

ELECTRONIC SUPPLEMENTARY MATERIAL to:

Dinuclear lanthanide(III)/ zinc(II) complexes from the use of methyl 2-pyridyl ketone oxime†

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SYNTHETIC DETAILS

All experiments were performed under aerobic conditions using materials (reagent grade) and solvents as received. The organic ligand mpko was prepared in typical yields of >80% following the reported method.¹

Preparation of [ZnEu(mpko)₃(mpkoH)₃](ClO₄)₂·2H₂O (1·2H₂O)

To a stirred, colourless solution of Zn(ClO₄)₂·6H₂O (0.074 g, 0.2 mmol), mpkoH (0.164 g, 1.2 mmol) and Et₃N (168 μL, 0.6 mmol) in MeOH (10 mL) was added solid Eu(NO₃)₃·6H₂O (0.178 g, 0.4 mmol). The solid soon dissolved and the resulting pale yellow solution was stirred for a further 5 min, filtered and the filtrate was stored in a closed vial at room temperature. After 2 d, pale yellow crystals of the product formed, which were collected by filtration, washed with cold MeOH (1 mL) and Et₂O (2x5 mL), and dried in air. The yield was 60% (based on the Zn^{II} available). The complex analysed satisfactorily as 1·2H₂O (calculated formula C₄₂H₄₉ZnEuN₁₂O₁₆Cl₂). Data are as follows (found values in parentheses): C, 39.84 (39.81); H, 3.90 (3.77); N, 13.28 (13.57) %. IR bands (KBr, cm⁻¹): 3430mb [ν (OH)], 3092w, 2802w, 1600s, 1561w, 1473m, 1439sh, 1375m, 1326w, 1256w, 1149m [ν (NO)_{oximate/oxime}], 1080vs [ν_3 (F₂) of ClO₄⁻, i.e. ν_d (ClO)], 1031vs, 1006sh, 958m, 782s, 747w, 695w, 679m [δ (2-pyridyl ring)], 624m [ν_4 (F₂) of ClO₄⁻, i.e. δ_d (OCIO)], 461w [γ (2-pyridyl ring)].

Preparation of [ZnDy(NO₃)₂(mpko)₃(mpkoH)](4)

To a stirred, almost colourless solution of Zn(ClO₄)₂·6H₂O (0.074 g, 0.2 mmol), mpkoH (0.164 g, 1.2 mmol) and Et₃N (168 μL, 0.6 mmol) in MeOH (10 mL) was added solid Dy(NO₃)₃·6H₂O (0.182 g, 0.4 mmol). The solid immediately dissolved and the resulting pale orange solution was stirred for a further 2 min, filtered and the filtrate was stored in a closed vial at room temperature. After 3 d, colourless crystals of the product were precipitated, collected by filtration, washed with cold MeOH (1 mL) and Et₂O (2x5 mL), and dried in air. The yield was 50% (based on the Zn^{II} available). The complex analysed satisfactorily as 4 (calculated formula C₂₈H₂₉ZnDyN₁₀O₁₀). Data are as follows (found values in parentheses): C, 37.64 (37.86); H, 3.27 (3.18); N, 15.68 (15.80) %. IR bands (KBr, cm⁻¹): 3220mb [ν (OH)],

3080w, 2930w, 1595vs, 1496s [$\nu_1(A_1)$ of the bidentate chelating nitrate groups, i.e. $\nu(N=O)$], 1444s, 1384w, 1350w, 1294s, [$\nu_5(B_2)$ of the bidentate chelating nitrate groups, i.e. $\nu_{as}(NO_2)$], 1167w, 1135w [$\nu(NO)_{oximate/oxime}$], 1101w, 1033s, 1012sh, 961w, 818w, 783m, 745w, 679m [$\delta(2\text{-pyridyl ring})$], 656w, 636w, 610w, 519w, 472w [$\gamma(2\text{-pyridyl ring})$], 415w.

