

Supporting Information

Novel Mixed-Valent $\text{Co}^{\text{II}}_2\text{Co}^{\text{III}}_4\text{Ln}^{\text{III}}_4$ Aggregates with Ligands Derived from *tris*-(hydroxymethyl)aminomethane (*tris*)

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Detailed Experiment:

Preparation of 1-3

All of the starting materials are commercially available and used without further purification. All the reactions were carried out under aerobic conditions. Elemental analyses for C, H and N were performed using an Elementar Vario EL analyzer and were carried out at the Institute of Inorganic Chemistry, University of Karlsruhe. FTIR spectra were measured on a Perkin-Elmer Spectrum spectrometer with samples prepared as KBr discs.

$[\text{Co}_6\text{Y}_4(\text{trisH})_8(\text{OAc})_6(\text{NO}_3)_4(\text{MeOH})_2] \cdot 7\text{H}_2\text{O} \cdot 6\text{MeOH}$ (1): Solid $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (498 mg, 2 mmol), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (913 mg, 2 mmol) and trisH_3 (242 mg, 2 mmol) were dissolved in 20 mL methanol. After stirring at about 50 °C about 10 minutes, to the peach

red mixture were added triethylamine (101 mg, 1 mmol) in 1 mL methanol. The result solution was continued to be heated about 10 minutes and then to be stirred for another 20 minutes. The final dark violet solution was allowed to cool, was filtered and was layered by n-hexane. Dark violet crystals (440 mg, 50% based on Co) were formed after about one week.

Found: C 21.74, H 4.29, N 7.31; $C_{48}H_{120}Co_6N_{14}O_{65}Y_4$ (loss of 4MeOH) requires C 21.81, H 4.57, N 7.42%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$: 3276, 2929, 2856, 1563, 1419, 1384, 1353, 1070, 1015, 815, 747, 682, 616, 582, 555, 515 and 473.

$[Co^{II}_2Co^{III}_4Gd^{III}_4(\text{trisH})_8(\text{OAc})_6(\text{NO}_3)_4(\text{H}_2\text{O})(\text{MeOH})](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot 5\text{MeOH}$ (2):

Compound **2** was obtained by the same procedure using $Gd(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in place of $Y(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Dark violet crystals (547 mg, 56% based on Co) were formed after about one week.

Found: C 20.37, H 4.15, N 6.56; $C_{50}H_{124}Co_6Gd_4N_{14}O_{65}$ requires C 20.25, H 4.22, N 6.61%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$: 3280, 2927, 2854, 1559, 1419, 1385, 1353, 1069, 1016, 815, 744, 679, 615, 581, 552, 516 and 471.

$[Co_6Dy_4(\text{trisH})_8(\text{OAc})_6(\text{NO}_3)_4(\text{MeOH})_2] \cdot 6\text{H}_2\text{O} \cdot 4\text{MeOH}$ (3): Compound **3** was obtained by the same procedure using $Dy(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in place of $Y(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Dark violet crystals (440 mg, 50% based on Co) were formed after about one week.

Found: C 19.33, H 4.01, N 6.54; $C_{48}H_{124}Co_6Dy_4N_{14}O_{67}$ (replacement of 2MeOH by 3H₂O) requires C 19.39; H 4.20; N 6.60%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$: 3285, 2933, 2868, 1563, 1420, 1385, 1353, 10766, 1016, 816, 746, 681, 614, 581, 516 and 478.

X-ray Crystallography

X-ray data for **1** and **3** were collected at 100(2) K on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data for **2** were collected at 123(2) K on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Cu- $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Semi-empirical absorption corrections were applied using the SADABS program.¹ The structures were solved using direct methods, and refined by full-matrix least-squares refinement against F^2 (all data) using the SHELXTL software package.² All ordered non-H atoms were assigned anisotropic temperature factors. All the organic hydrogen atoms of the ligands (and N-H and O-H H-atoms for **1**) were placed in calculated positions with riding isotropic thermal parameters; coordinates of ligand N-H and O-H H-atoms for **2** and **3** were refined.

