# ELECTRONIC SUPPLEMENTARY INFORMATION

## to

**"Switching on" the single-molecule magnet properties within a series of dinuclear cobalt(III)-dysprosium(III) 2-pyridyloximate complexes†**

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**Table S1.** Crystallographic data for complexes $[CoDy(pao)_3(NO_3)_3]$ (**1**), $[CoDy(mepao)_3(NO_3)_3]$ (**2**), $[CoDy(phpao)_3(NO_3)_3]$ (**3**) and $[CoDy(NH_2pao)_3(NO_3)_3]\cdot 3MeOH$ (**4**·3MeOH).

| | **1** | **2** | **3** | **4·3MeOH** |
|---|---|---|---|---|
| **Formula** | $C_{18}H_{15}CoDyN_9O_{12}$ | $C_{21}H_{21}CoDyN_9O_{12}$ | $C_{36}H_{27}CoDyN_9O_{12}$ | $C_{21}H_{30}CoDyN_{12}O_{15}$ |
| ***Fw*** | 770.82 | 812.90 | 990.09 | 912.00 |
| **Space group** | $R\bar{3}$ | $R3$ | $R3c$ | $P\bar{3}c1$ |
| ***a* (Å)** | 14.1257(3) | 15.0503(2) | 11.2364(2) | 16.5137(2) |
| ***b* (Å)** | 14.1257(3) | 15.0503(2) | 11.2364(2) | 16.5137(2) |
| ***c* (Å)** | 20.6905(4) | 10.2997(1) | 55.6273(10) | 20.9946(5) |
| ***α* (°)** | 90.00 | 90.00 | 90.00 | 90.00 |
| ***β* (°)** | 90.00 | 90.00 | 90.00 | 90.00 |
| ***γ* (°)** | 120.00 | 120.00 | 120.00 | 120.00 |
| ***V* (Å³)** | 3575.4(2) | 2020.44(6) | 6082.37(19) | 4958.23(13) |
| ***Z*** | 6 | 3 | 6 | 4 |
| ***T* (K)** | 160(2) | 170(2) | 160(2) | 160(2) |
| **Radiation** | Cu Kα (1.54178 Å) | | | |
| **$\rho_{calcd}$(g cm$^{-3}$)** | 2.148 | 2.004 | 1.637 | 1.222 |
| **$\mu$ (mm$^{-1}$)** | 22.812 | 20.224 | 13.570 | 11.104 |
| **Reflection collected** | 10087 | 6533 | 30781 | 48920 |
| **Independent reflections** | 1348 ($R_{int}$ = 0.0754) | 1486 ($R_{int}$ = 0.0679) | 2228 ($R_{int}$ = 0.0801) | 2819 ($R_{int}$ = 0.0615) |
| **Reflections with $I > 2\sigma(I)$** | 1283 | 1445 | 2145 | 2431 |
| **$R_1[I > 2\sigma(I)]$[a]** | 0.0348 | 0.0368 | 0.0423 | 0.0309 |
| **$wR_2[I > 2\sigma(I)]$[b,c]** | 0.0856 | 0.0713 | 0.1126 | 0.0866 |
| **$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ [e Å$^{-3}$]** | 1.410/-1.441 | 1.519/-0.663 | 0.983/-0.644 | 0.539/-0.567 |

**[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma(|F_o|)$.**

**[b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.**

**[c] $w = 1/[\sigma^2(F_o^2)+(\alpha P)^2+bP]$ and $P = [\max(F_o^2,0)+2F_c^2)]/3$. $\alpha$ = 0.0465, $b$ = 15.5519 for 1; $\alpha$ = 0.0140, $b$ = 0.0000 for 2; $\alpha$ = 0.0806, $b$ = 4.3217 for 3; $\alpha$ = 0.0445, $b$ = 3.1629 for 4·3MeOH.**

**Table S2.** Continuous Shape Measures (CShM) values for the possible coordination polyhedra of the 9-coordinate Dy ions in the molecular structures of **1**, **2**, **3** and **4**·3MeOH.

| Ideal polyhedron | 1 | 2 | 3 | 4·3MeOH |
|---|---|---|---|---|
| **Enneagon** | 30.88332 | 32.88982 | 35.40640 | 33.33234 |
| **Octagonal pyramid** | 22.44352 | 24.84877 | 24.65017 | 23.83295 |
| **Heptagonal bipyramid** | 19.13731 | 18.25268 | 20.66390 | 19.86454 |
| **Johnson triangular cupola** | 9.74068 | 11.86441 | 13.48457 | 12.73433 |
| **Capped cube J8** | 11.21531 | 10.17419 | 11.78072 | 11.29538 |
| **Spherical-relaxed capped cube** | 10.16580 | 9.02410 | 10.50435 | 10.17170 |
| **Capped square antiprism J10** | 4.04342 | 3.62828 | 3.58005 | 3.50544 |
| **Spherical capped square antiprism** | 3.12865 | 2.72964 | 2.50406 | 2.55199 |
| **Tricapped trigonal prism J51** | **2.8226** | 2.88247 | 3.06133 | 2.64178 |
| **Spherical tricapped trigonal prism** | 3.13332 | **2.31202** | **2.02651** | **2.27077** |
| **Tridiminished icosahedron J63** | 14.07676 | 11.27019 | 12.92923 | 13.28582 |
| **Hula-hoop** | 12.16811 | 12.76749 | 13.07646 | 12.88460 |
| **Muffin** | 3.33347 | 2.90445 | 2.54333 | 2.65181 |

**[a]The smallest values (in bold) define the best polyhedron. [b]Chemically significant distortions give CShM values of 0.1 or higher, while values larger than about 3 indicate important distortions.**

**Table S3** H-bonding interactions in the crystal structures of **1**, **2**, **3** and **4**·3MeOH.

| Interaction | D···A (Å) | H···A (Å) | D-H···A (°) | Symmetry operation of A |
|---|---|---|---|---|
| **Complex 1** | | | | |
| **C3-H3···O1** | 3.136 | 2.281 | 149.5 | 1/3+*y*,-1/3-*x*+*y*, 2/3+*z* |
| **C4-H4···O13** | 3.283 | 2.425 | 150.1 | 1/3-*y*, -2/3-*y*, 1/3-*z* |
| **Complex 2** | | | | |
| **C1-H1···O12**[a] | 3.159 | 2.538 | 123.1 | *x*, *y*, 1+*z* |
| **C4-H4···O1** | 3.168 | 2.317 | 148.8 | 2/3-*y*, 1/3+*x*-*y*, 1/3+*z* |
| **C7**[b]**-H7B···O12** | 3.394 | 2.679 | 130.1 | 2/3-*y*, 1/3+*x*-*y*, 1/3+*z* |
| **Complex 3** | | | | |
| **C8-H8···O11**[c] | 3.357 | 2.442 | 161.4 | *x*, *y*, *z* |
| **C10-H10···O11** | 3.381 | 2.634 | 135.8 | *x*, 1+*y*, *z* |
| **C10-H10···O1** | 3.354 | 2.465 | 155.8 | -*x*+*y*, 2-*x*, *z* |
| **C2-H2···O11** | 3.382 | 2.551 | 146.5 | 1/3-*y*,2/3-*x*, 1/6+*z* |
| **C2-H2···O12**[a] | 3.109 | 2.462 | 125.4 | -2/3+*x*, 2/3+*x*-*y*, 1/6+*z* |
| **C1-H1···O13** | 3.271 | 2.478 | 140.9 | 1/3-*y*,2/3-*x*, 1/6+*z* |
| **Complex 4·3MeOH** | | | | |
| **N3**[d]**-HB(N3) ···O1M** | 2.847 | 2.01 | 158 | *y*,-*x*+*y*,-*z* |
| **C3-H3···O11**[a] | 3.216 | 2.56 | 127 | *x*-*y*,- 1+*x*,-*z* |
| **O1M**[e] **–H(O1M)···O1** | 2.725 | 1.87 | 172 | *x*, *y*, *z* |
| **C4-H4···O11**[a] | 3.231 | 2.68 | 119 | *x*-*y*,-1+*x*,-*z* |

**[a]These H bonds are very weak and could not be considered. [b]This is the methyl C atom of mepao$^-$ not labelled in Fig. S1. [c]Intramolecular H bond. [d]This is the amino nitrogen atom not labelled in Fig. 2. [e]Lattice MeOH molecules. Abbreviations: A = acceptor, D = donor.**

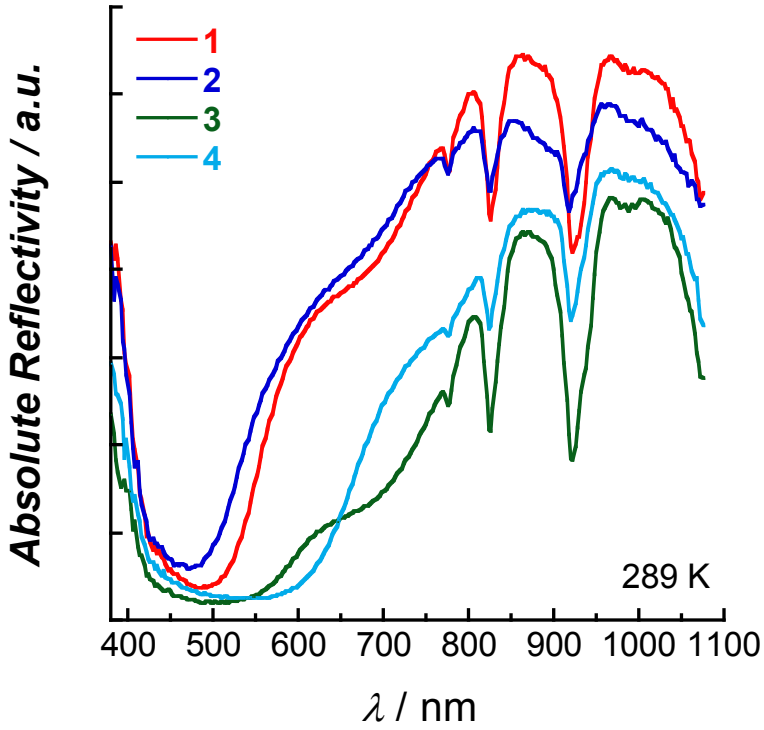



**Figure S1.** Optical reflectivity spectra for **1**, **2**, **3** and **4** at 289 K.

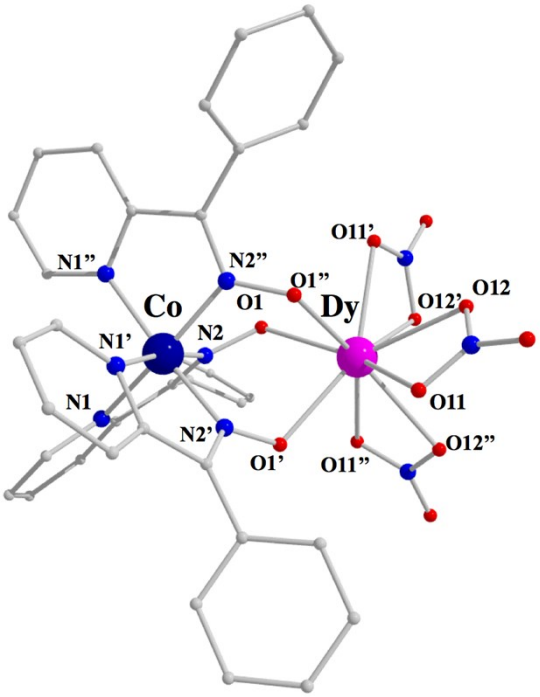



**Figure S2.** Partially labelled view of the molecular structure of complex $[CoDy(phpao)_3(NO_3)_3]$ (**3**). Symmetry operations used to generate equivalent atoms: (') –*y*+1, *x*-*y*+1, *z*; (") -*x*+*y*, -*x*+1, *z*. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

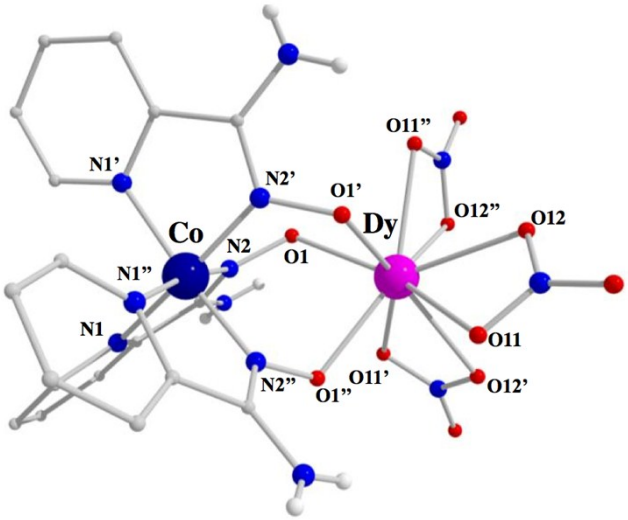



**Figure S3.** Partially labelled view of the structure of the dinuclear complex that is present in **4**·3MeOH. Only the H atoms of the $–NH_2$ groups are shown. Symmetry operations to generate equivalent atoms: (') -x+*y*+1, -*x*+1, *z*; (") -*y*+1, *x*-*y*, *z*. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey; H, white.

