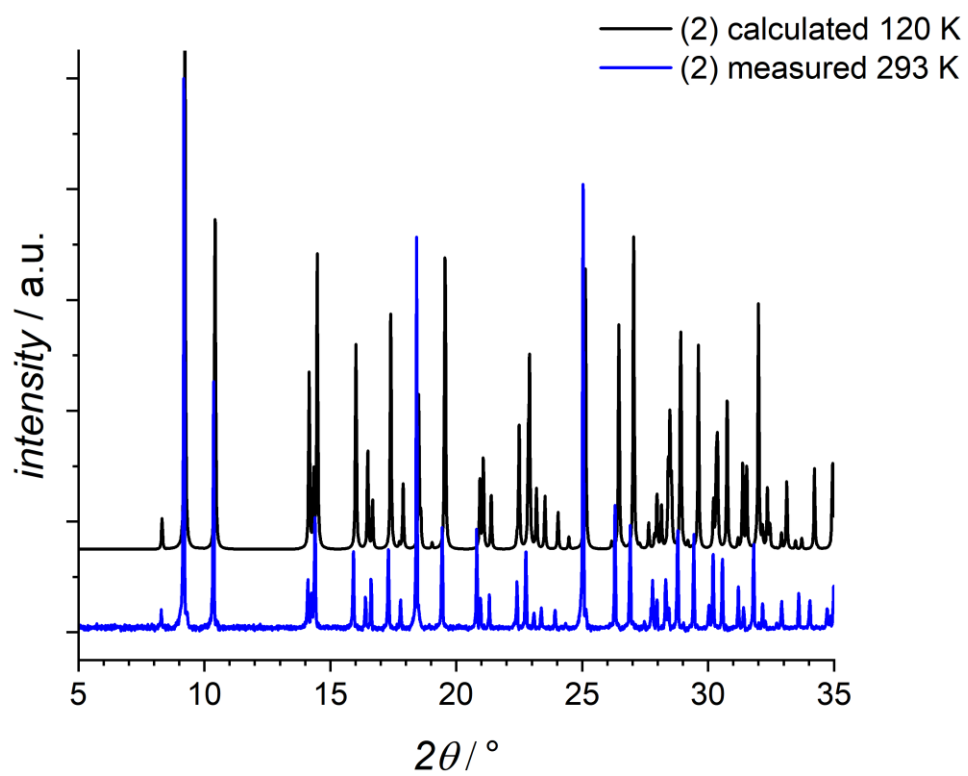
**Figure S5.** Crystal structure of compound **1-3** along the (a) a-, (b) b- and (c) c-axis.



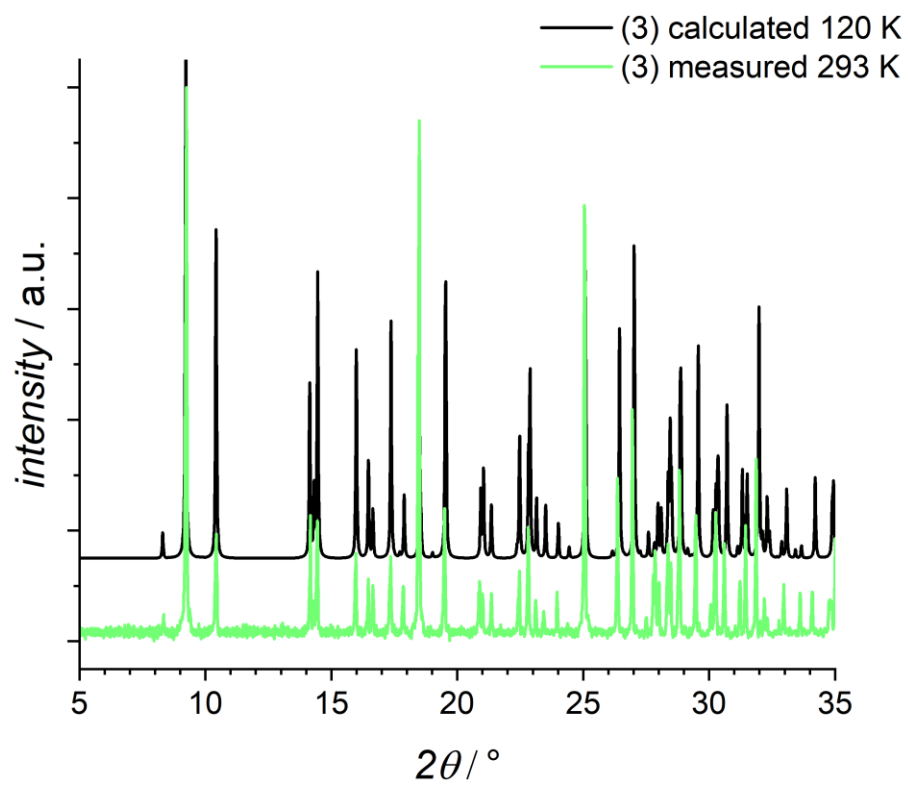
**Figure S6.** PXRD pattern of compounds **1**, **2** and **3** measured at 293 K – crystals were grinded before measurements (non-dehydrated sample).