The ligand hydroxyl oxygen O(9), the nitrate counterions and the lattice solvent were generally two-fold disordered, and were refined using partial C, N and O atoms, with geometrical restraints as necessary. In **2**, the terminal ligand on Gd(2) appears to be a superposition of a methanol and an aquo ligand, which were refined with a common full-occupancy oxygen and a half-occupancy carbon; each molecule thus has one aquo and one methanol ligand. No attempt was made to locate the H-atoms on the half-aquo ligand.

Several crystals were investigated; all showed poorly-resolved twinning to a certain extent, such that it did not prove possible to integrate the datasets with two twin domains, in consequence of the large proportion of overlapped reflections. The crystal used here showed only minor twinning, and could be refined reasonably satisfactorily, albeit with rather large residual density peaks near the Dy centres. The refined structure of **3** contains a void of *ca.* 110 \AA^3 in the unit cell, which presumably contains the two lattice MeOH

molecules found in the Co₆Y₄ analogue, but missing here. Electron density in this region could not be modelled satisfactorily; the formulation given here only includes the lattice solvent that was located and refined.

Selected bond lengths and angles for **1-3** are shown in Table S1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 758590-758592. 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.

Table S1. Selected bond lengths (Å) and angles (°) for **1-3**.

Compound	1 (Ln = Y)	2 (Ln = Gd)	3 (Ln = Dy)
Ln 1—O2	2.293(4)	2.297(6)	2.302(5)
Ln 1—O4	2.425(3)	2.458(6)	2.457(5)
Ln 1—O7	2.449(4)	2.513(6)	2.467(5)
Ln1—O8	2.199(4)	2.226(6)	2.192(6)
Ln 1—O10	2.263(3)	2.315(6)	2.299(6)
Ln 1—O14	2.408(3)	2.439(6)	2.414(6)
Ln 1—O15	2.463(4)	2.492(6)	2.471(6)
Ln 1—O16	2.456(4)	2.487(7)	2.466(8)
Ln 2—O11	2.239(4)	2.275(6)	2.243(6)
Ln 2—O15	2.323(4)	2.362(6)	2.343(6)
Ln 2—O18	2.298(4)	2.336(7)	2.320(6)
Ln 2—O19	2.504(4)	2.517(7)	2.510(7)
Ln 2—O20	2.458(4)	2.519(7)	2.481(6)
Ln 2—O22	2.468(4)	2.522(7)	2.497(7)
Ln 2—O23	2.451(5)	2.497(8)	2.488(8)
Ln 2—O25	2.400(4)	2.418(7)	2.400(7)

Ln 2—O7	2.520(4)	2.515(6)	2.521(6)
Co1—O1	2.121(4)	2.136(6)	2.123(6)
Co1—O1'	2.227(3)	2.230(6)	2.236(5)
Co1—O4	2.159(4)	2.149(6)	2.138(6)
Co1—O5'	1.997(4)	1.979(6)	1.994(6)
Co1—O8	2.094(3)	2.091(6)	2.104(5)
Co1—O13	2.047(4)	2.052(6)	2.050(6)
Co2—O1	1.908(4)	1.883(6)	1.897(6)
Co2—O2	1.902(3)	1.909(6)	1.903(5)
Co2—O4	1.910(4)	1.880(6)	1.901(6)
Co2—O5	1.886(3)	1.894(6)	1.895(5)
Co2—N1	1.948(4)	1.933(8)	1.937(7)
Co2—N2	1.946(5)	1.942(9)	1.929(8)
Co3—O7	1.913(3)	1.925(6)	1.911(6)
Co3—O10	1.889(4)	1.903(6)	1.889(6)
Co3—O11	1.890(4)	1.897(6)	1.905(6)
Co3—O17	1.920(4)	1.923(6)	1.918(6)
Co3—N3	1.928(5)	1.939(8)	1.945(8)
Co3—N4	1.938(4)	1.931(9)	1.936(8)
Co1-O1-Co1'	93.89(13)	93.6(2)	93.7(2)
Co1-O1-Co2	97.64(16)	98.5(3)	98.1(2)
Co2-O1-Co1'	95.29(15)	95.4(3)	95.5(2)
Co2-O2-Ln1	107.15(15)	107.4(3)	107.2(2)
Co2-O4-Co1	96.32(16)	98.1(3)	97.4(2)
Co2-O4-Ln1	101.95(14)	102.3(3)	101.5(2)
Co1-O4-Ln1	90.63(13)	90.8(2)	90.6(2)
Co2-O5-Co1'	104.14(17)	104.0(3)	104.1(3)
Co3-O7-Ln1	98.66(14)	98.0(2)	99.2(2)
Co3-O7-Ln2	93.95(14)	94.7(2)	94.3(2)
Ln1-O7-Ln2	108.11(14)	107.0(2)	107.8(2)
Co1-O8-Ln1	98.97(15)	99.1(3)	99.3(2)
Co3-O10-Ln1	106.16(16)	105.7(3)	105.9(3)
Co3-O11-Ln2	104.28(15)	103.7(3)	104.0(3)
Ln2-O15-Ln1	114.40(16)	112.7(3)	113.6(3)