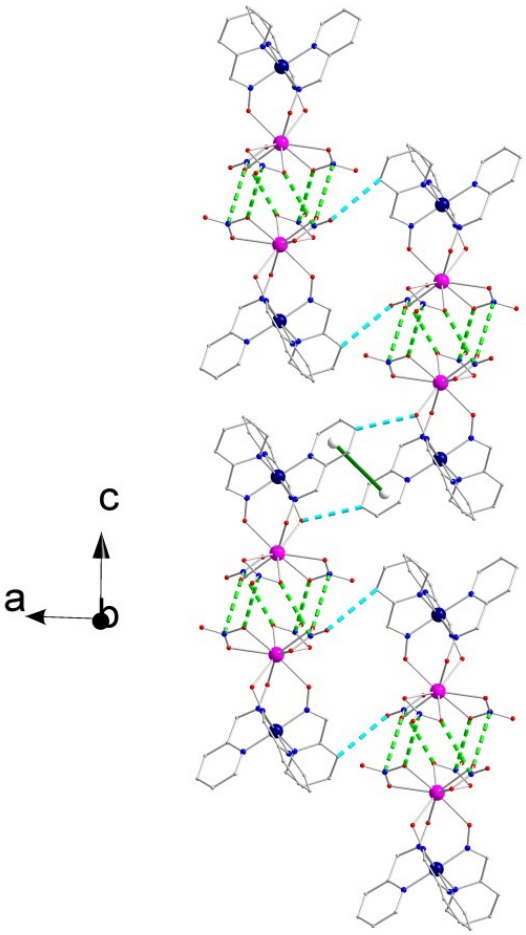



**Figure S4.** Side view of the intra- and inter-column inter-molecular interactions in $[CoDy(pao)_3(NO_3)_3]$ (**1**). The columns are situated along *c* formed by "dimers" as described in the text. The green, thick dashed lines represent the inter-dimer nitrato-nitrato O···N interactions, and the turquoise, dashed lines the $C_{aromatic}$-H···$O_{oximato}$ and $C_{aromatic}$-H···$O_{non\text{-}coord.nitrato}$ H bonds. The green solid line indicates a π-π stacking interaction. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

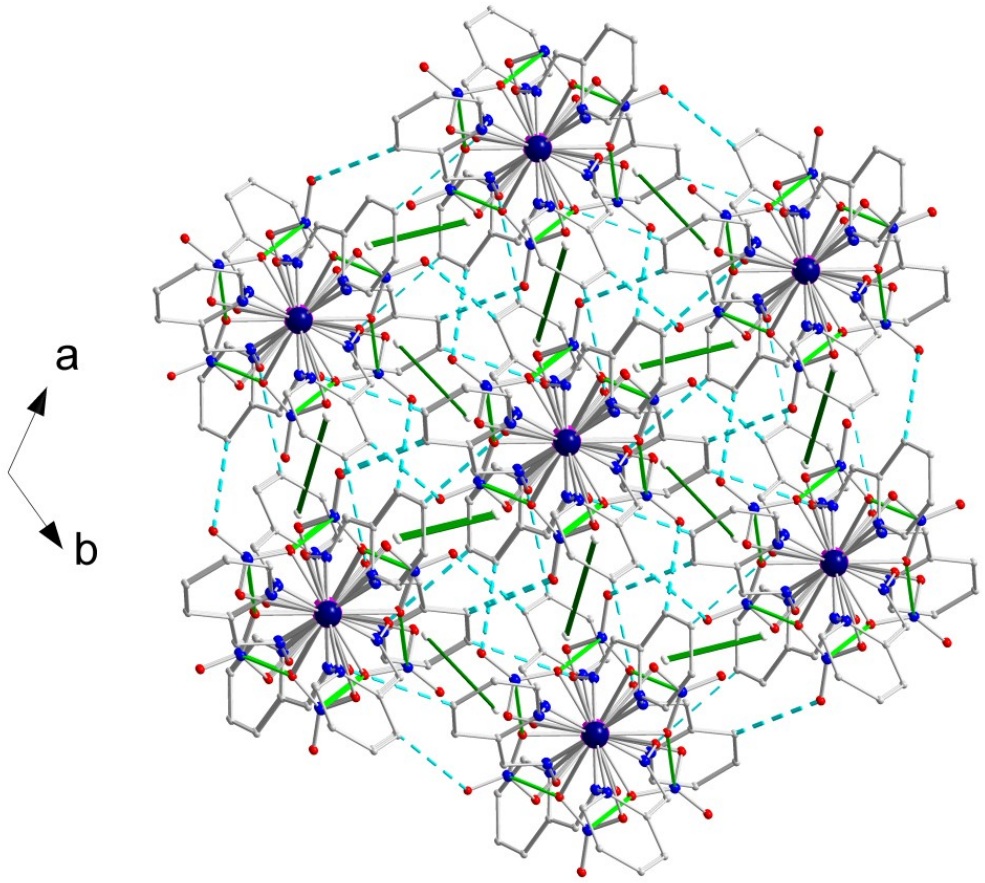



**Figure S5.** Top view of the 3D architecture in the crystal structure of $[CoDy(pao)_3(NO_3)_3]$ (**1**) viewed down the *c* axis. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

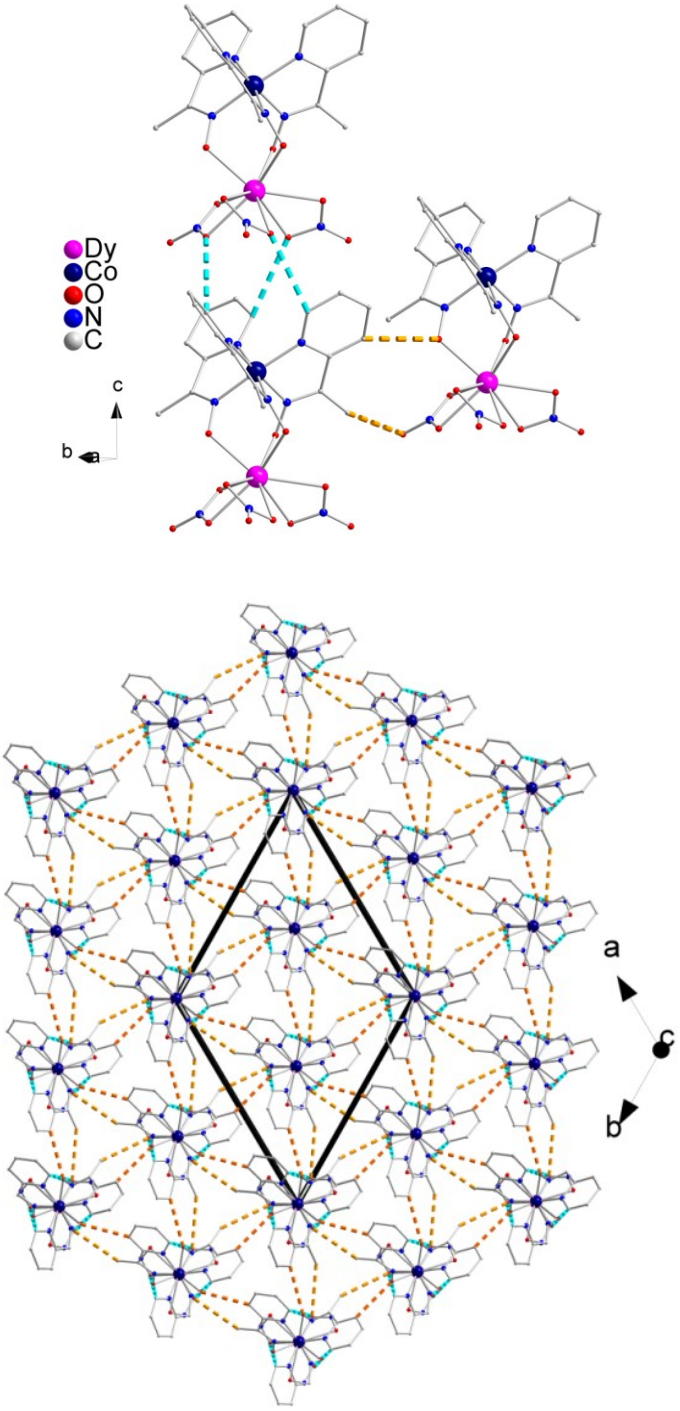



**Figure S6. (Top)** View of the inter-molecular interactions in the crystal structure of $[CoDy(mepao)_3(NO_3)_3]$ (**2**)**.** The intra-column C1-H1···O12 H bonds are indicated by turquoise dashed lines, while the orange-brown dashed lines represent the C4-H4···O1 and C7-H7B···O12 interactions, see Table S3. **(Bottom)** Top view of the 3D architecture in the crystal structure of complex **2** viewed down the *c* axis. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

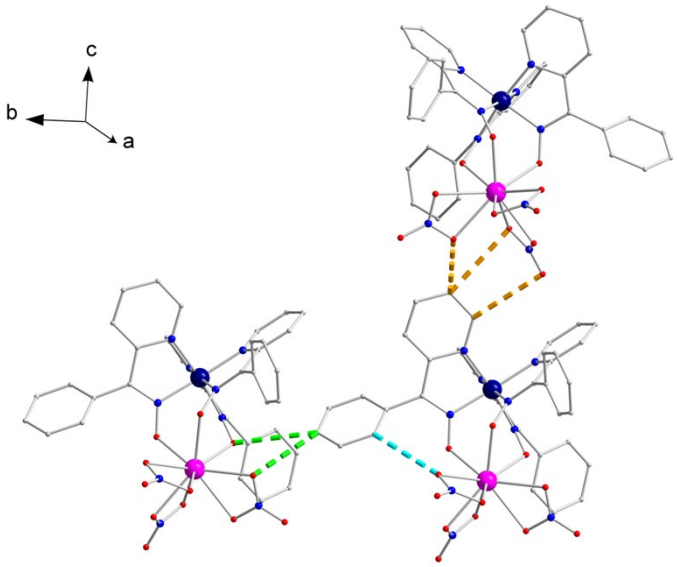



**Figure S7.** View of the inter-molecular H-bonding interactions in the crystal structure of $[CoDy(phpao)_3(NO_3)_3]$ (**3**)**.** The turquoise, bright green and orange-brown dashed lines represent the intra-molecular C8-H8···O11, the inter-molecular intra-layer C10-H10···O11 and C10-H10···O1, and the inter-layer C2-H2···O11, C2-H2···O12 and C1-H1···O13 H bonds. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

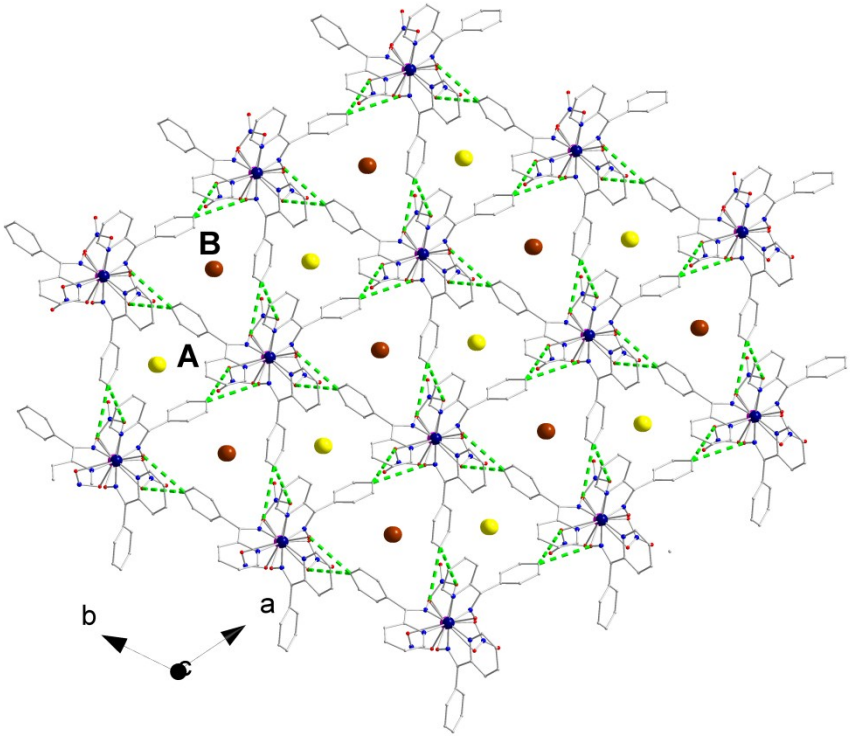



**Figure S8.** View of the layers composed of the dinuclear {CoDy} complexes in the crystal structure of $[CoDy(phpao)_3(NO_3)_3]$ (**3**). These layers are formed though the C10-H10···O11 and C10-H10···O1 H bonds (bright green dashed lines). Dinuclear complexes lying in the layers below (A sites, yellow colour) and above (B sites, brown colour) the main layer are also shown. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

