# ELECTRONIC SUPPLEMENTARY INFORMATION

# Opening up a dysprosium triangle by ligand oximation

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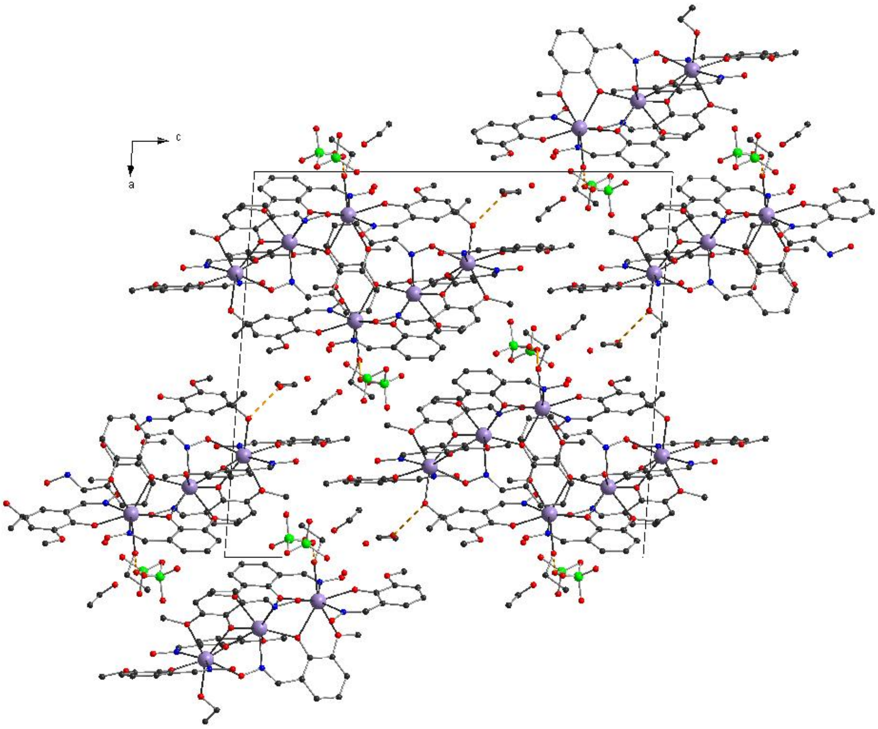


**Fig. S1** Molecular packing of **1** as viewed along the *b* axis with intermolecular hydrogen bonding highlighted with fragmented lines.

## Experimental details

Synthesis of $H_2$vanox: A suspension of 3.31g (24.2 mmol) of o-vanillin in 11ml $H_2O$ was stirred while heating to 45°C. A solution containing 1.80g (26.1 mmol) $NH_2OH{\cdot}HCl$ and 1.78g (21.8 mmol) $CH_3CO_2Na$ was added and the reaction was heated with stirring at 80°C for 2h.

Upon cooling to room temperature the resulting white microcrystalline precipitate was filtered and washed with cold $H_2O$ and recrystallized from EtOH. The resulting compound is light sensitive. Yield 3.82g (95%). IR (KBr disk, cm$^{-1}$): 3337, 1636, 1623, 1579, 1481, 1420, 1303, 1267, 1243, 1092, 1078, 996, 963, 839, 720, 620. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.41-6.89 (m, 3H), 3.96 (s, 3H).

Magnetic susceptibility measurements were obtained with a Quantum Design SQUID magnetometer MPMS-XL. The measurements were performed on 17.6 mg of a polycrystalline powder restrained in 6.8 mg of Apeizon grease. Ac susceptibility measurements were measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. Corrections considering diamagnetic contributions of the sample holder were applied to the raw magnetic data.