Primed atoms at 1-x, 1-y, 1-z

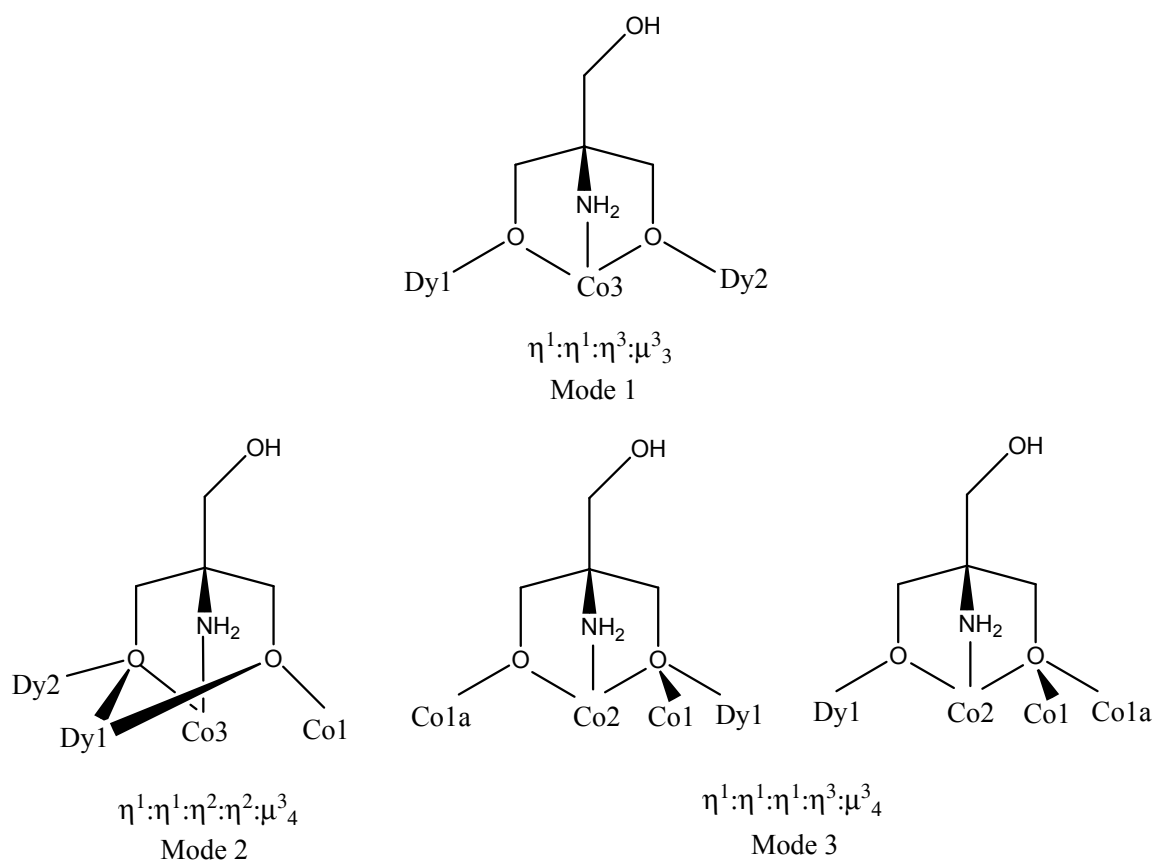
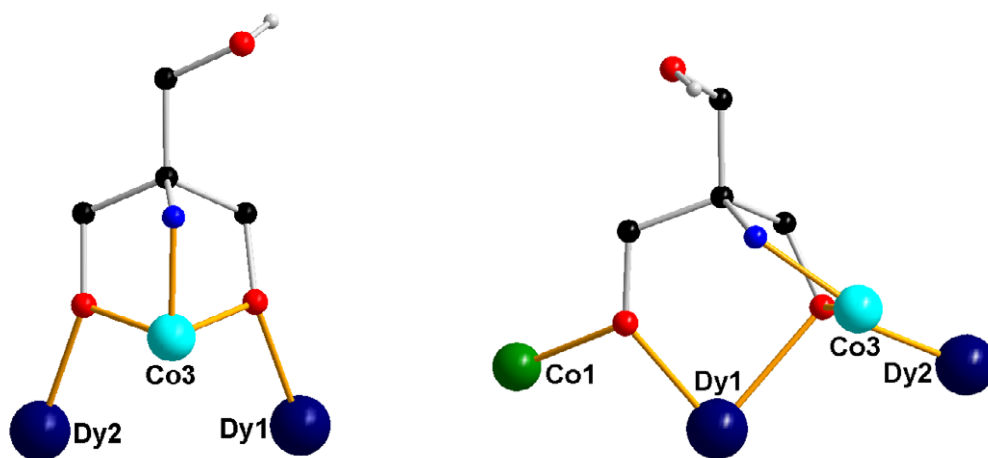