Preparation of complexes [ZnGd(mpko)₃(mpkoH)₃](ClO₄)₂·2H₂O (2·2H₂O), [ZnTb(mpko)₃(mpkoH)₃](ClO₄)₂·2H₂O (3·2H₂O), and [ZnHo(NO₃)₂(mpko)₃(mpkoH)](5)

Complexes 2·2H₂O and 3·2H₂O were prepared in an identical manner with complex 1·2H₂O by simply replacing Eu(NO₃)₃·6H₂O with the corresponding hydrated nitrates of Gd(III) and Tb(III). The IR spectra of 1·2H₂O (see above), 2·2H₂O and 3·H₂O are almost identical (superimposable) with a maximum wavenumber difference of 3 cm⁻¹. Analytical data: For 2·2H₂O (calculated formula C₄₂H₄₉ZnGdN₁₂O₁₆Cl₂, found values in parentheses): C, 39.67 (39.82); H, 3.89 (3.79); N, 13.22 (13.46) %. For 3·2H₂O (calculated formula C₄₂H₄₉ZnTbN₁₂O₁₆Cl₂, found values in parentheses): C, 39.62 (39.48); H, 3.89 (3.97); N, 13.20 (13.36) %.

Complex 5 was prepared in an identical manner with complex 4 by simply replacing Dy(NO₃)₃·6H₂O with Ho(NO₃)₃·6H₂O. The IR spectra of 4 and 5 are almost identical (superimposable) with a maximum wavenumber difference of 2 cm⁻¹. Analytical data for 5 (calculated formula C₂₈H₂₉ZnHoN₁₀O₁₀, found values in parentheses): C, 37.53 (37.81); H, 3.27 (3.19); N, 15.64 (15.25) %.

SINGLE-CRYSTAL X-RAY CRYSTALLOGRAPHY IN BRIEF

Data for $1\cdot 2\text{H}_2\text{O}$ and **4** were collected at 180 K on a Stoe IPDS II area detector diffractometer using graphite-monochromated Mo α radiation. Semi-empirical absorption corrections were applied using XPREP in SHELXTL.² The structures were solved using direct methods, followed by a full-matrix least-squares refinement against F^2 (all data) using SHELXTL.² Anisotropic refinement was used for all ordered non-H atoms. Organic H atoms were placed at calculated positions, while coordinates of hydroxyl and aqua H atoms were either placed in calculated positions or located from the difference Fourier map and then constrained to ride on their parent atom with $U_{\text{iso}}=1.5 U_{\text{eq}}$ (parent atom). CCDC numbers 1021513 ($1\cdot 2\text{H}_2\text{O}$) and 1021514 (**4**).

HYDROGEN BONDS IN THE CRYSTAL STRUCTURE OF $1\cdot 2\text{H}_2\text{O}$

Intracationic H bonds

D-H \cdots A	D \cdots A (Å)	H \cdots A (Å)	D-H \cdots A (Å)	Symmetry operation
O1-H1 \cdots O6	2.554(8)	1.850	140.7	x, y, z
O2-H2 \cdots O4	2.478(8)	1.760	142.2	x, y, z
O3-H3 \cdots O5	2.538(9)	1.830	141.4	x, y, z

There are also H bonds between the ClO_4^- counterions (acceptors) and lattice H_2O molecules (donors). Metric parameters: O16 \cdots O10 2.933 Å, H16B \cdots O10 2.333 Å, O16-H16B \cdots O10 126.3°; O15 \cdots O11 2.931 Å, H15D \cdots O11 2.328 Å, O15-H15D \cdots O11 126.6°; O15 \cdots O14 2.648 Å, H15E \cdots O14 2.024 Å, O15-H15E \cdots O14 157.6°.

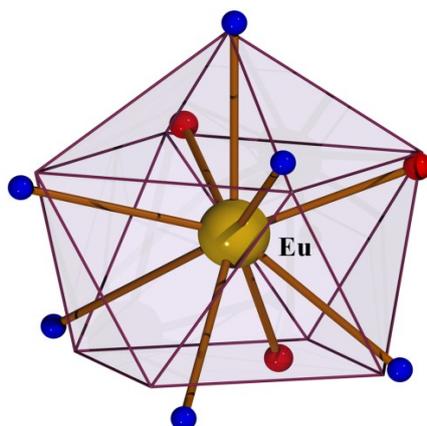


Fig. S1 The capped square antiprismatic geometry of the Eu^{III} centre in the structure of $1 \cdot 2\text{H}_2\text{O}$; the very small spheres define the vertices of the ideal polyhedron.