**Figure S7.** Comparison of calculated (on the basis of single crystal structural data at 120 K) and measured (at 293 K) PXRD patterns of compound **1** (non-dehydrated sample).



**Figure S8.** Comparison of calculated (on the basis of single crystal structural data at 120 K) and measured (at 293 K) PXRD patterns of compound **2** (non-dehydrated sample).



**Figure S9.** Comparison of calculated (on the basis of single crystal structural data at 120 K) and measured (at 293 K) PXRD patterns of compound **3**(non-dehydrated sample).

**Table S6.** Bond lengths of Dy1, K1 and K2 centres.

Atom names	Bond length / Å	Atom names	Bond length / Å
Dy1 K1	4.2346(5)	K1 N1	3.0505(19)
Dy1 K1 <sup>a</sup>	4.2346(5)	K1 N3 <sup>b</sup>	2.906(2)
Dy1 K1	4.2345(5)	K1 N3	2.820(2)
Dy1 O1	2.4881(16)	K1 N2 <sup>a</sup>	3.380(2)
Dy1 O1 <sup>a</sup>	2.4881(16)	K1 C1	3.223(2)
Dy1 O2	2.4290(16)	K1 O3	3.084(3)
Dy1 O2 <sup>a</sup>	2.4289(15)	K2 S2 <sup>d</sup>	3.3972(8)
Dy1 N1 <sup>a</sup>	2.3869(19)	K2 S2 <sup>a</sup>	3.4072(8)
Dy1 N1	2.3868(19)	K2 S2 <sup>e</sup>	3.3292(8)
Dy1 N2 <sup>a</sup>	2.4091(19)	K2 S3 <sup>f</sup>	3.2816(7)
Dy1 N2	2.4091(19)	K2 S1 <sup>b</sup>	3.2352(7)
K1 K1 <sup>b</sup>	4.0284(9)	K2 S4 <sup>b</sup>	3.405(3)
K1 S3 <sup>c</sup>	3.2514(7)	K2 N3	2.873(2)
K1 S1 <sup>b</sup>	3.4686(7)	K2 C3	3.474(2)
K1 S1 <sup>c</sup>	3.2681(7)	K2 O3 <sup>b</sup>	3.313(2)
K1 O2	2.9953(16)	K2 N4 <sup>b</sup>	3.168(11)

<sup>a</sup>  $-x+1/2, y, -z+1$ ; <sup>b</sup>  $-x+1/2, -y+3/2, -z+1/2$ ; <sup>c</sup>  $x, y+1, z$ ; <sup>d</sup>  $x-1/2, y-1/2, z-1/2$ ; <sup>e</sup>  $x-1/2, y+1/2, z-1/2$ ; <sup>f</sup>  $-x, y+1/2, -z+1/2$