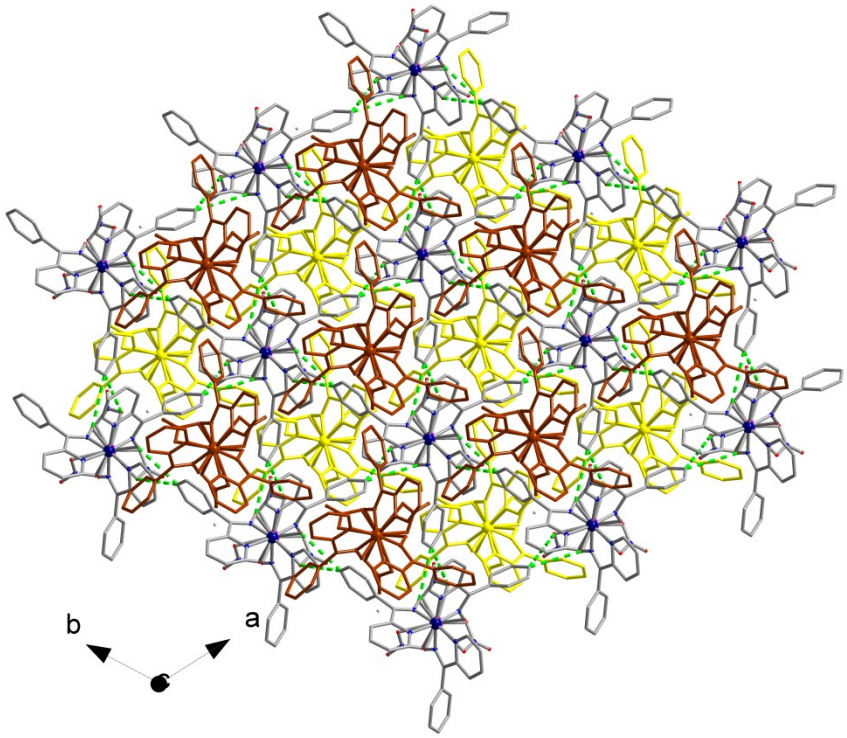



**Figure S9.** Top view of three successive layers in the crystal structure of $[CoDy(phpao)_3(NO_3)_3]$ (**3**). The complexes coloured in yellow and brown form the layers, which lie below and above the middle layer. The intra-molecular and inter-layer H bonds are not shown for clarity. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

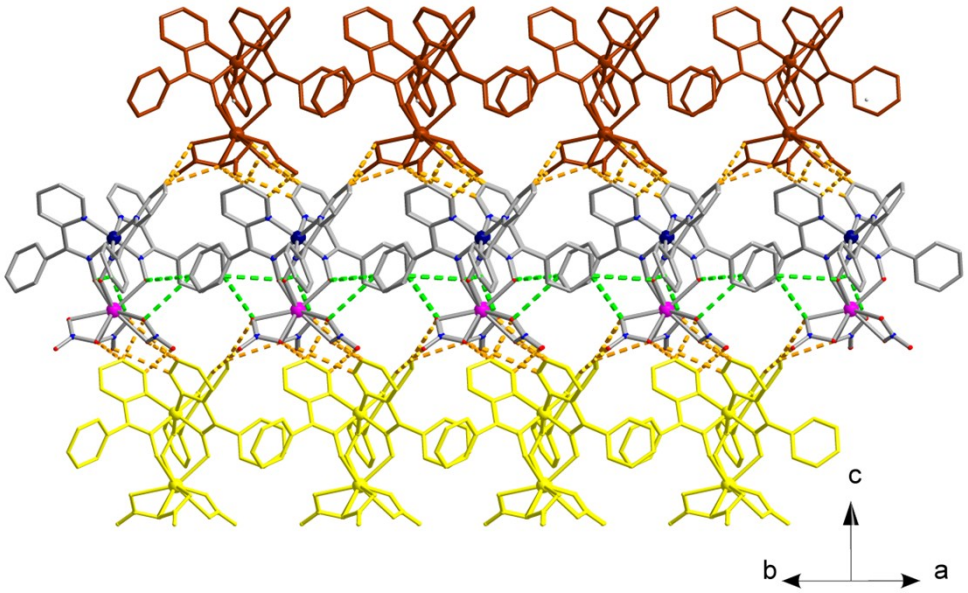



**Figure S10.** Side view of three successive layers of complexes in the crystal structure of $[CoDy(phpao)_3(NO_3)_3]$ (**3**). The intra-molecular H bonds are not shown for clarity. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

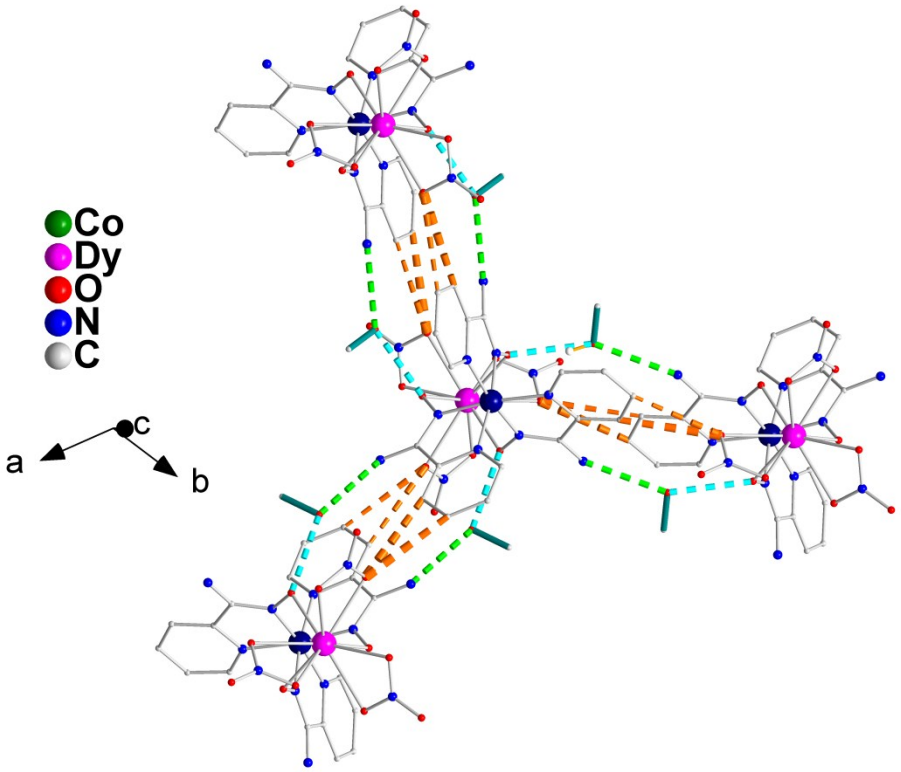



**Figure S11.** H-bonding interactions in the crystal structure of $[CoDy(NH_2pao)_3(NO_3)_3]$ ·3MeOH (**4**·3MeOH). The dark green solid lines indicate the ordered C1M-O1M MeOH lattice molecules. Colour scheme: Co, dark blue; Dy, dark pink; O, red; N, blue; C, grey.

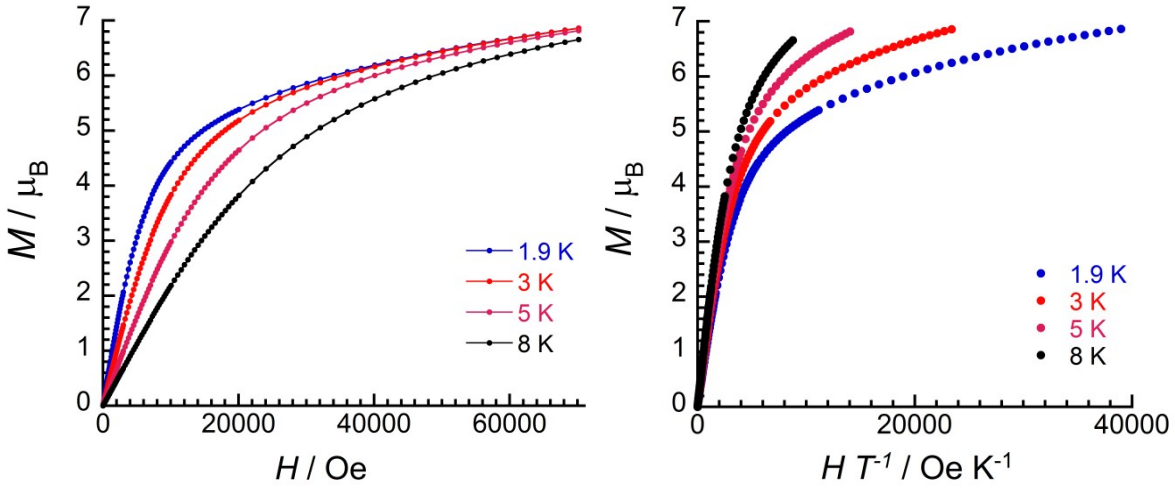



**Figure S12.** Field dependence of magnetisation for complex $[CoDy(pao)_3(NO_3)_3]$ (**1**) plotted as *M* versus *H* (left; solid lines are visual guides) or *M* versus *H/T* (right) at the indicated temperatures, scanning at 80 – 400 Oe.min$^{-1}$ for *H* < 1 T and 500 – 2500 Oe.min$^{-1}$ for *H* > 1 T.

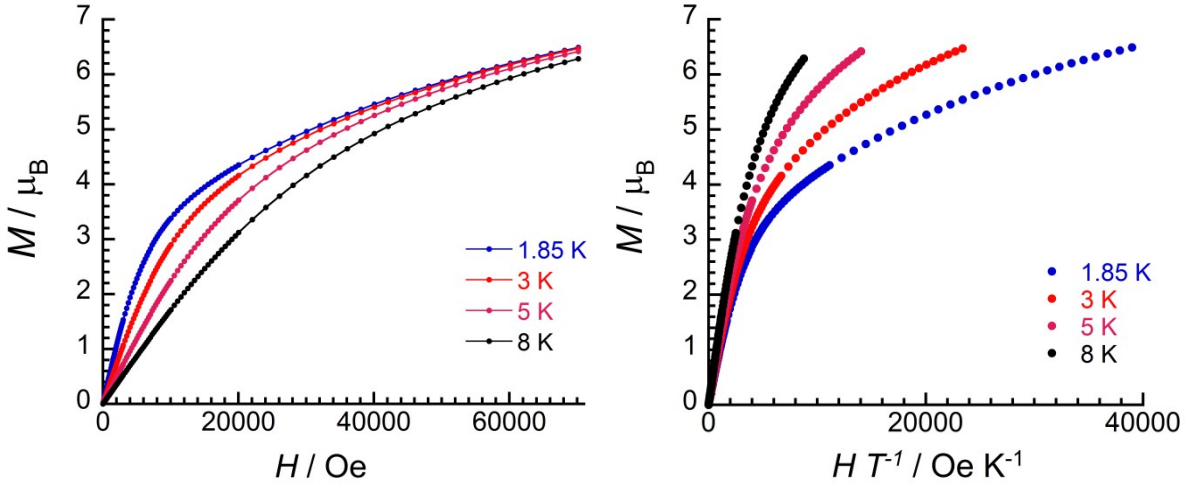



**Figure S13.** Field dependence of magnetisation for complex $[CoDy(mepao)_3(NO_3)_3]$ (**2**) plotted as *M* versus *H* (left; solid lines are visual guides) or *M* versus *H/T* (right) at the indicated temperatures, scanning at 80 – 400 Oe.min$^{-1}$ for *H* < 1 T and 500 – 2500 Oe.min$^{-1}$ for *H* > 1 T.

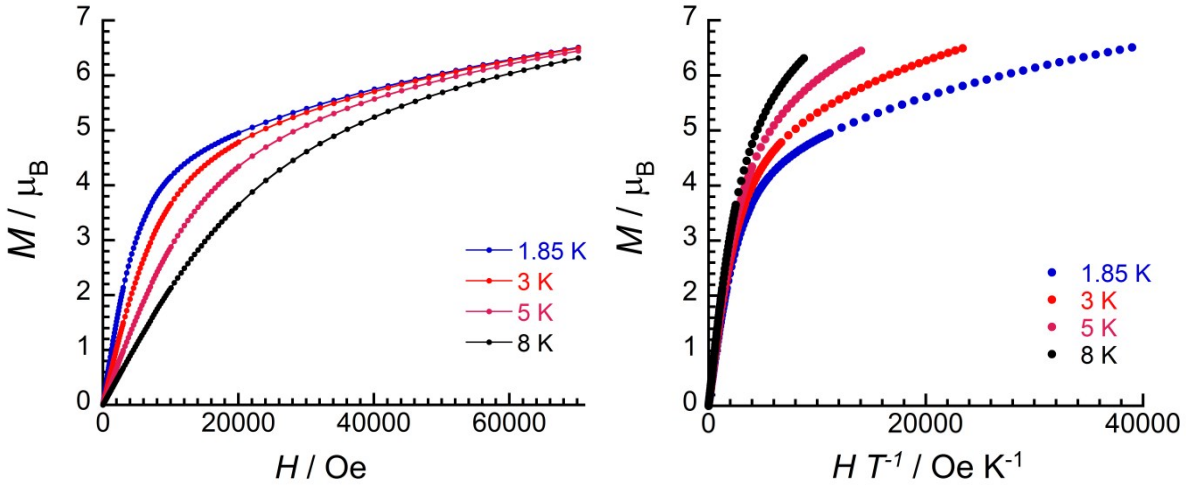



**Figure S14.** Field dependence of magnetisation for complex [CoDy(phpao)$_3$(NO$_3$)$_3$] (**3**) plotted as *M* versus *H* (left; solid lines are visual guides) or *M* versus *H/T* (right) at the indicated temperatures, scanning at 80 – 400 Oe.min$^{-1}$ for *H* < 1 T and 500 – 2500 Oe.min$^{-1}$ for *H* > 1 T.