Figure S1. The binding modes of TrisH^{2-} ligands in **1-3**.



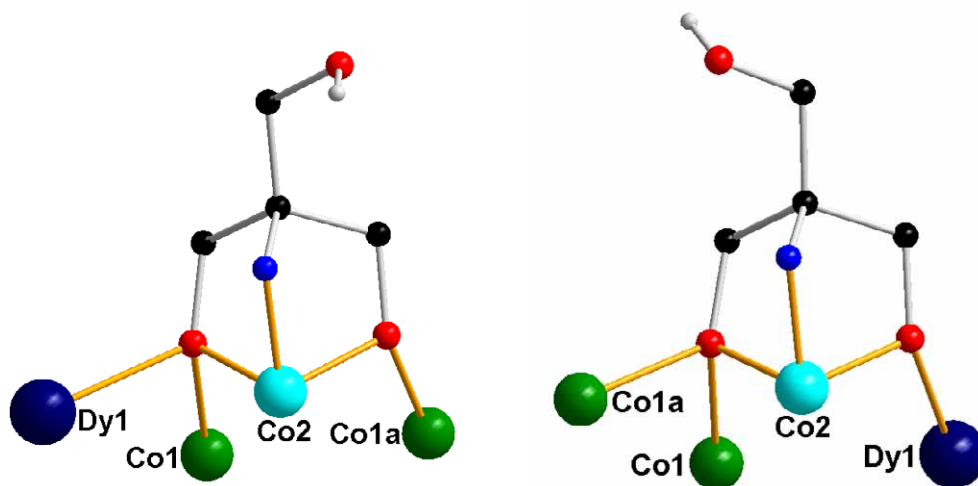


Figure S1. Binding Mode 1 (top left), Binding Mode 2 (top right) and Binding Mode 3 (bottom) of TrisH^{2-} ligands in **1-3**. [symmetric equivalent: $a = 1 - x, 1 - y, 1 - z$].

