ELECTRONIC SUPPLEMENTARY MATERIAL to:

Squashed {$Fe^{III}_2M^{III}_4$} octahedra (M = Y, Gd, Dy) from the first use of the cyanoacetate ligand in 3d/4f coordination chemistry†

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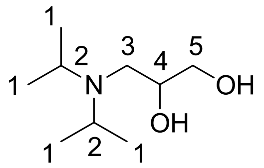
SYNTHESIS AND CHARACTERIZATION OF (±) – 3 – (DIISOPROPYLAMINO) PROPANE - 1,2 - DIOL

This compound is no longer commercially available.

General information

All solvents were of reagent quality, and all commercial reagents were used without additional purification. Removal of all solvents was carried out under reduced pressure. Column chromatography was carried out using chromatographic silica gel 40-60 µm Merck. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} Merck aluminium plates and visualized by UV lamp (254 nm) and by $KMnO_4$ exposure. ^1H and ^{13}C NMR spectra were obtained at ambient temperature in $CDCl_3$ on a Brucker Advance 300 spectrometer at 300 MHz, and 75 MHz, respectively. Chemical shifts (δ) are given in ppm relative to the resonance of their respective residual solvent peak, $CHCl_3$ (^1H: δ=7.26, ^{13}C: 77.23 ppm, the middle peak). Low-resolution mass spectrometry was performed on an Agilent MSD with Agilent 1200 SL HPLC equipped with DAD.



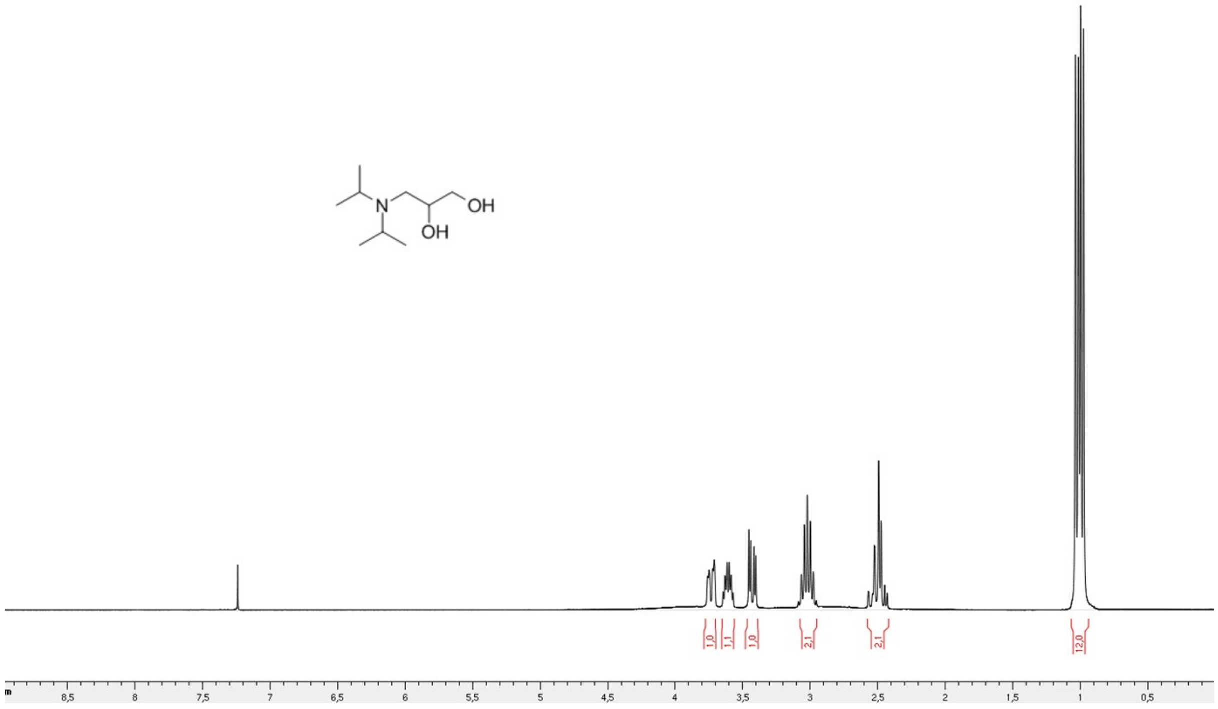
Chemical Formula: $C_9H_{21}NO_2$
Exact Mass: 175.1572
Molecular Weight: 175.2685