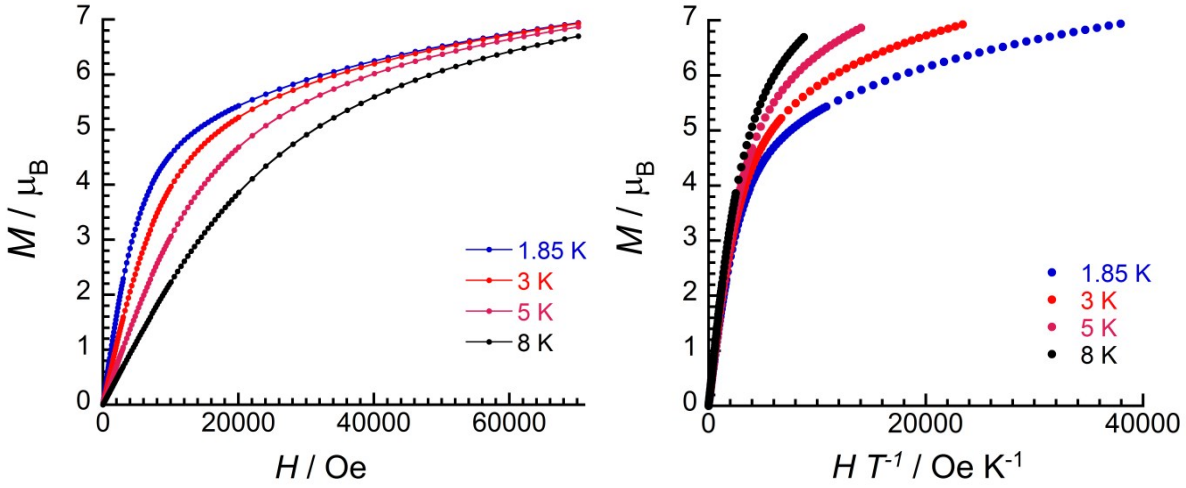



**Figure S15.** Field dependence of magnetisation for complex [CoDy(NH$_2$pao)$_3$(NO$_3$)$_3$] (a dried sample of **4**·3MeOH) plotted as *M* versus *H* (left; solid lines are visual guides) or *M* versus *H/T* (right) at the indicated temperatures, scanning at 80 – 400 Oe.min$^{-1}$ for *H* < 1 T and 500 – 2500 Oe.min$^{-1}$ for *H* > 1 T.

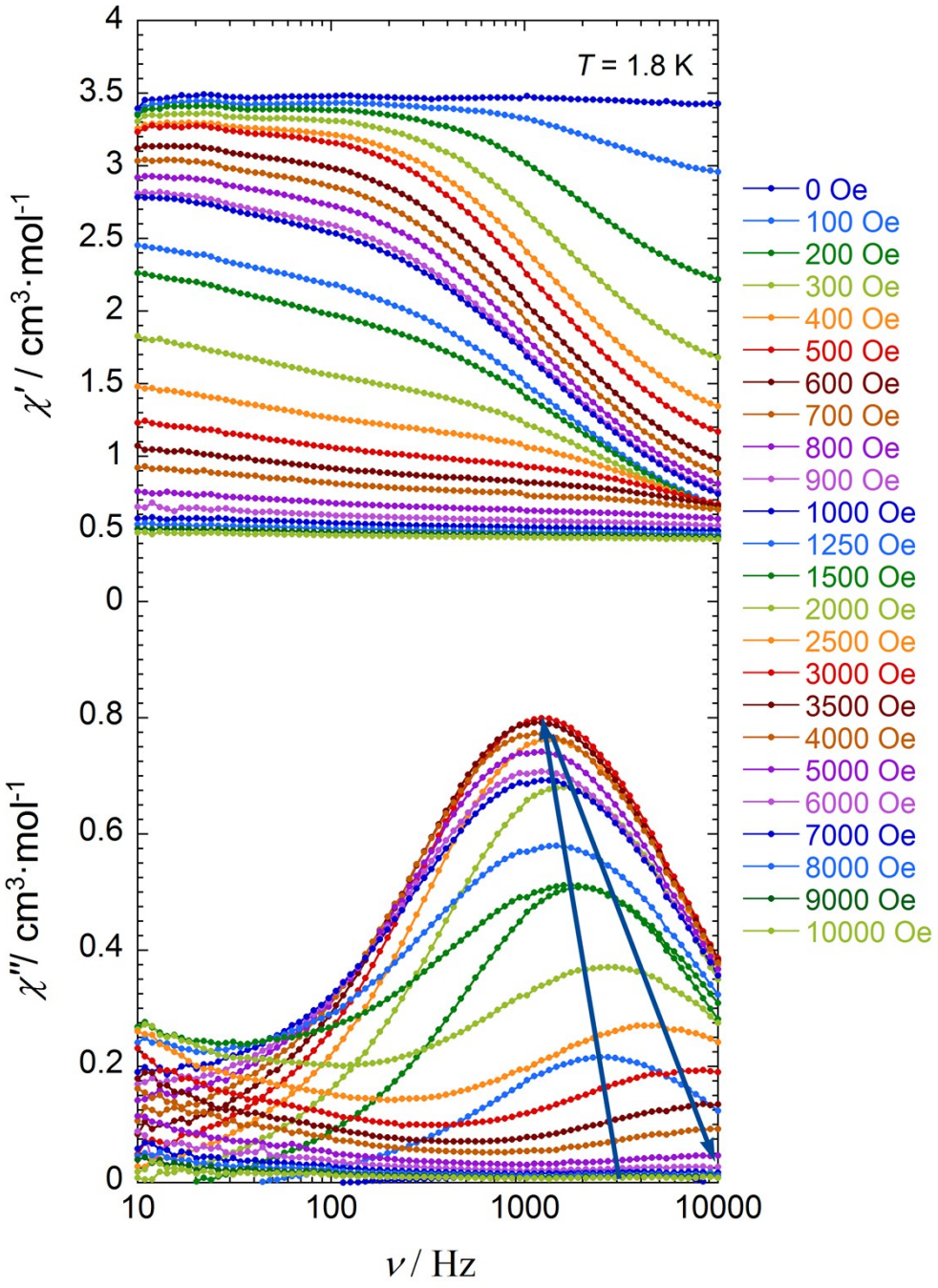



**Figure S16.** Frequency dependence of the real ($\chi'$, top) and imaginary ($\chi''$, bottom) components of the *ac* susceptibility, at the indicated *dc* fields (between 0 and 1 T) for $[CoDy(mepao)_3(NO_3)_3]$ (**2**) at 1.8 K. Solid lines and arrows are visual guides.

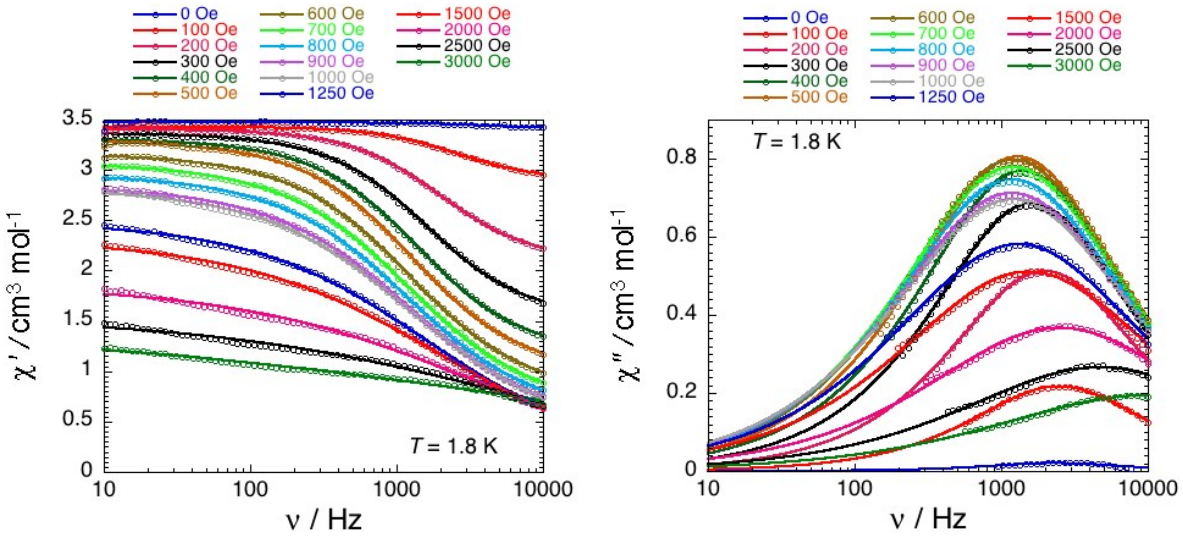



**Figure S17.** Frequency dependence of the real ($\chi'$, left) and imaginary ($\chi''$, right) components of the *ac* susceptibility, at the indicated *dc* fields (between 0 and 0.3 T) for $[CoDy(mepao)_3(NO_3)_3]$ (**2**) at 1.8 K. The solid lines are the best fits of the main relaxation mode seen in the experimental data (Figure S16) to the generalized Debye model.

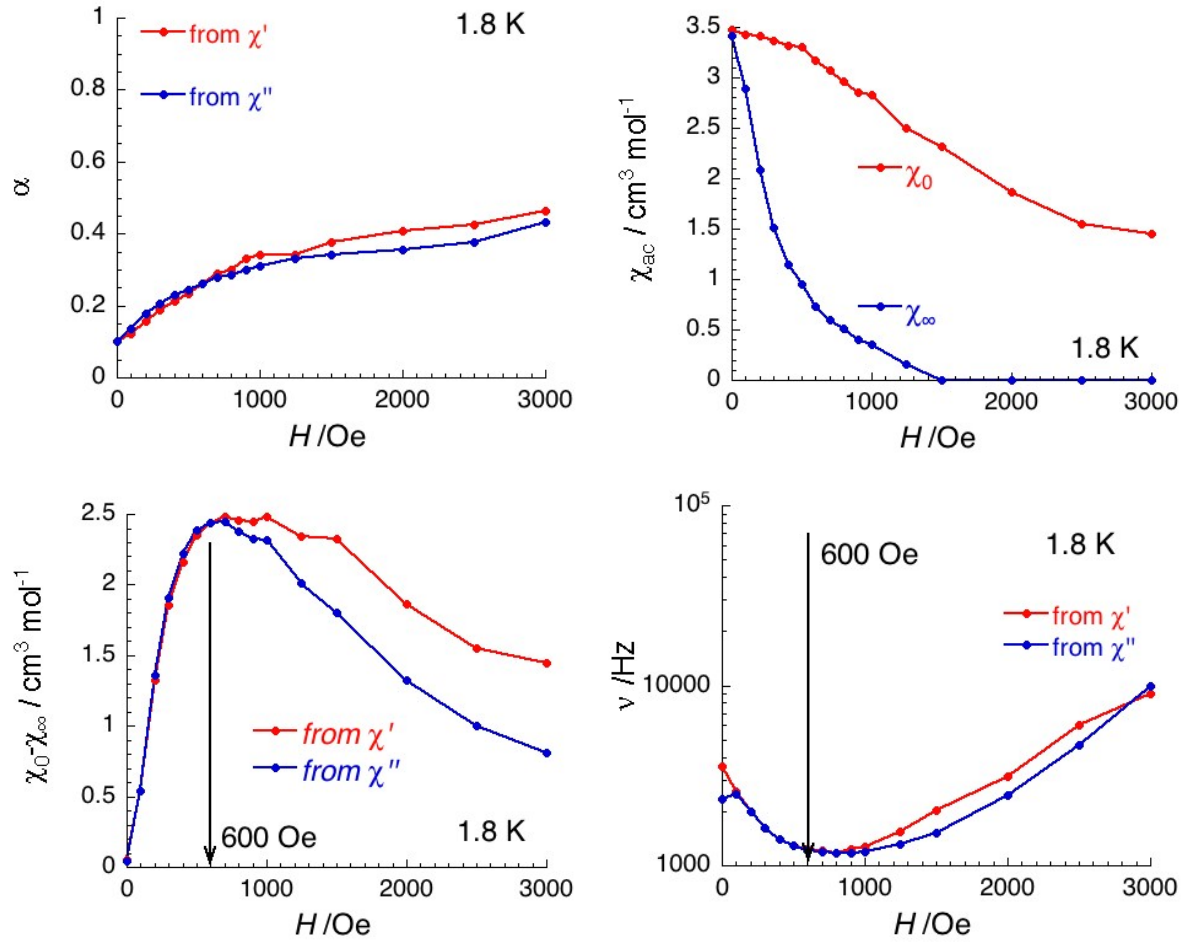



**Figure S18**. Field dependence of the parameters ($\alpha$, $\chi_0$, $\chi_\infty$, $\chi_0$-$\chi_\infty$, and the characteristic frequency, ν) deduced from the Debye generalized fits of the experimental data for complex $[CoDy(mepao)_3(NO_3)_3]$ (**2**) at 1.8 K (Figure S17). Solid lines are visual guides.