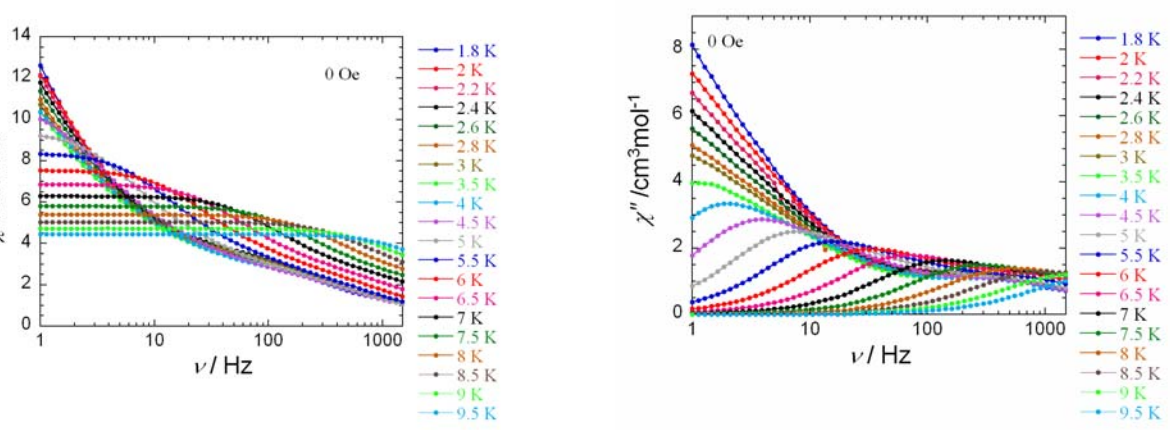


**Fig. S2** Frequency dependence of the in-phase, $\chi'$, left, and out-of-phase, $\chi''$, right, components of the ac magnetic susceptibility obtained for **1** in a zero dc applied field.

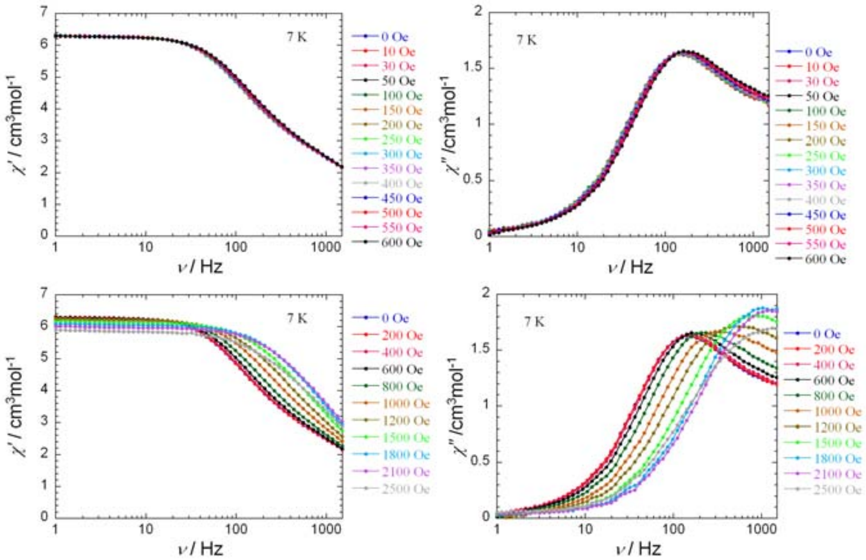
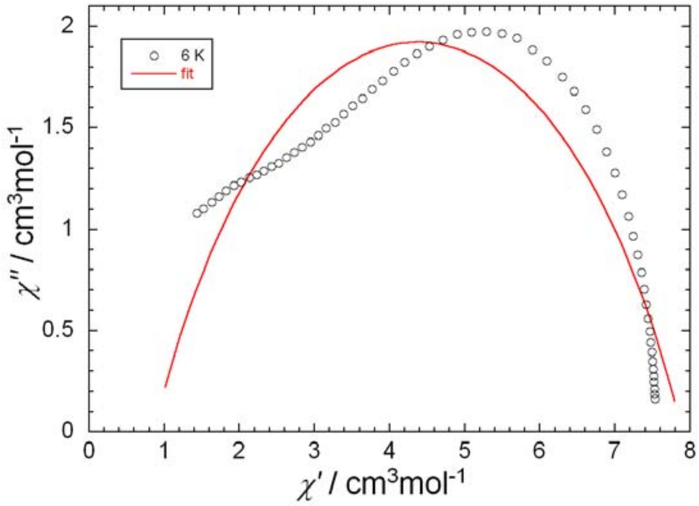