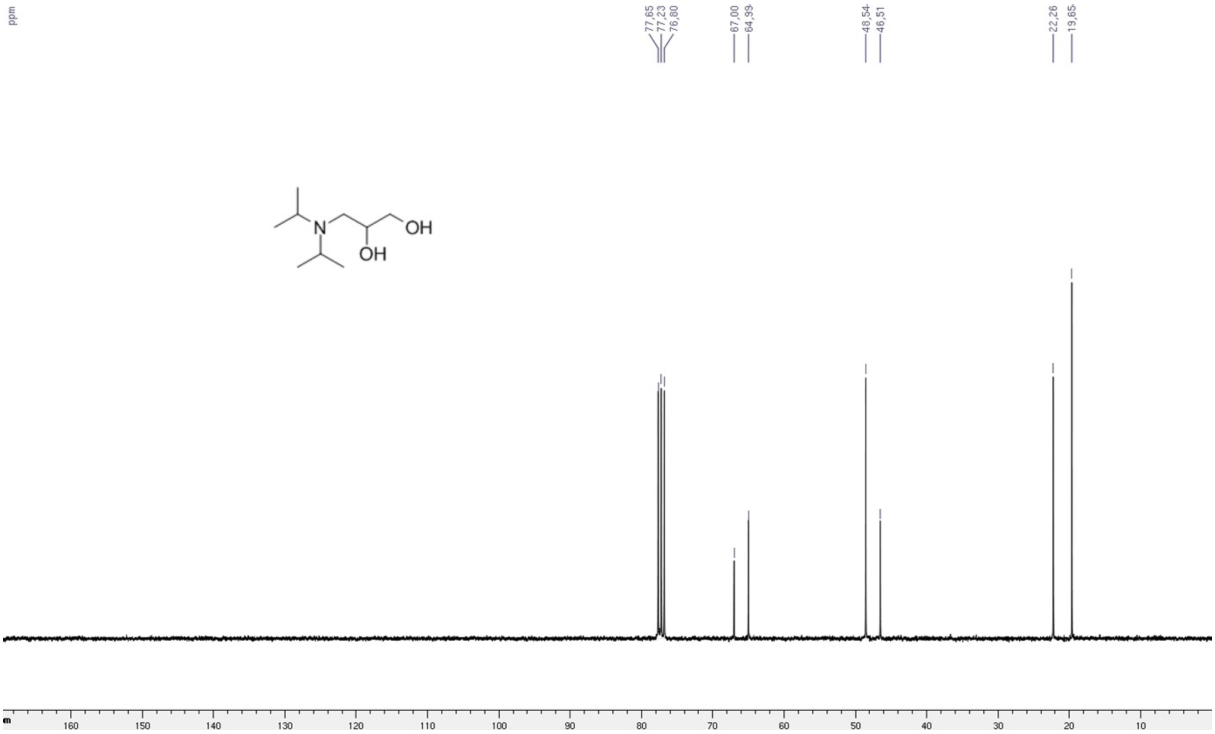
(±)-3-(diisopropylamino)propane-1,2-diol or **(±)-3-diisopropylamino-1,2-propanediol**

To a solution of (±)-3-chloro-1,2-propanediol (1.50 g, 13.57 mmol) in 50 mL of acetonitrile were added K_2CO_3 (13.13 g, 94.99 mmol) and diisopropylamine (11.41 mL, 81.42 mmol). The reaction mixture was stirred for 48 h at reflux. The solution was then filtered and concentrated. The crude residue was purified by chromatography over silica gel using a mixture of CH_2Cl_2/saturated solution of ammonia in MeOH (95/5 v/v) as eluant to yield the desired product as a colorless oil (1.45 g, 61%).