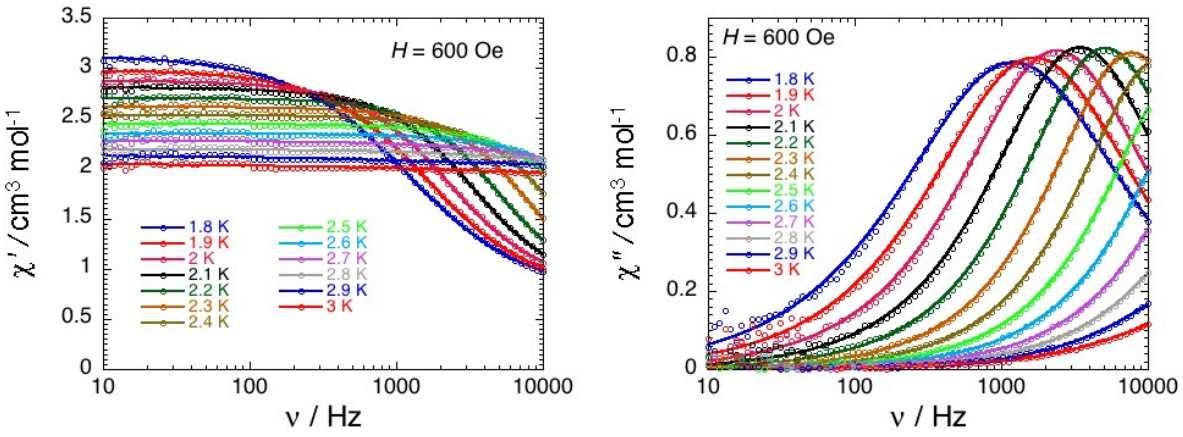



**Figure S19.** Frequency dependence of the real (χ′, left) and imaginary (χ″, right) components of the *ac* susceptibility, at the indicated temperatures (between 1.8 and 3 K) for $[CoDy(mepao)_3(NO_3)_3]$ (**2**) at 600 Oe. The solid lines at the best fit of experimental data to the generalized Debye model.

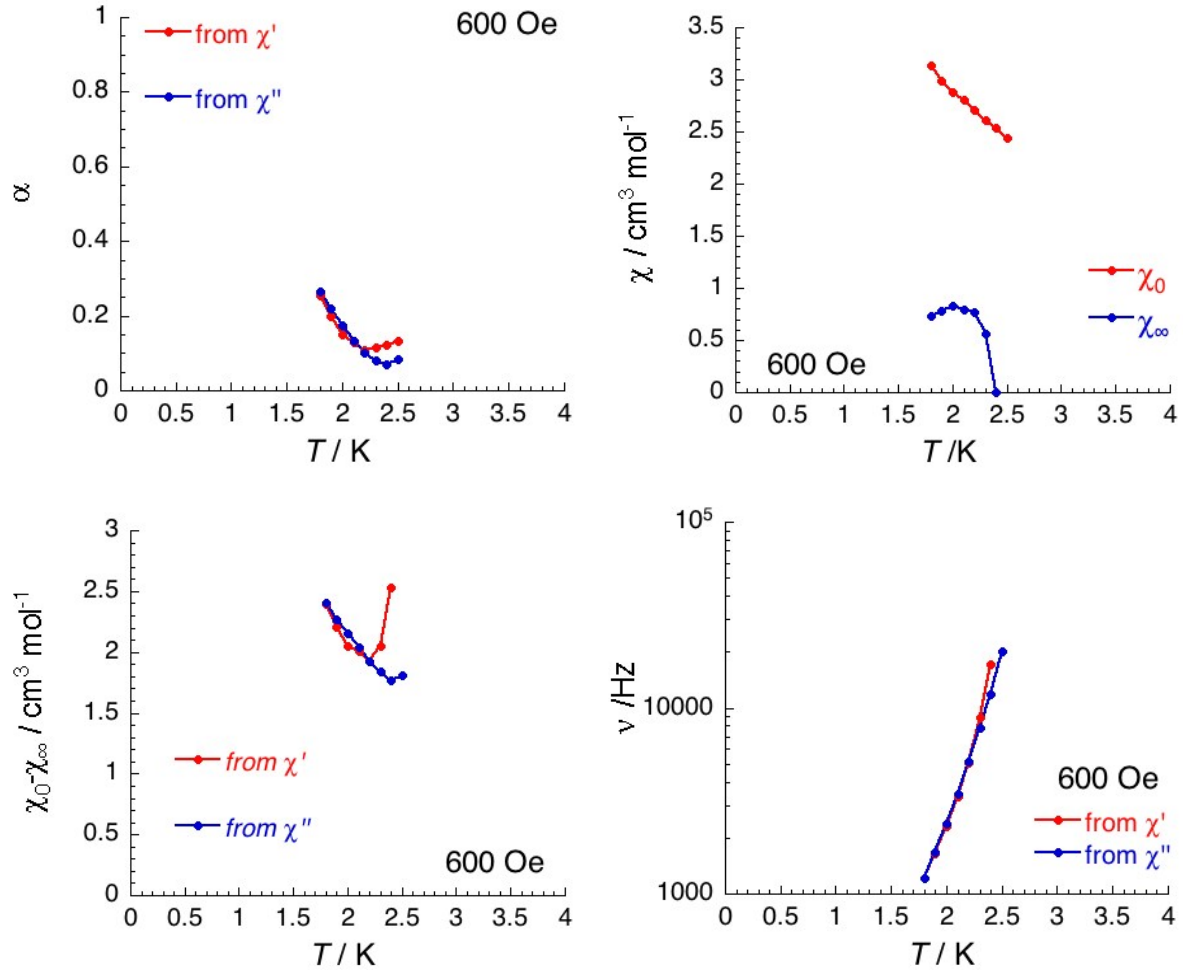



**Figure S20**. Temperature dependence of the parameters ($\alpha$, $\chi_0$, $\chi_\infty$, $\chi_0$-$\chi_\infty$, and the characteristic frequency, ν) deduced from the Debye generalized fits of the experimental data for complex $[CoDy(mepao)_3(NO_3)_3]$ (**2**) at 600 Oe (Figure S19). Solid lines are visual guides.

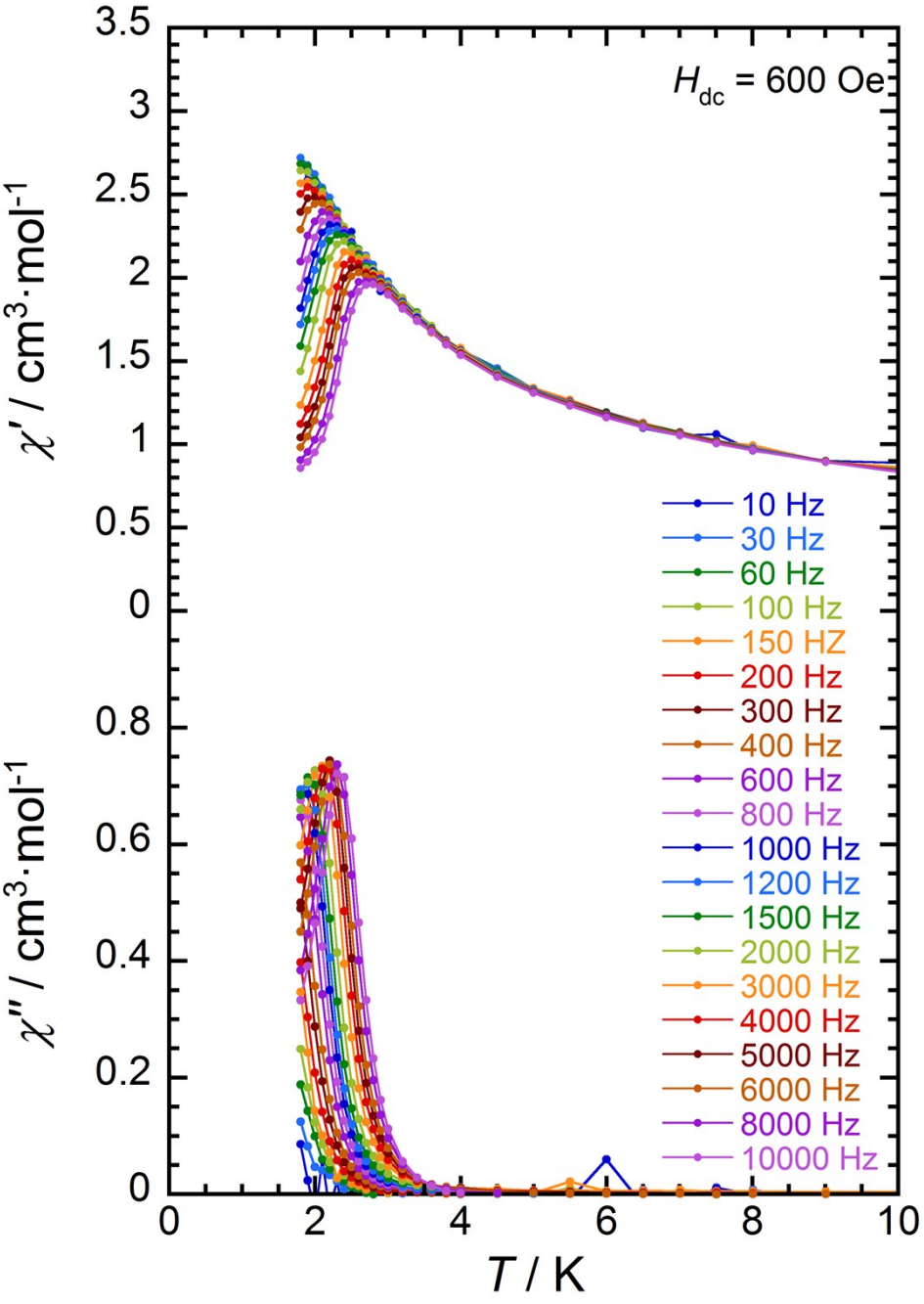



**Figure S21.** Temperature dependence of the real ($\chi'$, top) and imaginary ($\chi''$, bottom) components of the *ac* susceptibility at different *ac* frequencies (between 10 and 10000 Hz) for $[CoDy(mepao)_3(NO_3)_3]$ (**2**) with a 600-Oe *dc* field between 1.8 and 10 K. Solid lines are visual guides.

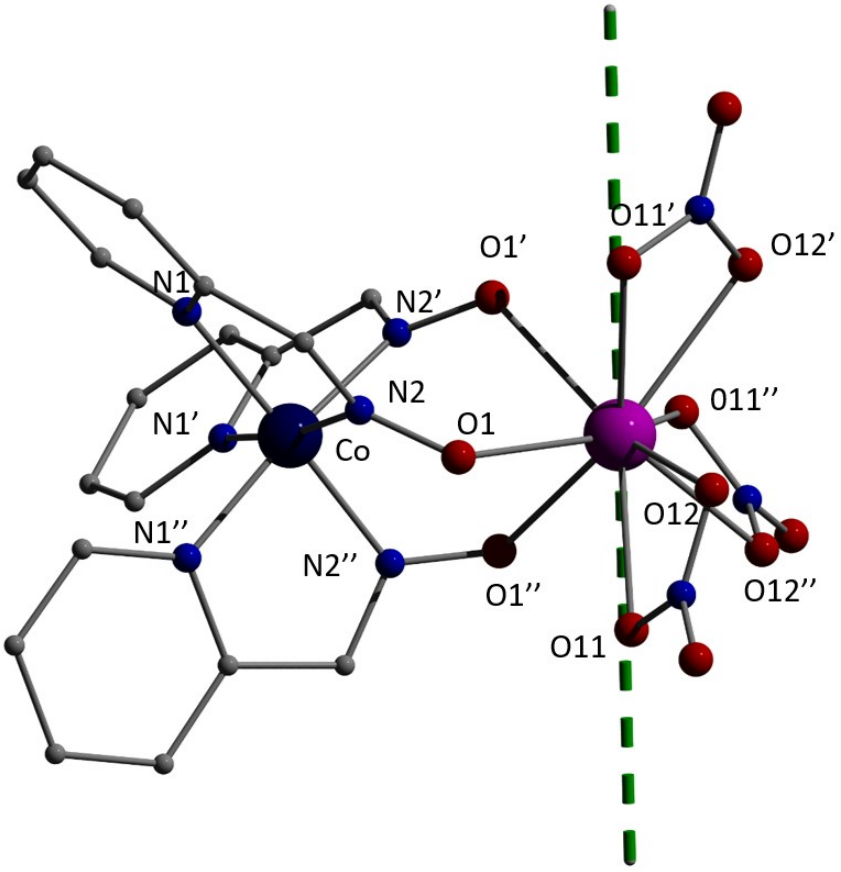



**Figure S22.** Ground-state magnetic anisotropy axis (dashed line) for the Dy ion that is present in the molecule of **1**.