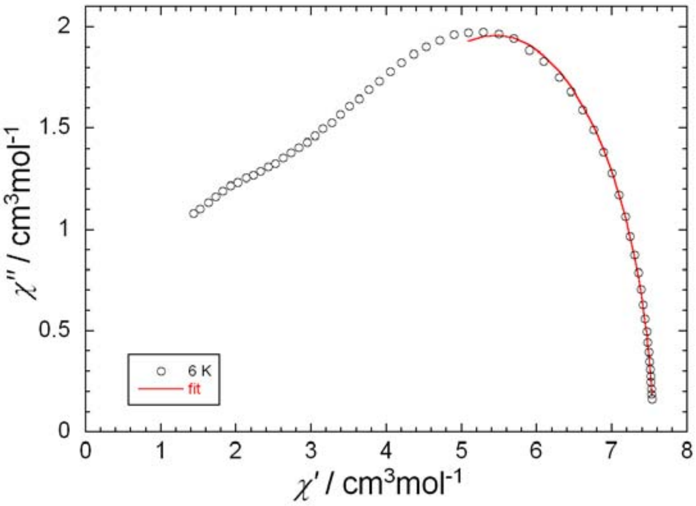
**Fig. S3** Frequency dependence obtained at 7 K of the in-phase, $\chi'$, left, and the out-of-phase, $\chi''$, right, ac susceptibility measured in different dc applied fields for **1**.

## Relaxation Processes.

We fitted the Cole-Cole diagrams of the using a generalized Debye model. Two temperatures (4.5 and 6 K) located in different relaxation regime are selected.

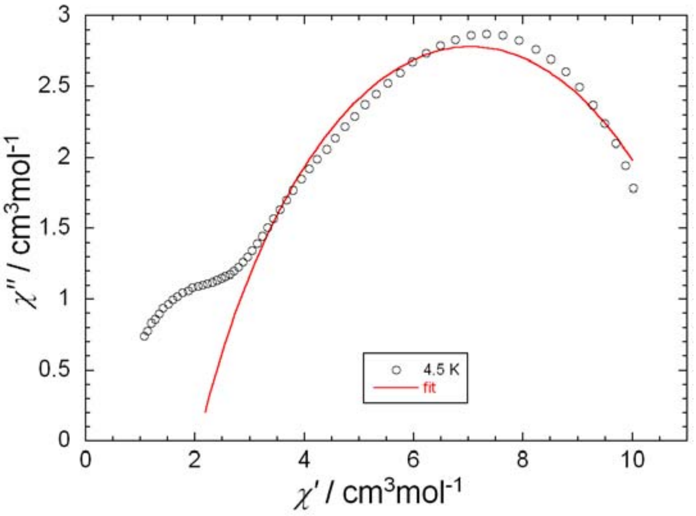


As seen from the fit above, the full range of Cole-Cole plot at 6K cannot be fit well, indicating there is more than one relaxation process.



The part of Cole-Cole diagram at 6K can be fit well by the following parameters:

$\alpha = 0.0452$ (4), $\chi_0 = 7.552(3)$ cm$^3$/mol, $\chi_{inf} = 3.345(37)$ cm$^3$/mol.



Same as that demonstrated in the fit of Cole-Cole diagram at 4.5K, the fit of the data without the first peak leads to the parameters: $\alpha = 0.352$ (12), $\chi_0 = 12.032(12)$ cm$^3$/mol, $\chi_{inf} = 2.048(68)$ cm$^3$/mol.

In conclusion, two relaxation processes are clearly observed from the study of the Cole-Cole diagrams.