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 3.77-3.69 (m, 1H, **H_5**), 3.65-3.56 (m, 1H, **H_4**), 3.43 (dd, *J* = 11.3 Hz, 4.1 Hz, 1H, **H_5**), 3.09-2.95 (m, 2H, **H_2**), 2.58-2.42 (m, 2H, **H_3**), 1.05-0.96 (m, 12H, **H_1**); **^{13}C NMR** (75 MHz, $CDCl_3$): δ(ppm) 67.0 (CH), 64.9 (CH_2), 48.5 (CH), 46.5 (CH_2), 22.3 (CH_3), 19.7 (CH_3); **LRMS-ESI**: *m/z* 176.1 $[M+H]^+$.

^{1}H NMR, ^{13}C NMR and DEPT ^{13}C NMR data are shown below.

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PREPARATION OF THE HEXANUCLEAR CLUSTERS

Method A:

$[Fe_2Ln_4(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_{2.36}(\mu_3\text{-}OMe)_{1.64}(O_2CCH_2CN)_{10}(MeOH)_5(H_2O)]\cdot 0.36H_2O\cdot 3MeOH$ (Ln = Dy, $1\cdot 0.36H_2O\cdot 3MeOH$; M = Y, $2\cdot 0.36H_2O\cdot 3MeOH$; M = Gd, $3\cdot 0.36H_2O\cdot 3MeOH$)

To an orange suspension of $[Fe_3O(O_2CCH_2CN)_6(H_2O)_3](NO_3)\cdot 5H_2O$ (160 mg, 0.18 mmol) in MeOH (10 mL) was added (±)-3-diisopropylamino-1,2-propanediol (175 mg, 1.00 mmol) and solid $M(NO_3)_3\cdot xH_2O$ (0.25 mmol). The resulting yellow-orange suspension was stirred for ~2 h and filtered. Storage of the filtrate in a closed flask at room temperature gave a yellow powder which was removed by filtration. The new yellow-orange filtrate was allowed to stand undisturbed at room temperature. Small orange crystals formed over 1 week. The crystals were collected by filtration, washed with cold MeOH (1 x 2 mL) and dried in air. Yields were ~10% (based on the Fe^{III} triangle available). The complexes analyzed satisfactorily as $[Fe_2M_4O_2(OH)_2(OMe)_2(O_2CCH_2CN)_{10}(MeOH)_6]\cdot H_2O$ (calculated formulae $C_{38}H_{54}Fe_2M_4N_{10}O_{33}$). Data are as follows (found values in parentheses): Fe_2Dy_4 cluster: C 23.43 (22.95); H 2.80 (2.93); N 7.20 (7.27)%. Fe_2Y_4 cluster: C 27.71 (27.66); H 3.31 (3.22); N 8.51 (8.60)%. The IR spectra of the two samples are identical. The IR data (KBr, cm^{-1}) of the representative Fe_2Dy_4 complex are as follows: 3426 (sb), 2969 (m), 2935 (m), 2893 (w), 1626 (sb), 1416 (s), 1381 (s), 1275 (m), 1204 (w), 1010 (m), 940 (m), 917 (m), 882 (w), 713 (m), 588 (m), 520 (sh), 509 (s), 472 (s), 423 (w). The initially precipitated yellow powder is clearly a byproduct containing $CNCH_2CO_2^-$ groups. Its IR wavenumbers are as follows: 3420 (sb), 2968 (m), 2932 (m), 1616 (s), 1420 (s), 1384 (s), 1276 (m), 1036 (w), 938 (m), 718 (m), 670 (w), 536 (m).

Method B:

$[Fe_2Ln_4(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_{2.36}(\mu_3\text{-}OMe)_{1.64}(O_2CCH_2CN)_{10}(MeOH)_5(H_2O)]\cdot 0.36H_2O\cdot 3MeOH$ (Ln = Dy, $1\cdot 0.36H_2O\cdot 3MeOH$; M = Y, $2\cdot 0.36H_2O\cdot 3MeOH$; M = Gd, $3\cdot 0.36H_2O\cdot 3MeOH$)

A brown-green mixture of $[Fe_3O(O_2CCH_2CN)_6(H_2O)_3)]Cl\cdot H_2O\cdot 2EtOH$ (80 mg, 0.09 mmol), 3-diisopropylamino-1,2-propanediol (175 mg, 1.00 mmol) and