Magnetic Measurements

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on finely ground polycrystalline samples. M versus H measurements were performed at 100 K to check for the presence of ferromagnetic impurities that were found to be systematically absent. The ac susceptibility measurements were measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

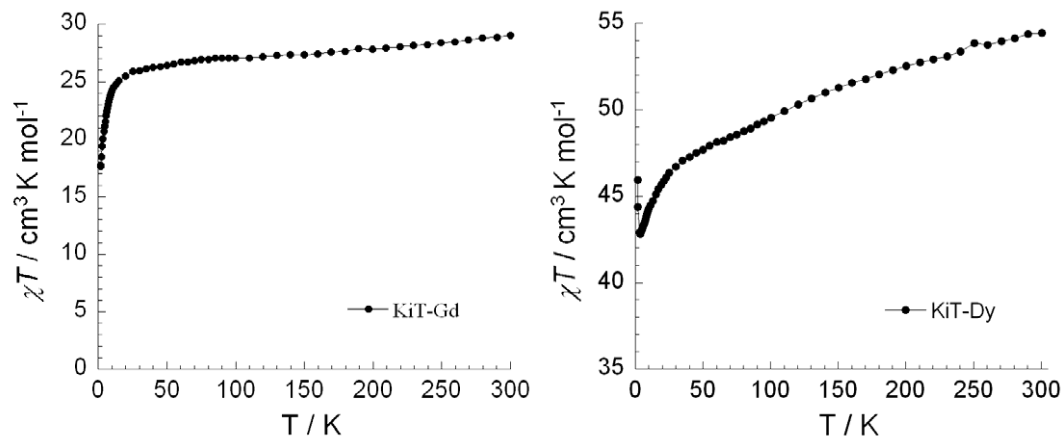


Figure S2. The χT vs T plots for **2** and **3** with the data for **1** subtracted, i.e. without the magnetic contribution of the Co_6 unit.

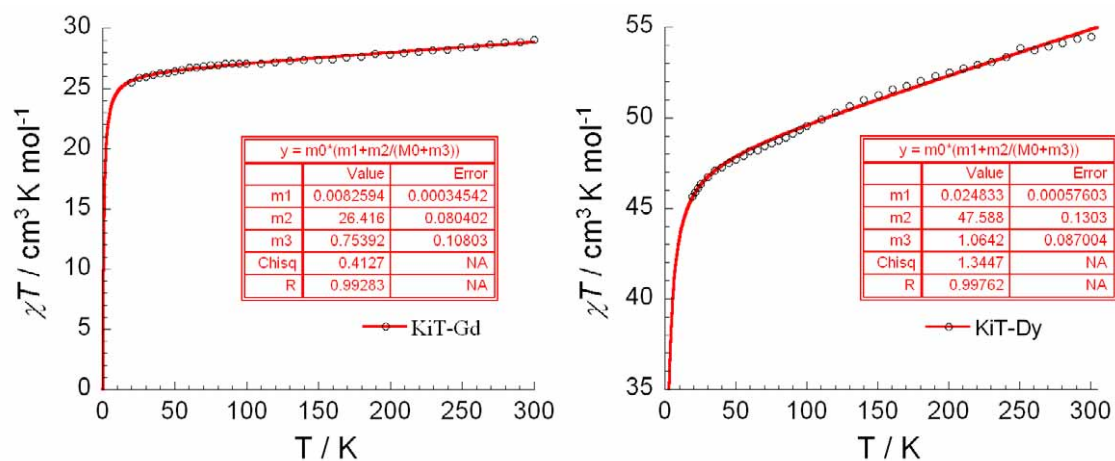


Figure S3. The Curie-Weiss fittings (above 20 K) of the χT vs T plots in Figure S2, i.e. for **2** and **3** without the magnetic contribution of the Co_6 unit. Here m_1 is a constant corresponding to diamagnetic or TIP contribution to the total susceptibility.