**Table S7.** Bond lengths of Tb1, K1 and K2 centres.

Atom names	Bond length / Å	Atom names	Bond length / Å
<b>Tb1 K1</b>	4.2319(5)	K1 N2	3.354(3)
<b>Tb1 K1<sup>a</sup></b>	4.2318(5)	K1 N3	2.821(2)
<b>Tb1 O1</b>	2.4985(16)	K1 N3 <sup>b</sup>	2.905(2)
<b>Tb1 O1<sup>a</sup></b>	2.4985(16)	K1 C1 <sup>a</sup>	3.229(2)
<b>Tb1 O3</b>	2.4389(16)	K1 O2 <sup>b</sup>	3.084(3)
<b>Tb1 O3<sup>a</sup></b>	2.4389(16)	K2 S3 <sup>f</sup>	3.2811(8)
<b>Tb1 N1<sup>a</sup></b>	2.395(2)	K2 S2 <sup>f</sup>	3.3324(8)
<b>Tb1 N1</b>	2.395(2)	K2 S2	3.3987(9)
<b>Tb1 N2<sup>a</sup></b>	2.423(2)	K2 S2 <sup>g</sup>	3.4005(8)
<b>Tb1 N2</b>	2.423(2)	K2 S1 <sup>d</sup>	3.2341(8)
<b>K1 K1<sup>b</sup></b>	4.0310(10)	K2 N3	2.874(2)
<b>K1 S3<sup>c</sup></b>	3.2529(8)	K2 C3	3.478(2)
<b>K1 S1<sup>d</sup></b>	3.4648(8)	K2 S4 <sup>h</sup>	3.405(3)
<b>K1 S1<sup>e</sup></b>	3.2698(7)	K2 O2 <sup>b</sup>	3.313(2)
<b>K1 O3</b>	2.9972(17)	K2 N4 <sup>h</sup>	3.164(12)
<b>K1 N1<sup>a</sup></b>	3.047(2)		

<sup>a</sup>  $-x+3/2, y, -z+1$ ; <sup>b</sup>  $-x+3/2, -y+3/2, -z+3/2$ ; <sup>c</sup>  $x, y+1, z$ ; <sup>d</sup>  $x, -y+3/2, z+1/2$ ; <sup>e</sup>  $-x+3/2, y+1, -z+1$ ; <sup>f</sup>  $-x+2, y+1/2, -z+3/2$ ; <sup>g</sup>  $-x+2, y-1/2, -z+3/2$ ; <sup>h</sup>  $x+1/2, y+1/2, z+1/2$



**Table S8.** Bond lengths of Gd1, K1 and K2 centres.

Atom names	Bond length / Å	Atom names	Bond length / Å
<b>Gd1 K1<sup>a</sup></b>	4.2373(4)	K1 N1 <sup>a</sup>	3.0480(17)
<b>Gd1 K1</b>	4.2373(4)	K1 C1 <sup>a</sup>	3.2324(17)
<b>Gd1 O2</b>	2.4513(13)	K1 N3 <sup>b</sup>	2.9059(17)
<b>Gd1 O2<sup>a</sup></b>	2.4513(13)	K1 N3	2.8217(17)
<b>Gd1 O1</b>	2.5122(13)	K1 O3	3.093(2)
<b>Gd1 O1<sup>a</sup></b>	2.5122(13)	K2 S3 <sup>f</sup>	3.2836(6)
<b>Gd1 N2<sup>a</sup></b>	2.4404(17)	K2 S2	3.3935(7)
<b>Gd1 N2</b>	2.4404(16)	K2 S2 <sup>f</sup>	3.3369(7)
<b>Gd1 N1<sup>a</sup></b>	2.4125(15)	K2 S2 <sup>g</sup>	3.4017(7)
<b>Gd1 N1</b>	2.4125(15)	K2 S1 <sup>e</sup>	3.2348(6)
<b>K1 K1<sup>b</sup></b>	4.0366(8)	K2 S4	3.411(3)
<b>K1 S3<sup>c</sup></b>	3.2547(6)	K2 N3	2.8765(17)
<b>K1 S1<sup>d</sup></b>	3.2703(6)	K2 O3 <sup>b</sup>	3.3128(19)
<b>K1 S1<sup>e</sup></b>	3.4589(6)	K2 C3	3.4811(18)
<b>K1 O2</b>	3.0029(14)	K2 N4	3.151(9)
<b>K1 N2</b>	3.3533(19)		