$Gd(NO_3)_3 \cdot 6H_2O$ (64 mg, 0.14 mmol) in $MeOH/CHCl_3$ (10 mL/15 mL) was stirred for 2h at room temperature. The solids soon dissolved and the colour of the solution gradually changed to yellow-orange. The solution was filtered (very little yellow precipitate is observed in comparison to method A and in case of Gd no precipitate at all) and the filtrate was allowed to stand undisturbed in a closed vial at room temperature. Small orange crystals formed over 1 week. The crystals were collected by filtration, washed with cold MeOH (1 x 2 mL) and dried in air. Typical yields were ~10% (method A) (based on the Fe^{III} triangle available) and 31% for method B.

The complex analyzed satisfactorily as $Fe_2Gd_4O_2(OH)_2(OMe)_2(O_2CCH_2CN)_{10}(MeOH)_6 \cdot H_2O$ (calculated formula $C_{38}H_{54}Fe_2Gd_4N_{10}O_{33}$). Data are as follows (found values in parentheses): C 23.73 (23.39); H 2.83 (2.99); N 7.29 (7.35) %. The IR spectrum of the complex is almost identical with the spectra of the Fe_2Dy_4 and Fe_2Y_4 clusters. Data (KBr, cm^{-1}) are as follows: 3422 (sb), 2970 (m), 2934 (m), 2892 (w), 1623 (sb), 1414 (s), 1381 (s), 1274 (m), 1203 (w), 1010 (m), 939 (m), 916 (w), 713 (m), 587 (m), 521 (sh), 505 (m), 470 (m), 423 (w).

SINGLE X-RAY CRYSTALLOGRAPHY

Data for **1**$\cdot 0.36H_2O \cdot 3MeOH$ (Fe_2Dy_4) were measured on a Bruker SMART Apex diffractometer at the SCD beamline at the ANKA synchrotron, Karlsruhe Institute of Technology, using Si-monochromated radiation of wavelength 0.80000 Å. *f'* and *f''* were calculated using the method of Brennan and Cowan [1] as implemented on http://skuld.bmsc.washington.edu/scatter/AS_periodic.html.

Structure solution by direct methods and full-matrix least-squares refinement (all data) were carried out using the SHELXTL software package [2]. Ordered non-H atoms were refined with anisotropic thermal parameters. The triply-bridging ligand based on O(3) was modelled as a disordered superposition of methoxo (with methyl carbon C3A having 82% occupancy) and hydroxo (forming a hydrogen bond to lattice water O33B, 18% occupancy). Over the molecule as a whole this comes to 1.64 (OMe) and 0.36 ($OH \cdot\cdot OH_2$). One of the cyanoacetate ligands has its CN group 55:45 disordered in the compound. These partial atoms were refined anisotropically, with geometrical similarity restraints. The neutral monodentate ligands on Dy1 and

Dy2 were also disordered. Those based on O15 and O16 were methanol, with their respective carbons 55:45 disordered. That on O14 was a 50:50 mixture of MeOH and water (i.e. 50% occupancy for the carbon); it was not possible to model the second H-atom of the water component. Similarity restraints were applied to the C-O distances. The molecule thus has a total of one H_2O and five MeOH ligands. A lattice MeOH on a general site was disordered; the major component could be refined anisotropically, the minor component isotropically (without hydrogens). Another MeOH was badly disordered over an inversion centre, and was refined with partial occupancy isotropic C and O atoms. Similarity restraints were applied to the C-O bond distances of the lattice MeOH. There are thus three lattice MeOH per cluster, in addition to the partial-occupancy lattice waters.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1021088. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

References:

1: S. Brennan and P.L. Cowan, *Rev. Sci. Instrum.,* 1992, **63**, 850.

2: G.M. Sheldrick, *Acta Cryst. A,* 2008, **64**, 112.

Details of data collection and refinement for **1**$\cdot 0.36H_2O\cdot 3MeOH$ are summarised in Table S1.