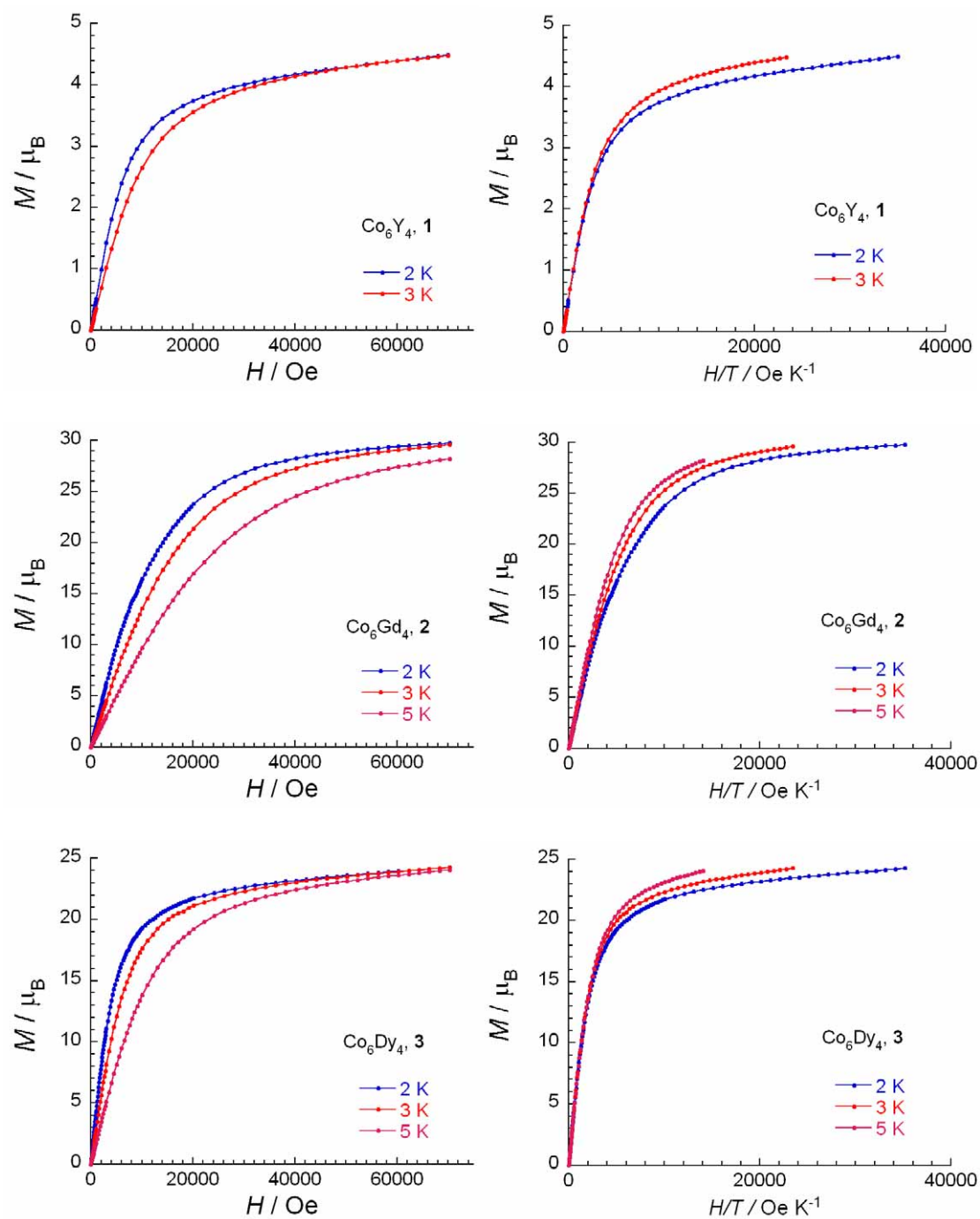


Figure S4. Plots of magnetization M vs H and M vs H/T between 2 and 5 K for complexes 1-3.