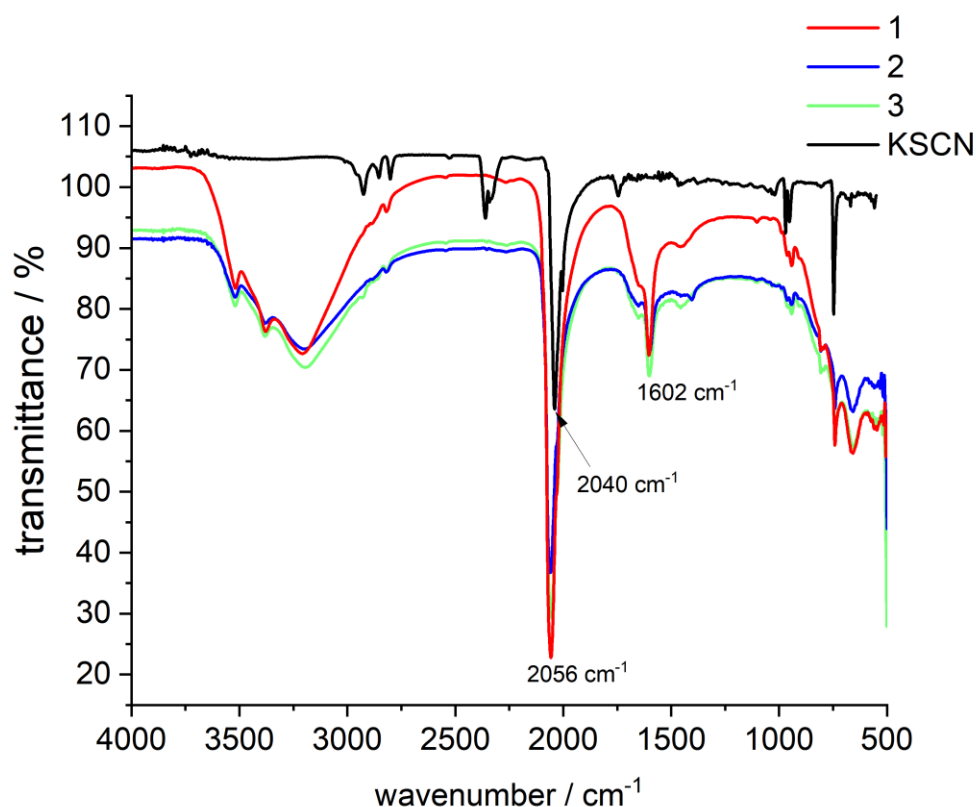
<sup>a</sup>  $-x+3/2, y, -z+1$ ; <sup>b</sup>  $-x+3/2, -y+3/2, -z+1/2$ ; <sup>c</sup>  $x, y+1, z$ ; <sup>d</sup>  $-x+3/2, y+1, -z+1$ ; <sup>e</sup>  $x, -y+3/2, z-1/2$ ; <sup>f</sup>  $-x+1, y+1/2, -z+1/2$ ; <sup>g</sup>  $-x+1, y-1/2, -z+1/2$

Continuous Shape Measure Analysis (CSHM) of all lanthanide ions in 1, 2 and 3 residing in eight-coordinate environments was performed using SHAPE program.[1-3] Calculated “Sx” parameters (x = selected idealized shape) provide insight into coordination geometry of the ions: the closer the value of Sx to 0, the closer the geometry of the coordination polyhedra to an idealized shape. The geometries of lanthanide ions coordination environments, encompassing four N and four O atoms each, were tested against all 8-vertex idealized polyhedra available in SHAPE program. Only the results with Sx below 4 are gathered below in the Table S6. According to CSHM analysis the Dy, Gd and Tb complexes, in compounds 1, 2 and 3 respectively, adapt the geometries of distorted square antiprisms (corresponding to distorted D4d symmetry) with very similar “Sx” parameters.

Table S9. Results of the Continuous Shape Measure Analysis of lanthanide ion coordination spheres in compounds 1, 2 and 3 and symmetry of the corresponding ideal shapes.

Ion	S <sub>SAPR</sub>	S <sub>TDD</sub>	S <sub>BTPR</sub>	S <sub>JSD</sub>
Dy <sup>3+</sup>	<b>0.562</b>	1.519	1.774	3.507
Tb <sup>3+</sup>	<b>0.502</b>	1.577	1.776	3.582
Gd <sup>3+</sup>	<b>0.509</b>	1.562	1.783	3.610
Symmetry of the ideal shape	<b>D4d</b>	D2d	C2v	D2d

SAPR - Square antiprism; TDD - Triangular dodecahedron; BTPR - Biaugmented trigonal prism; JSD - Snub diphennoid.