Table S1: Crystal Data for **1**·0.36H_2O·3MeOH

Compound	**1**·0.36H_2O·3MeOH
Formula	$C_{39.64}H_{62}Dy_4Fe_2N_{10}O_{35.36}$
Formula weight	2006.13
Crystal System	triclinic
Space Group	$P\bar{1}$
a / Å	10.226(2)
b / Å	12.250(3)
c / Å	13.744(3)
α / °	102.500(3)
β / °	97.563(3)
γ / °	104.646(3)
V / Å^3	1594.3(6)
Z	1
T / K	150(2)
F(000)	969
D_c / Mg m^{-3}	2.090
λ / Å	0.80000
μ / mm^{-1}	7.134
Data Measured	20261
Unique Data	7495
R_{int}	0.0437
Data with $I \geq 2\sigma(I)$	7000
wR_2 (all data)	0.0657
S (all data)	1.029
R_1 [$I \geq 2\sigma(I)$]	0.0257

Parameters/Restraints	481 / 21
Biggest diff. peak/hole / eÅ^{-3}	+1.72 / -1.47

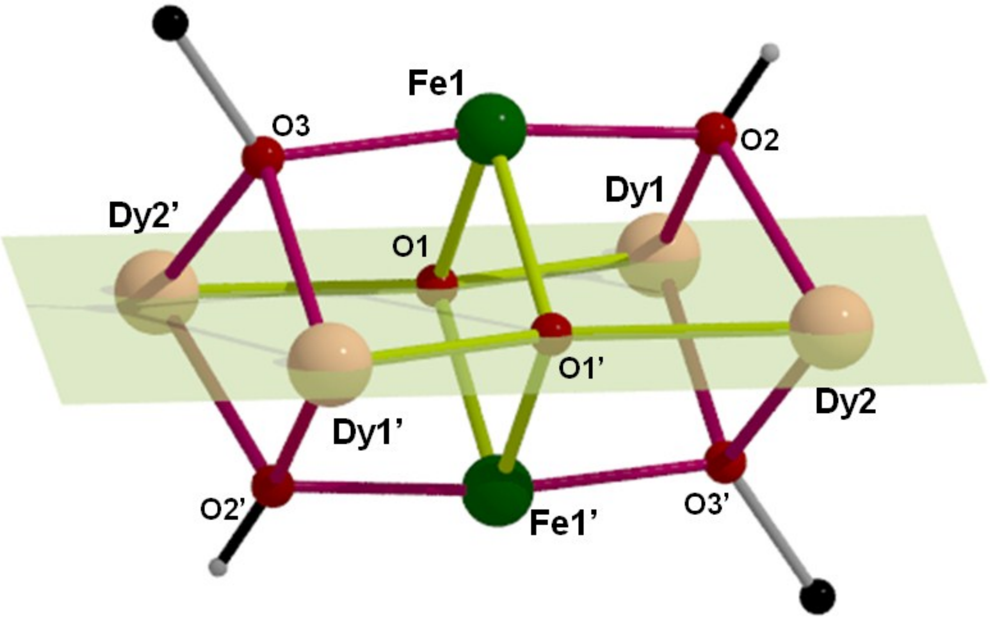

Fig. S1 The $\{Fe_2Dy_4(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_{2.36}(\mu_3\text{-}OH)_{1.64}\}^{10+}$ core of complex **1**·0.36H$_2$O·3MeOH.