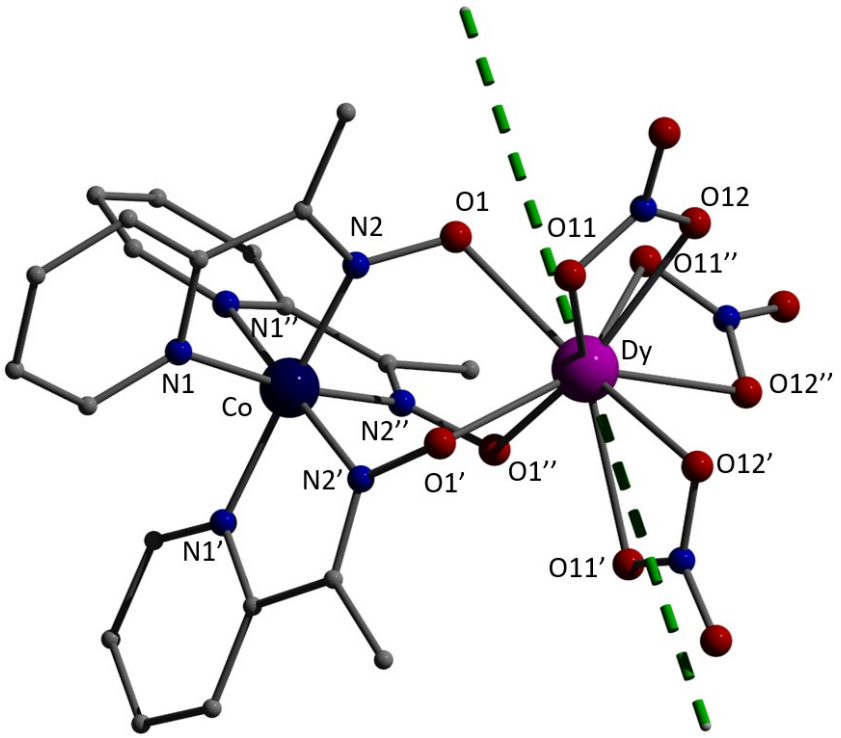



**Figure S23.** Ground-state magnetic anisotropy axis (dashed line) for the Dy ion that is present in the molecule of **2**.

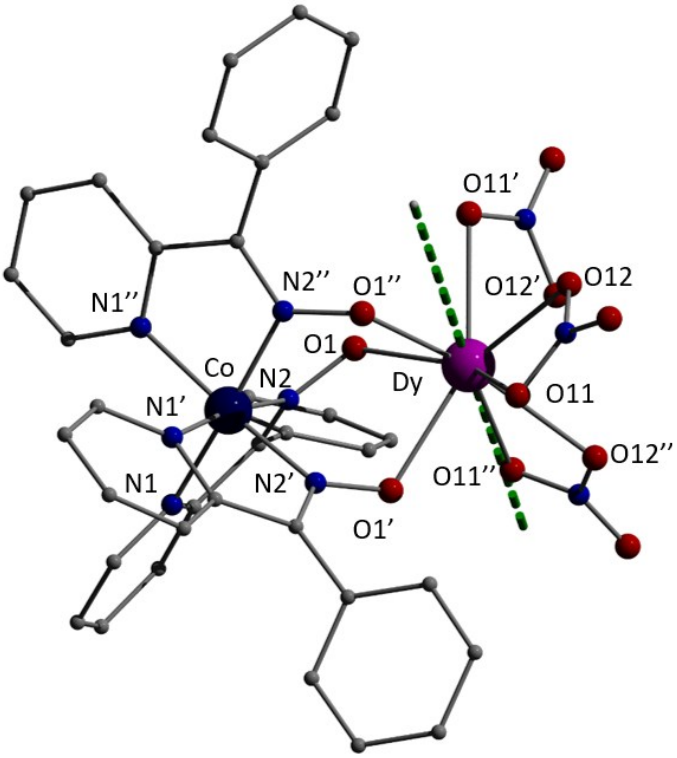



**Figure S24.** Ground-state magnetic anisotropy axis (dashed line) for the Dy ion that is present in the molecule of **3**.

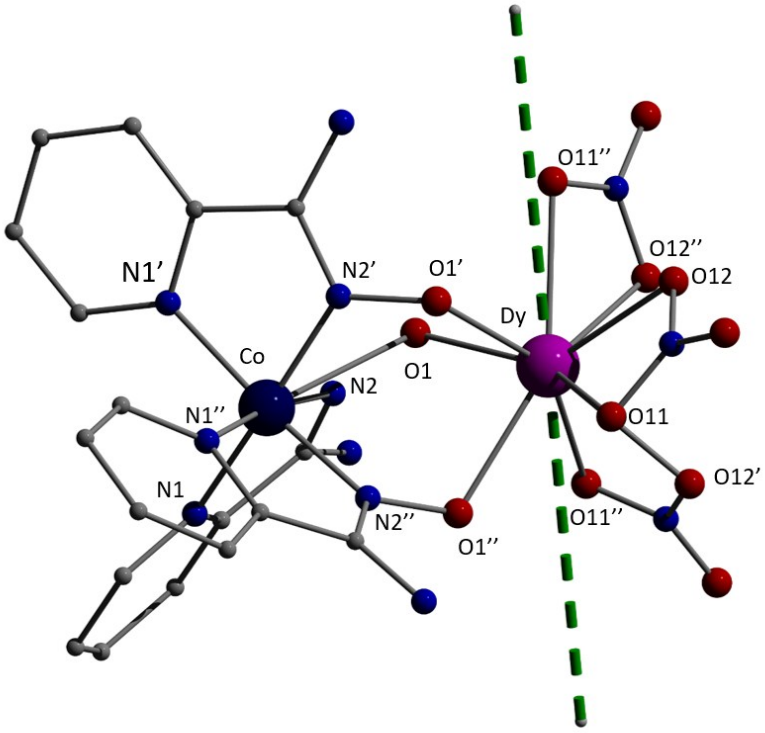
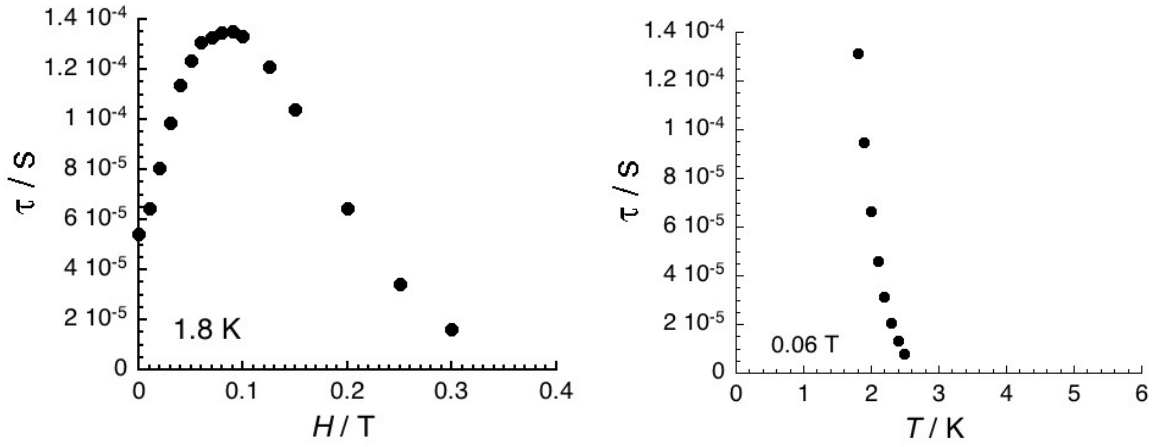



**Figure S25.** Ground-state magnetic anisotropy axis (dashed line) for the Dy ion that is present in the molecule of **4**.

**ALTERNATIVE IDEAS ABOUT THE NATURE OF THE MAGNETIZATION RELAXATION IN COMPLEX [CoDy(mepao)$_3$(NO$_3$)$_3$] (2)**

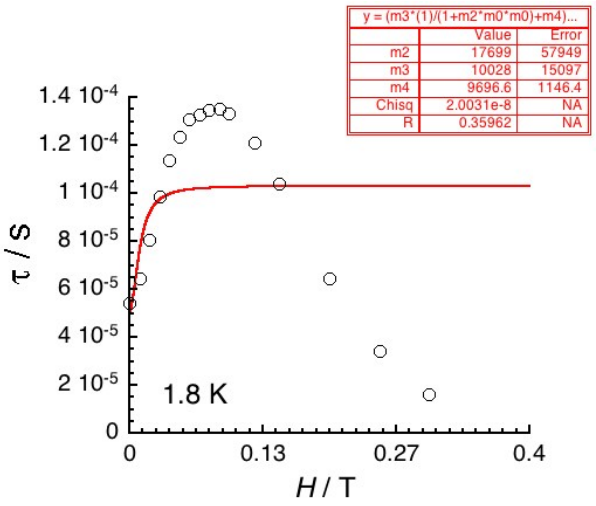



As shown above, from the fit of the *ac* data, the field and temperature dependence of the relaxation time can be deduced. Now the question is : can we fit or understand this dependence? In the text, we talk about two relaxation processes: Quantum tunnelling of the Magnetization (minimized by applying a *dc* magnetic field) and Orbach relaxation (thermally activated but field independent). Unfortunately, it is impossible to fit the data with these two mechanisms!!!

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1}$$

$$\tau^{-1} = \frac{B_1}{1 + B_2 H^2} + K$$

with *K* being a constant in field:



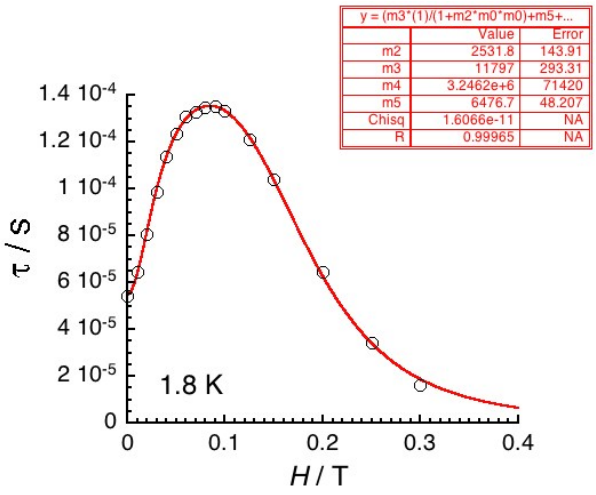
Thus we need to include other pathways of relaxation that explain the fast decrease of the relaxation time above 0.06 T. The only process that can do that is a direct process that has a relaxation time in $H^4$:

$$\tau_{Direct}^{-1} = ATH^4$$

Then we tried to fit with:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Direct}^{-1} + \tau_{Orbach}^{-1}$$

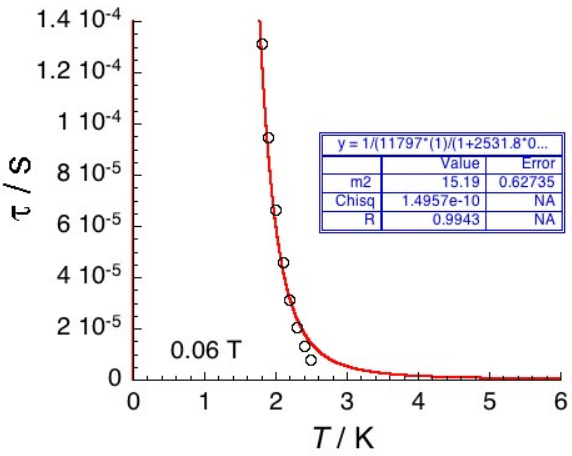
$$\tau^{-1} = \frac{B_1}{1 + B_2 H^2} + ATH^4 + K$$




And it is working… with (four parameters) $B_1$ = 2532 $s^{-1}$, $B_2$ = 11797 $T^{-2}$, $A$ = 3.25 $10^6$ $K^{-1}T^{-4}s^{-1}$ and $K$ = 6477 $s^{-1}$. Then we tried to fit the temperature dependence accordingly fixing these parameters:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Direct}^{-1} + \tau_{Orbach}^{-1}$$

$$\tau^{-1} = \frac{B_1}{1 + B_2 H^2} + ATH^4 + \tau_0^{-1} exp\left(-\frac{\Delta}{k_B T}\right)$$



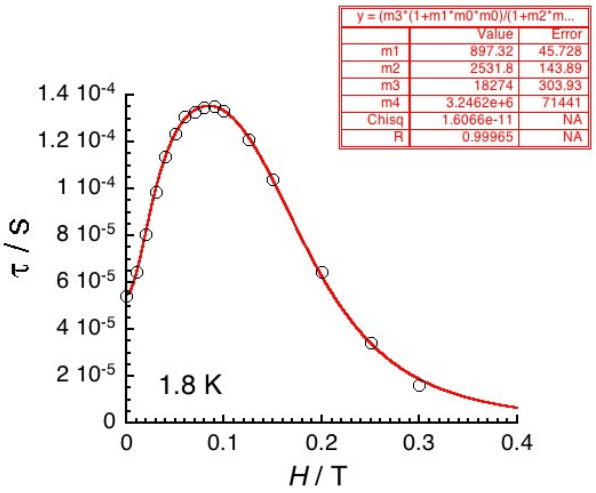

In agreement with the text of the main ms., this is working with $\Delta/k_B$ = 15.2 K (a total of 5 fitting parameters) which implies (based on $K$ = 6477 $s^{-1}$) $\tau_0$ = 3.3 $10^{-8}$ s. But this $\tau_0$ value is a little suspicious. The time to reverse the magnetization from the phonon should be around $10^{-10}$ to $10^{-12}$ s. So we tried a different approach changing our point of view of the problem. Can we fit the data with only two relaxation processes?