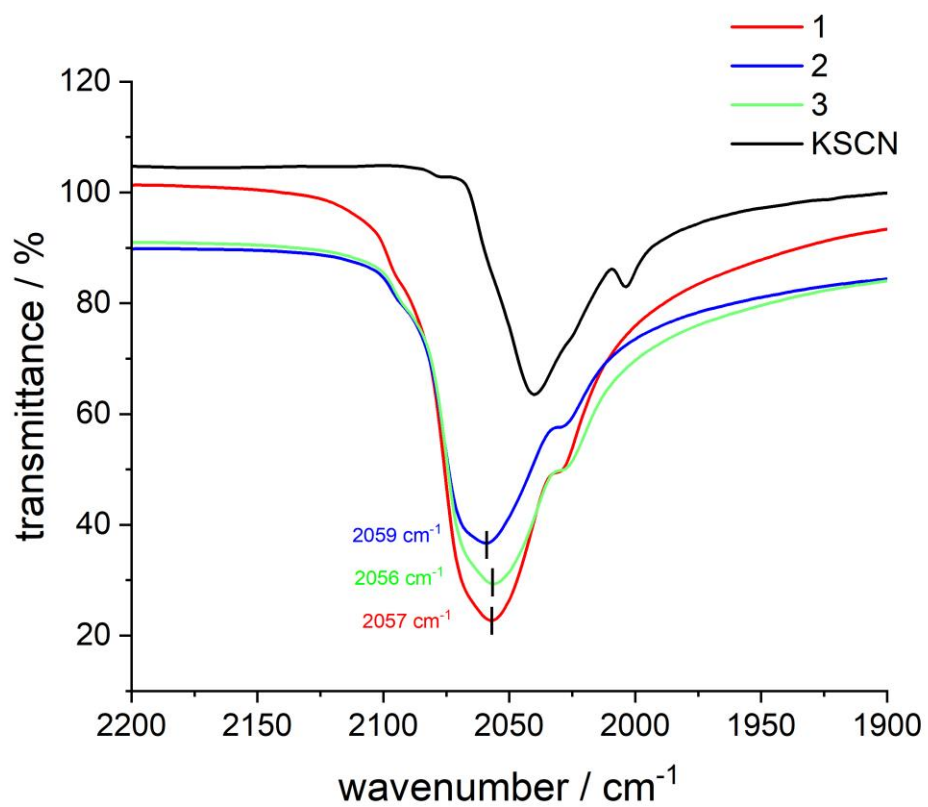
**Figure S10.** IR spectra of 1 (red), 2 (blue), 3 (green) and KSCN (black) in the range of 4000 - 500  $\text{cm}^{-1}$ . Selected vibration peaks are marked.

Fourier transform infrared spectra (FTIR) of powdered air-dried samples of 1, 2 and 3 were measured on Jasco FT/IR-4200 equipped with ATR PR0450-S system over range 4000-500  $\text{cm}^{-1}$ . For ATR (attenuated total reflection) a diamond crystal was used with a 1.5 mm diameter of sample contact area. KSCN spectra (Wako guaranteed reagent) was also measured for comparison with 1-3.

The collected results of IR spectra measurements are presented in Figure S10. Figure S11 shows close-up view of the 2200-1900  $\text{cm}^{-1}$  region where some finer details can clearly be seen.

Stretching C-N vibrations are found in the 2100-2000  $\text{cm}^{-1}$  range. Coordination of  $\text{SCN}^-$  to  $\text{Ln}^{3+}$  in 1, 2 and 3 causes visible shift to higher wavenumbers (2056  $\text{cm}^{-1}$ ) as can be observed by comparison with KSCN salt (2040  $\text{cm}^{-1}$ ). Little difference has been found between the CN vibrations of different presented lanthanides (Figure S11).

We have assigned a series of peaks centred around 1602  $\text{cm}^{-1}$  to H-O-H bending vibrations of various coordinated and uncoordinated  $\text{H}_2\text{O}$  molecules. Difference between KSCN showing no peaks in this region and 1, 2 and 3 can be traced to the presence of water molecules in the latter. Moreover, this is a well-known region of bending vibrations of  $\text{H}_2\text{O}$  [4].



**Figure S11.** IR spectra of 1 (red), 2 (blue), 3 (green) and KSCN (black) in the range of 2200 - 1900  $\text{cm}^{-1}$ . Selected vibration peaks are marked.

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