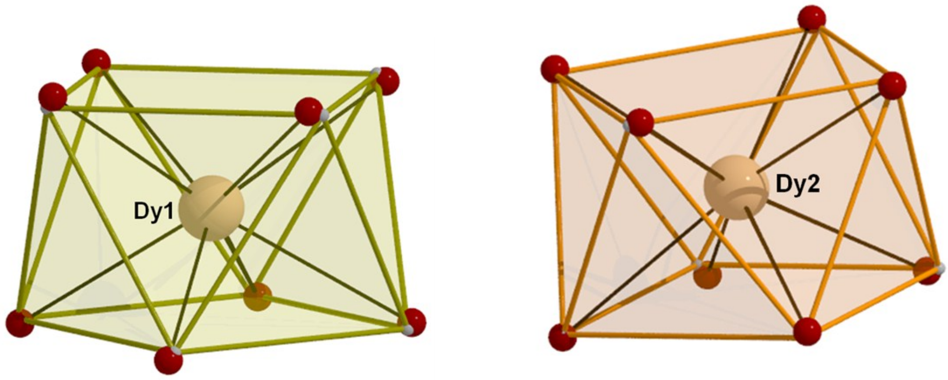

Fig. S2 The square antiprismatic geometries of Dy1 (left) and Dy2 (right) in the structure of cluster **1**·0.36H$_2$O·3MeOH; the very small spheres define the vertices of the ideal polyhedron.

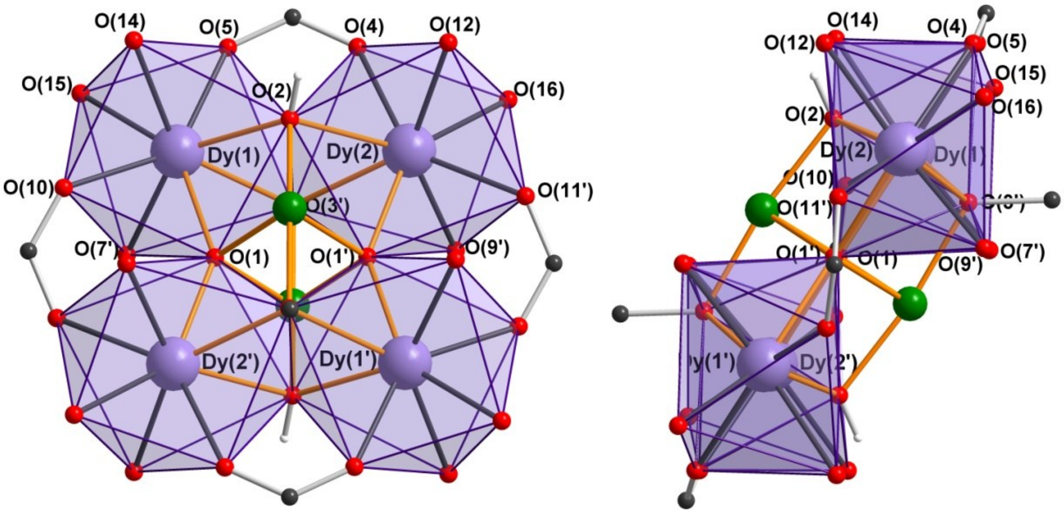

Fig. S3 View of the molecular structure of **1** showing the square antiprismatic Dy coordination polyhedra, viewed along the fourfold axes of the antiprisms (left) and perpendicular to these axes (right).

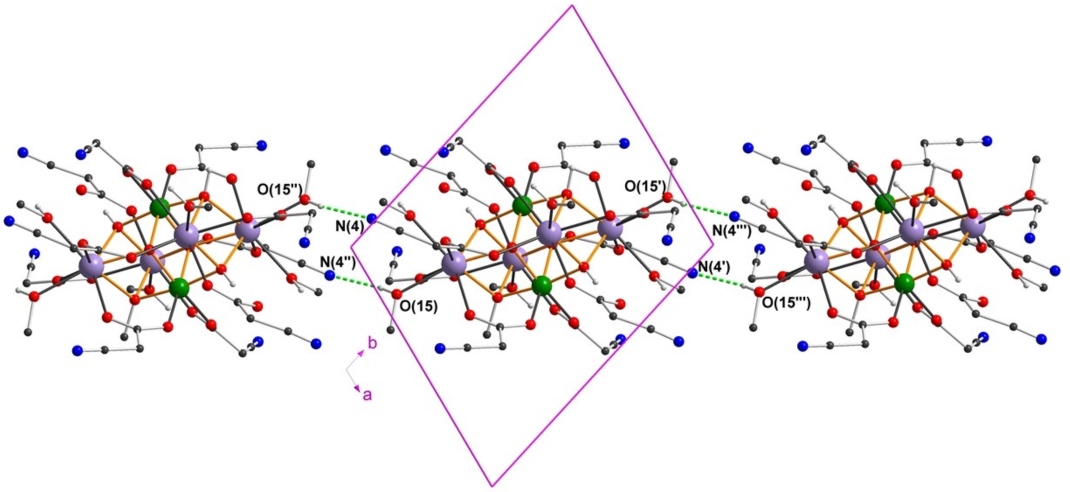

Fig. S4 View of the chains of $\{Fe_2Dy_4\}$ coordination clusters in **1**. The chains run parallel to the a + b vector with the chain viewed along the c direction. Symmetry equivalents are: ' 1-x,1-y,1-z; '' -x,-y,1-z and ''' 1+x,1+y,z