Obviously, we need the direct process to explain the field dependence above 0.06 T. At low field, we can try to replace QTM with a Raman process that has almost the same field dependence:

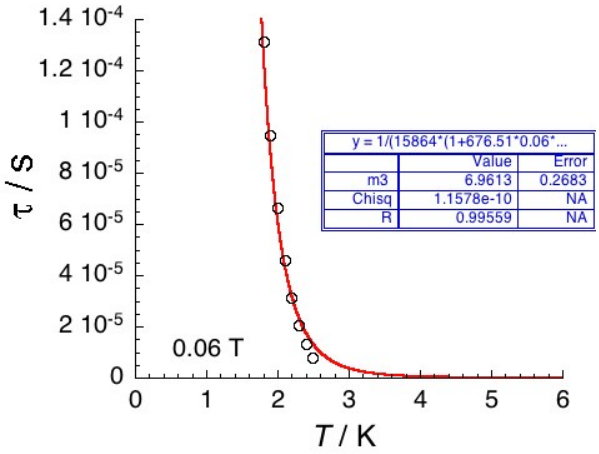
$$\tau^{-1} = \tau_{Raman}^{-1} + \tau_{Direct}^{-1}$$

$$\tau^{-1} = C\frac{1 + B_1H^2}{1 + B_2H^2}T^n + ATH^4$$

We can fit the field dependence without any problem!




The best set of the four parameters is then $B_1$ = 897 $T^{-2}$, $B_2$ = 2532 $T^{-2}$, $CT^n$ = 18274 $s^{-1}$ and $A$ = 3.25 $10^6$ $K^{-1}T^{-4}s^{-1}$. Fixing these four parameters, only $n$ is an additional parameter (fifth one) to fit the temperature dependence:




And this is working with $n$ = 7 (which is very much what we expect for Raman processes) leading to $C$ = 305.2 $s^{-1}$ $K^{-7}$.

In conclusion, based on the above mentioned, it is difficult to decide which model is the best one to describe the magnetization relaxation in **2**. May be none! Both have five (5) parameters. The second model (Direct Raman) has a $n$ number that is making sense and involves only two relaxation processes. Thus, we might favour this. Our hypothesis is supported by the fact that the $\tau_0$ value in the first approach (QTM+ Direct+ Orbach) is a little too high.

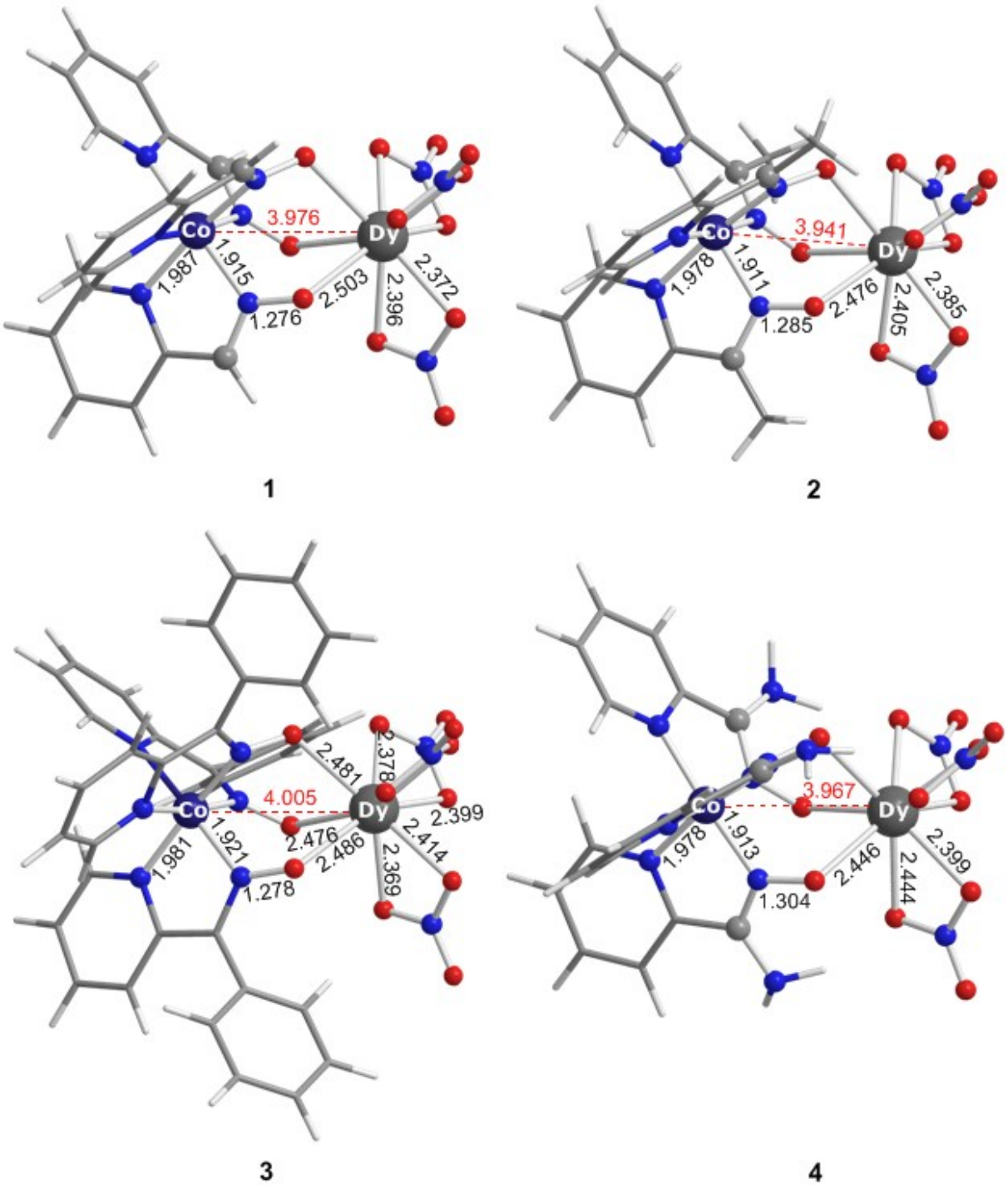



**Figure S26.** Equilibrium geometries of **1**-**4** with selected structural parameters optimized at the BP86/SDD(Co,Dy) ∪ 6-31G(d,p)(E) (E = main group element) level in the gas phase.

**Computational Details**. All calculations were performed in gas phase using the Gaussian09, D.01 program suite. The geometries of **1 - 4** were fully optimized, without symmetry constraints, employing DFT electronic structure calculations using the BP86 pure functional1 as implemented in the Gaussian09, D.01 program suite. For the geometry optimizations we used the SDD ECP basis set[1-3] for Co and Dy metal centers and the 6-31G(d,p) basis set for all non metal elements, E. Hereafter the computational protocol used in DFT calculations is abbreviated as BP86/SDD(Co,Dy)$\cup$6-31G(d,p)(E) (E = main group element). The stationary points were identified as local minima by the absence of imaginary frequencies ($N_{Imag}$ = 0). The natural bond orbital (NBO) population analysis was performed using Weinhold's methodology.

**Table S4.** Cartesian coordinates and energies of **1** - **4** at the BP86/SDD(Co,Dy)$\cup$6-31G(d,p)(E) (E = main group element) level.

**1**

| | | | |
|---|---|---|---|
| Dy | 2.343150000 | -0.000105000 | 0.000340000 |
| O | 0.562384000 | -0.945016000 | -1.483895000 |
| O | 0.562181000 | -0.813380000 | 1.559990000 |
| O | 0.562338000 | 1.757368000 | -0.075439000 |
| O | 2.379483000 | 1.093240000 | -2.130918000 |
| O | 2.380235000 | -2.392564000 | 0.118520000 |
| O | 2.379317000 | 1.298064000 | 2.013468000 |
| O | 3.879906000 | -0.461047000 | -1.747085000 |
| O | 3.879521000 | -1.282768000 | 1.273891000 |
| O | 3.877047000 | 1.746487000 | 0.473963000 |
| Co | -1.632806000 | -0.000292000 | -0.000131000 |
| N | -0.528566000 | -0.285620000 | -1.538998000 |
| N | -0.528921000 | -1.190474000 | 1.016554000 |
| N | -0.528942000 | 1.475274000 | 0.522528000 |
| N | 3.372617000 | 0.388615000 | -2.590923000 |
| N | 3.372881000 | -2.438486000 | 0.959324000 |
| N | 3.370411000 | 2.050991000 | 1.632357000 |
| N | -2.672796000 | 1.128271000 | -1.263018000 |
| N | -2.673098000 | -1.657907000 | -0.346188000 |
| N | -2.673561000 | 0.529048000 | 1.608276000 |
| C | -0.939328000 | 0.306955000 | -2.654795000 |
| C | -0.940127000 | -2.452920000 | 1.061424000 |
| C | -0.940599000 | 2.145632000 | 1.593035000 |
| O | 3.792506000 | 0.511949000 | -3.736296000 |
| O | 3.793062000 | -3.492057000 | 1.424975000 |

| | | | |
|---|---|---|---|
| O | 3.789022000 | 2.982011000 | 2.311609000 |
| C | -3.769648000 | 1.881585000 | -1.027723000 |
| C | -2.125186000 | 1.105307000 | -2.527878000 |
| C | -3.769899000 | -1.830494000 | -1.116347000 |
| C | -2.125976000 | -2.741900000 | 0.306425000 |
| C | -3.770321000 | -0.051609000 | 2.142956000 |
| C | -2.126563000 | 1.636362000 | 2.220611000 |
| C | -4.388351000 | 2.640974000 | -2.025708000 |
| C | -2.706229000 | 1.852565000 | -3.578096000 |
| C | -4.389126000 | -3.074237000 | -1.274787000 |
| C | -2.707568000 | -4.024810000 | 0.184620000 |
| C | -4.389572000 | 0.433218000 | 3.299209000 |
| C | -2.708237000 | 2.172574000 | 3.392385000 |
| C | -3.841464000 | 2.622682000 | -3.323220000 |
| C | -3.842800000 | -4.188840000 | -0.609831000 |
| C | -3.843388000 | 1.566578000 | 3.931782000 |
| H | -0.322177000 | 0.249955000 | -3.554107000 |
| H | -0.323293000 | -3.203389000 | 1.560622000 |
| H | -0.323996000 | 2.953367000 | 1.993354000 |
| H | -4.148855000 | 1.865213000 | -0.002354000 |
| H | -4.148809000 | -0.934211000 | -1.614914000 |
| H | -4.149159000 | -0.931660000 | 1.616262000 |
| H | -5.272369000 | 3.236180000 | -1.784871000 |
| H | -2.248065000 | 1.822675000 | -4.570239000 |
| H | -5.273135000 | -3.163028000 | -1.910715000 |
| H | -2.249868000 | -4.869162000 | 0.706866000 |
| H | -5.273486000 | -0.073172000 | 3.694209000 |
| H | -2.250614000 | 3.047155000 | 3.862334000 |
| H | -4.297999000 | 3.210525000 | -4.125337000 |
| H | -4.299775000 | -5.177238000 | -0.717616000 |
| H | -4.300429000 | 1.967577000 | 4.841556000 |

Sum of electronic and zero-point Energies= -3120.738965
Sum of electronic and thermal Energies= -3120.700200
Sum of electronic and thermal Enthalpies= -3120.699256
Sum of electronic and thermal Free Energies= -3120.815402

**2**

| | | | |
|---|---|---|---|
| Dy | -2.321332000 | -0.000221000 | -0.000134000 |
| O | -0.574661000 | 1.660443000 | -0.567180000 |
| O | -0.574673000 | -0.339869000 | 1.721683000 |

| | | | |
|---|---|---|---|
| O | -0.574670000 | -1.321572000 | -1.154409000 |
| O | -2.414740000 | 0.438767000 | -2.362539000 |
| O | -2.414313000 | 1.826335000 | 1.560782000 |
| O | -2.415095000 | -2.265403000 | 0.801322000 |
| O | -3.873398000 | 1.454271000 | -1.078349000 |
| O | -3.873447000 | 0.206989000 | 1.798503000 |
| O | -3.872970000 | -1.661402000 | -0.721116000 |
| Co | 1.619172000 | -0.000076000 | 0.000198000 |
| N | 0.528175000 | 1.186707000 | -1.025138000 |
| N | 0.527907000 | 0.294058000 | 1.540491000 |
| N | 0.528076000 | -1.481387000 | -0.515007000 |
| N | -3.372573000 | 1.315682000 | -2.267122000 |
| N | -3.372336000 | 1.305736000 | 2.272607000 |
| N | -3.372493000 | -2.621426000 | -0.006236000 |
| N | 2.650277000 | -0.079278000 | -1.685900000 |
| N | 2.649601000 | 1.500239000 | 0.774635000 |
| N | 2.650256000 | -1.420740000 | 0.911870000 |
| C | 0.933153000 | 1.472630000 | -2.265002000 |
| C | 0.932254000 | 1.225243000 | 2.407901000 |
| C | 0.932876000 | -2.698072000 | -0.142542000 |
| O | -3.756516000 | 1.972808000 | -3.230803000 |
| O | -3.756190000 | 1.812144000 | 3.323379000 |
| O | -3.756261000 | -3.784620000 | -0.093539000 |
| C | 3.738358000 | -0.829716000 | -1.964196000 |
| C | 2.125153000 | 0.751330000 | -2.655078000 |
| C | 3.737282000 | 2.117189000 | 0.263863000 |
| C | 2.123885000 | 1.924306000 | 1.978286000 |
| C | 3.738442000 | -1.286824000 | 1.700855000 |
| C | 2.124736000 | -2.675283000 | 0.677342000 |
| C | 0.103627000 | 2.362418000 | -3.140075000 |
| C | 0.102415000 | 1.538161000 | 3.615823000 |
| C | 0.103448000 | -3.900840000 | -0.475748000 |
| H | 4.094259000 | -1.471352000 | -1.153851000 |
| C | 4.379175000 | -0.798221000 | -3.206492000 |
| C | 2.732905000 | 0.822192000 | -3.930524000 |
| H | 4.093484000 | 1.736297000 | -0.696896000 |
| C | 4.377111000 | 3.178021000 | 0.912094000 |
| C | 2.730647000 | 2.994112000 | 2.677159000 |
| H | 4.094809000 | -0.264374000 | 1.851131000 |
| C | 4.378855000 | -2.378575000 | 2.294899000 |
| C | 2.732031000 | -3.815380000 | 1.253945000 |

| | | | |
|---|---|---|---|
| H | -0.816383000 | 1.832578000 | -3.448629000 |
| H | 0.654809000 | 2.693635000 | -4.032371000 |
| H | -0.217335000 | 3.247880000 | -2.567534000 |
| H | -0.817253000 | 2.070812000 | 3.311110000 |
| H | 0.653685000 | 2.144727000 | 4.349219000 |
| H | -0.219199000 | 0.599607000 | 4.095923000 |
| H | -0.816585000 | -3.903533000 | 0.137356000 |
| H | 0.654883000 | -4.839101000 | -0.316812000 |
| H | -0.217596000 | -3.847445000 | -1.528790000 |
| H | 5.255412000 | -1.426628000 | -3.382712000 |
| C | 3.860559000 | 0.047054000 | -4.204532000 |
| H | 2.303355000 | 1.474633000 | -4.693796000 |
| H | 5.253056000 | 3.645413000 | 0.456023000 |
| C | 3.857901000 | 3.619682000 | 2.142899000 |
| H | 2.300657000 | 3.328918000 | 3.623624000 |
| H | 5.255174000 | -2.217180000 | 2.927162000 |
| C | 3.859721000 | -3.665384000 | 2.062225000 |
| H | 2.302162000 | -4.802529000 | 1.070813000 |
| H | 4.331167000 | 0.094575000 | -5.191371000 |
| H | 4.327775000 | 4.451057000 | 2.677328000 |
| H | 4.330017000 | -4.543846000 | 2.514670000 |