# Details of the *ab intio* calculations

*Computational details*:

In the CASSCF/RASSI-SO[1] approach relativistic effects are treated in two steps, both based on the Douglas–Kroll Hamiltonian[2]. Scalar terms are included in the basisset generation and are used to determine spin-free wavefunctions and energies, through the use of Complete Active Space Self Consistent Field(CASSCF) method. Then, Spin–Orbit coupling is treated with a Restricted Active Space State Interaction computation(RASSI-SO), which uses the CASSCF wavefunctions as the basis states. By using the resulting eigenstates of the previous method, the gyromagnetic tensor of the ground doublet Kramer's state can be computed and diagonalized in order to obtain the three main anisotropy axes and the gyromagnetic values along those axes($g_x$, $g_y$ and $g_z$).

All the calculations were performed using the MOLCAS 7.0 quantum chemistry package[3]. In the quantum cluster employed for each calculation the *o-vanillin oxime* not coordinated with the studied $Dy^{3+}$ ion were replaced by $OH^-$ or $H_2O$ groups bonded the other $Dy^{3+}$ ions in order to get the same bond order for those first neighbour ligand atoms as they had in the replaced ligand groups. In addition, the other Dy(III) were also replaced by Y(III) ions.

All the atoms were represented by basis sets of atomic natural orbitals from the ANO-RCC library as implemented in the MOLCAS-7.4 quantum chemistry package. The following contractions were used: [8s7p4d3f2g] for Dy, TZP for all the atoms in the first shell around the studied Dy ion and DZ for all the other atoms.

Two different CASSCF calculations were performed for computing the gyromagnetic factors and the direction of the easy axis for each $Dy^{3+}$ ion. First, a CASSCF state average calculations of the roots of all the sextets ($^6H$, $^6F$ and $^6P$) in order to confirm the existence of a large energy gap between the $^6H$ and $^6F$ (the lowest excited multiplet). In the three cases this energy gap was larger than 7500 $cm^{-1}$ and therefore in the final CASSCF state average calculations only the 11 roots of the $^6H$ ground multiplet were included.

[1.] P. A. Malmqvist, B. O. Roos, B. Schimmelpfennig, *Chem. Phys. Lett.* **2002,** *357,* 230.

[2.] B. A. Hess, C. M. Marian, U. Wahlgren, O. Gropen, *Chem. Phys. Lett.* **1996,** 251, 365

[3.] G. Karlstrom, R. Lindh, P. A. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P. O. Widmark, M. Cossi B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, *28*, 222-239.

[4.] F. Aquilante, T. B. Pedersen, R. Lindh, *J. Chem. Phys.* **2007,** 126, 194106

*Computational results*:

**UU** = transformation matrix from local to crystal coordinates.
$\Delta$=energy difference from the ground to the first excited Kramer's doublet

**Dy1(central)**:

$g_x$= 0.0541
$g_y$= 0.0421
$g_z$=19.8585

$\Delta$=106 cm$^{-1}$

**UU**=

| | | |
|---|---|---|
| -0.721015 | 0.689038 | -0.0691647 |
| -0.663408 | -0.657186 | 0.357118 |
| -0.200902 | -0.303595 | -0.931638 |

**Dy2:**

$g_x$= 0.0054
$g_y$= 0.0037
$g_z$=19.8676

$\Delta$=125 cm$^{-1}$

**UU**=

| | | |
|---|---|---|
| -0.239594 | -0.961489 | 0.134983 |
| -0.897039 | 0.271578 | 0.349389 |
| -0.372461 | -0.0373833 | -0.927791 |

**Dy3:**

$g_x$= 0.0076
$g_y$= 0.0050
$g_z$=19.9068

$\Delta$=134 cm$^{-1}$

**UU**=

| | | |
|---|---|---|
| 0.0804038 | 0.970837 | -0.226983 |
| 0.938268 | -0.150061 | -0.312179 |
| 0.336537 | 0.187634 | 0.923187 |