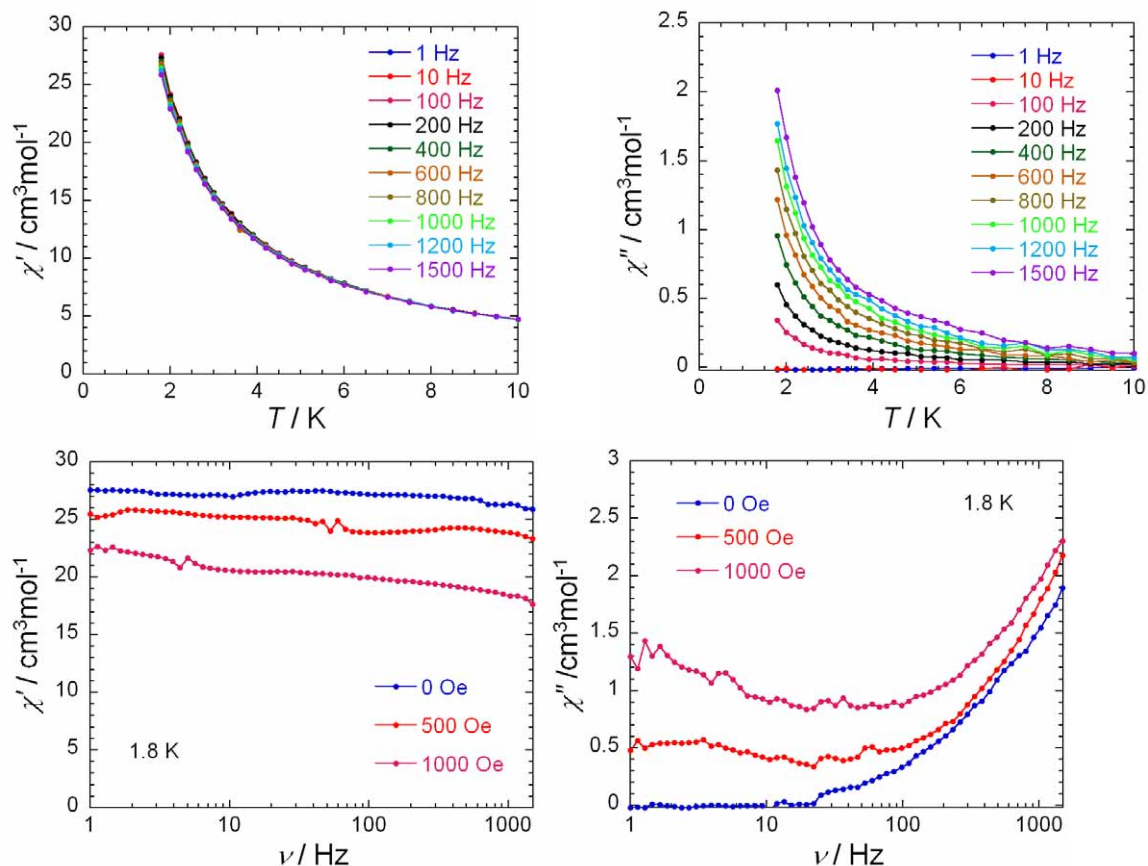


Figure S5. ac susceptibility data for complex 3.

References.

1. G. M. Sheldrick, SADABS (the Siemens Area Detector Absorption Correction), University of Göttingen, 1996.
2. G. M. Sheldrick, SHELXTL 6.14, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719 – 1173, USA, 2003.
3. a) G. S. Papaefstathiou, A. Escuer, M. Font-Bardi'a, S. P. Perlepes, X. Solans and R. Vicente, *Polyhedron* 2002, **21**, 2027-2032. b) G. S. Papaefstathiou, A. Escuer, C. P. Raptopoulou, A. Terzis, S. P. Perlepes, and R. Vicente, *Eur. J. Inorg. Chem.* 2001, 1567-1574. c) G. A. Seisenbaeva, M. Kritikos and V. G. Kessler, *Polyhedron* 2003, **22**, 2581-2586. d) P. King, R. Clérac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2004, 2670-2676.