Sum of electronic and zero-point Energies= -3238.629778
Sum of electronic and thermal Energies= -3238.586253
Sum of electronic and thermal Enthalpies= -3238.585309
Sum of electronic and thermal Free Energies= -3238.709939

**3**

| | | | |
|---|---|---|---|
| Dy | 2.360180000 | -0.018712000 | -0.018344000 |
| O | 0.579780000 | 1.111997000 | -1.325947000 |
| O | 0.563493000 | -1.699829000 | -0.300482000 |
| O | 0.588732000 | 0.581710000 | 1.619662000 |
| O | 2.571138000 | 2.287637000 | 0.518893000 |
| O | 2.511335000 | -0.742628000 | -2.278574000 |
| O | 2.566836000 | -1.609943000 | 1.724172000 |
| O | 4.000299000 | 1.467587000 | -0.927120000 |
| O | 3.980728000 | -1.565214000 | -0.875837000 |
| O | 4.045330000 | 0.007124000 | 1.709664000 |
| Co | -1.644466000 | 0.017808000 | 0.006678000 |
| N | -0.561894000 | 1.375451000 | -0.815823000 |
| N | -0.583684000 | -1.384242000 | -0.768010000 |

| | | | |
|---|---|---|---|
| N | -0.564387000 | 0.032523000 | 1.594393000 |
| N | 3.576707000 | 2.507668000 | -0.288347000 |
| N | 3.527103000 | -1.543831000 | -2.084924000 |
| N | 3.596347000 | -1.044022000 | 2.304691000 |
| N | -2.711904000 | 1.584538000 | 0.579129000 |
| N | -2.732388000 | -0.262564000 | -1.624485000 |
| N | -2.733721000 | -1.245164000 | 1.076129000 |
| C | -1.099606000 | 2.605504000 | -0.861084000 |
| C | -1.143846000 | -2.041673000 | -1.796286000 |
| C | -1.112033000 | -0.533867000 | 2.682589000 |
| O | 4.060228000 | 3.626883000 | -0.432639000 |
| O | 3.991526000 | -2.233140000 | -2.989086000 |
| O | 4.072583000 | -1.486293000 | 3.346763000 |
| C | -3.772356000 | 1.629592000 | 1.416014000 |
| C | -2.290961000 | 2.737173000 | -0.046488000 |
| C | -3.787854000 | 0.451384000 | -2.075074000 |
| C | -2.334528000 | -1.390978000 | -2.306711000 |
| C | -3.805482000 | -1.975513000 | 0.695300000 |
| C | -2.315071000 | -1.286310000 | 2.387828000 |
| C | -4.480115000 | 2.807043000 | 1.673852000 |
| C | -2.970665000 | 3.958863000 | 0.173559000 |
| C | -4.513800000 | 0.087535000 | -3.212876000 |
| C | -3.033663000 | -1.810586000 | -3.463322000 |
| C | -4.526933000 | -2.776814000 | 1.584738000 |
| C | -3.007886000 | -2.078488000 | 3.334296000 |
| C | -4.067293000 | 3.991208000 | 1.035164000 |
| C | -4.125474000 | -1.068751000 | -3.914802000 |
| C | -4.115723000 | -2.823434000 | 2.929907000 |
| H | -4.053772000 | 0.684181000 | 1.885341000 |
| H | -4.050172000 | 1.338610000 | -1.494235000 |
| H | -4.084860000 | -1.904565000 | -0.358379000 |
| H | -5.328702000 | 2.789994000 | 2.361982000 |
| H | -2.608399000 | 4.858161000 | -0.329620000 |
| H | -5.357514000 | 0.701476000 | -3.537146000 |
| H | -2.689653000 | -2.704710000 | -3.988051000 |
| H | -5.384437000 | -3.350391000 | 1.224724000 |
| H | -2.646687000 | -2.099462000 | 4.364938000 |
| H | -4.594159000 | 4.933110000 | 1.216639000 |
| H | -4.667365000 | -1.381948000 | -4.812553000 |
| H | -4.652687000 | -3.444111000 | 3.653881000 |
| C | -0.568732000 | -3.269081000 | -2.405487000 |

| | | | |
|---|---|---|---|
| C | -1.324212000 | -4.464175000 | -2.378962000 |
| C | 0.703448000 | -3.264379000 | -3.014236000 |
| C | -0.810574000 | -5.638262000 | -2.949253000 |
| H | -2.307157000 | -4.474562000 | -1.893990000 |
| C | 1.212281000 | -4.443700000 | -3.578009000 |
| H | 1.287271000 | -2.339483000 | -3.047486000 |
| C | 0.460239000 | -5.629396000 | -3.547791000 |
| H | -1.399206000 | -6.561113000 | -2.916531000 |
| H | 2.206437000 | -4.425183000 | -4.034333000 |
| H | 0.864373000 | -6.547615000 | -3.986785000 |
| C | -0.498160000 | 3.742231000 | -1.605611000 |
| C | -1.235407000 | 4.343748000 | -2.651575000 |
| C | 0.783157000 | 4.236899000 | -1.285081000 |
| C | -0.695107000 | 5.421380000 | -3.368824000 |
| H | -2.225547000 | 3.952634000 | -2.912560000 |
| C | 1.318826000 | 5.311508000 | -2.010099000 |
| H | 1.353477000 | 3.782743000 | -0.469135000 |
| C | 0.584532000 | 5.905031000 | -3.049800000 |
| H | -1.270021000 | 5.875498000 | -4.182738000 |
| H | 2.319652000 | 5.673514000 | -1.756742000 |
| H | 1.009483000 | 6.741586000 | -3.614367000 |
| C | -0.508822000 | -0.467112000 | 4.038681000 |
| C | -1.245215000 | 0.129497000 | 5.088247000 |
| C | 0.774639000 | -0.990335000 | 4.300682000 |
| C | -0.702616000 | 0.204280000 | 6.379587000 |
| H | -2.236354000 | 0.551124000 | 4.884814000 |
| C | 1.312303000 | -0.907536000 | 5.593491000 |
| H | 1.345111000 | -1.463237000 | 3.495423000 |
| C | 0.578668000 | -0.312757000 | 6.632974000 |
| H | -1.276998000 | 0.675518000 | 7.184098000 |
| H | 2.314250000 | -1.307457000 | 5.775509000 |
| H | 1.005307000 | -0.248190000 | 7.639439000 |

Sum of electronic and zero-point Energies= -3813.663932
Sum of electronic and thermal Energies= -3813.610722
Sum of electronic and thermal Enthalpies= -3813.609778
Sum of electronic and thermal Free Energies= -3813.755821

**4**

| | | | |
|---|---|---|---|
| Dy | 2.263212000 | -0.000104000 | 0.000328000 |
| O | 0.545713000 | -0.952051000 | -1.459015000 |
| O | 0.545779000 | -0.786873000 | 1.554431000 |

| | | | |
|---|---|---|---|
| O | 0.545737000 | 1.738938000 | -0.095150000 |
| O | 2.502281000 | 0.788862000 | -2.300684000 |
| O | 2.502358000 | -2.387066000 | 0.467954000 |
| O | 2.502853000 | 1.599370000 | 1.833018000 |
| O | 3.893875000 | -0.750058000 | -1.591074000 |
| O | 3.894811000 | -1.002977000 | 1.444576000 |
| O | 3.894108000 | 1.753227000 | 0.145107000 |
| Co | -1.704164000 | -0.000128000 | 0.000115000 |
| N | -0.571744000 | -0.283011000 | -1.515495000 |
| N | -0.571642000 | -1.170697000 | 1.003261000 |
| N | -0.571696000 | 1.453626000 | 0.512648000 |
| N | 3.482020000 | -0.033744000 | -2.582838000 |
| N | 3.482970000 | -2.220059000 | 1.320499000 |
| N | 3.482517000 | 2.254691000 | 1.261037000 |
| N | -2.717594000 | 1.111785000 | -1.283717000 |
| N | -2.717142000 | -1.668286000 | -0.320923000 |
| N | -2.717544000 | 0.556106000 | 1.604899000 |
| C | -0.865514000 | 0.423343000 | -2.608349000 |
| C | -0.865111000 | -2.470392000 | 0.938271000 |
| C | -0.865232000 | 2.047183000 | 1.670660000 |
| O | 3.949988000 | -0.118894000 | -3.714239000 |
| O | 3.951500000 | -3.157232000 | 1.959580000 |
| O | 3.950374000 | 3.277544000 | 1.752127000 |
| C | -3.857161000 | 1.805753000 | -1.078939000 |
| C | -2.117578000 | 1.151182000 | -2.521429000 |
| C | -3.856175000 | -1.838536000 | -1.024988000 |
| C | -2.116956000 | -2.759540000 | 0.264233000 |
| C | -3.857070000 | 0.031829000 | 2.103598000 |
| C | -2.117398000 | 1.608396000 | 2.257636000 |
| H | -4.275216000 | 1.747988000 | -0.070129000 |
| C | -4.473524000 | 2.560846000 | -2.083956000 |
| C | -2.697970000 | 1.882446000 | -3.581170000 |
| H | -4.274265000 | -0.936239000 | -1.479805000 |
| C | -4.471937000 | -3.086726000 | -1.176619000 |
| C | -2.696731000 | -4.043189000 | 0.160635000 |
| H | -4.275045000 | -0.812908000 | 1.549030000 |
| C | -4.473301000 | 0.524818000 | 3.260055000 |
| C | -2.697690000 | 2.160708000 | 3.420735000 |
| H | -5.392836000 | 3.109181000 | -1.865053000 |
| C | -3.880907000 | 2.590903000 | -3.358937000 |
| H | -2.227200000 | 1.873330000 | -4.567599000 |
| H | -5.390816000 | -3.171804000 | -1.761549000 |
| C | -3.879188000 | -4.205583000 | -0.564691000 |
| H | -2.225859000 | -4.892681000 | 0.662034000 |
| H | -5.392546000 | 0.061128000 | 3.625706000 |
| C | -3.880566000 | 1.614028000 | 3.923326000 |
| H | -2.226862000 | 3.019562000 | 3.905969000 |

| | | | |
|---|---|---|---|
| H | -4.339519000 | 3.162458000 | -4.171570000 |
| H | -4.337286000 | -5.195343000 | -0.653530000 |
| H | -4.339062000 | 2.032096000 | 4.824646000 |
| N | -0.033198000 | 2.991539000 | 2.236685000 |
| H | -0.093259000 | 3.024520000 | 3.255401000 |
| H | 0.948359000 | 2.826361000 | 1.950179000 |
| N | -0.033432000 | -3.432772000 | 1.473610000 |
| H | -0.093539000 | -4.331617000 | 0.993057000 |
| H | 0.948194000 | -3.102323000 | 1.473937000 |
| N | -0.033768000 | 0.441656000 | -3.709459000 |
| H | -0.093767000 | 1.307738000 | -4.246852000 |
| H | 0.947814000 | 0.275866000 | -3.423506000 |

Sum of electronic and zero-point Energies= -3286.804425
Sum of electronic and thermal Energies= -3286.761938
Sum of electronic and thermal Enthalpies= -3286.760994
Sum of electronic and thermal Free Energies= -3286.881801

**References of the ESI**

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2. M. Kaupp, P. v. R. Schleyer, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1991, **94**, 1360.
3. M. Dolg, H. Stoll, H. Preuss and R.M. Pitzer, *J. Phys. Chem.*, 1993, **97**, 5852.