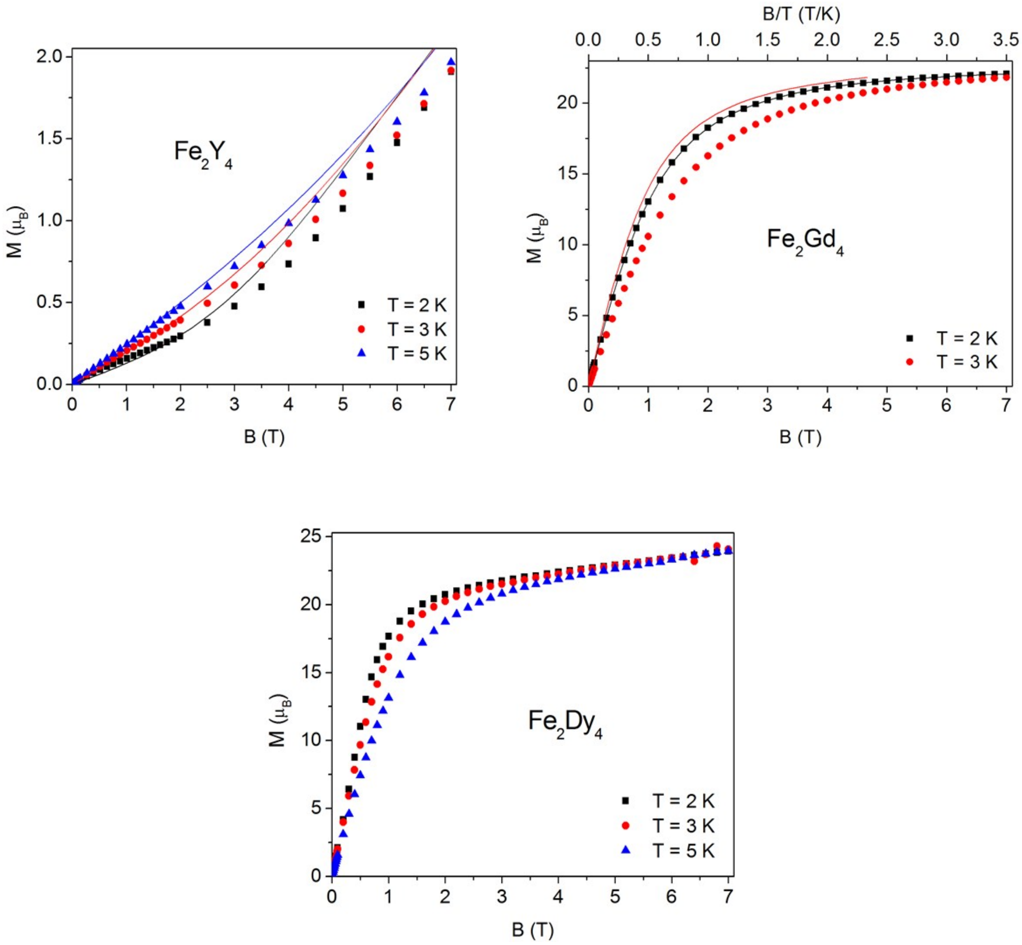

Fig. S5 Magnetization M versus applied field B for the Fe_2M_4 (M = Y, Gd, Dy) clusters at the indicated temperatures. The solid lines in the top left panel are the calculated curves, shown for comparison. The solid lines in the top right panel are the reduced magnetization curves, i.e. M versus B/T (the corresponding horizontal axis is at the top of the graph).