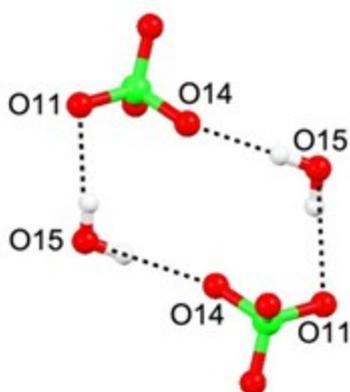


Fig. S2 The H- bonded parallelogram of the type $\text{HOH} \cdots \text{O}(\text{ClO}_2)\text{O} \cdots \text{HOH} \cdots \text{O}(\text{ClO}_2)\text{O}$ that is present in the crystal structure of $1 \cdot 2\text{H}_2\text{O}$; this involves two symmetry-related H_2O molecules and ClO_4^- anions that belong to neighbouring unit cells.

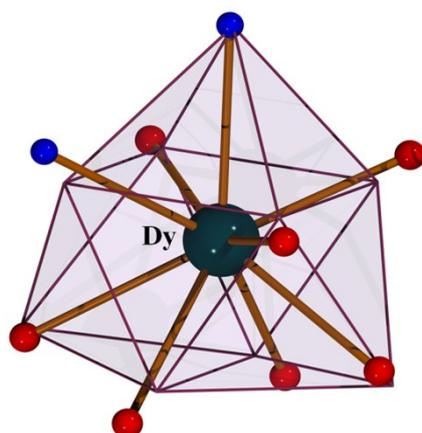


Fig. S3 The capped square antiprismatic geometry of the Dy^{III} centre in the structure of **4**; the very small spheres define the vertices of the ideal polyhedron.

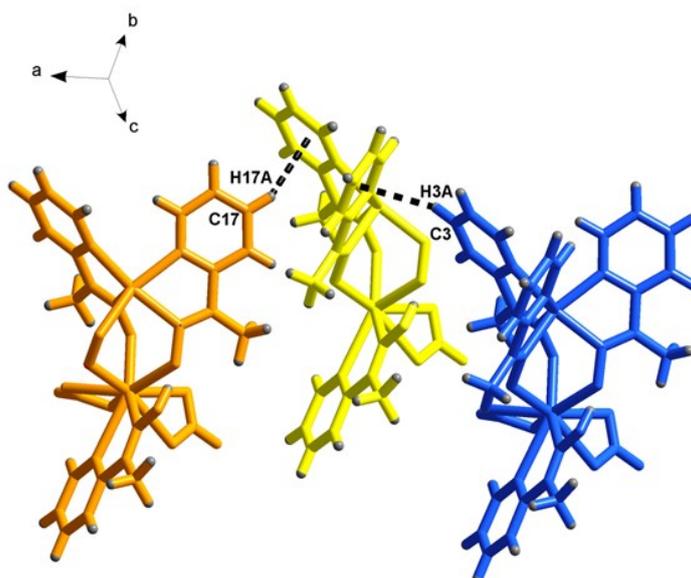


Fig. S4 C-H... π interactions (black dashed lines) in the crystal lattice of **4**; parts of the molecules have been omitted for clarity.

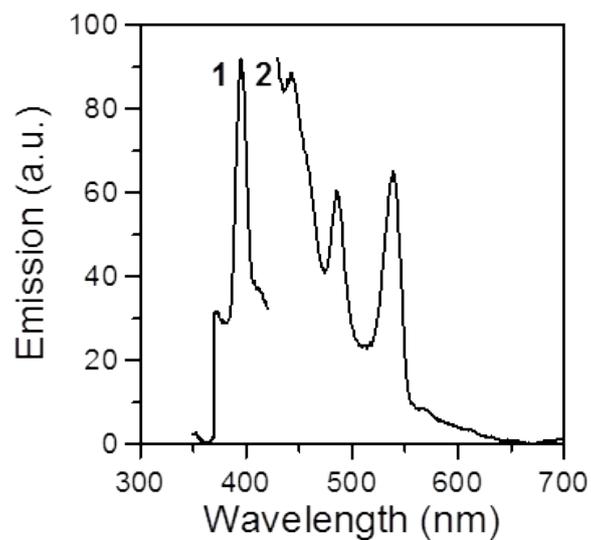


Fig. S5 Solid-state room-temperature excitation (emission at 540 nm, curve 1) and emission (excitation at 400 nm, curve 2) for complex 1·2H₂O.

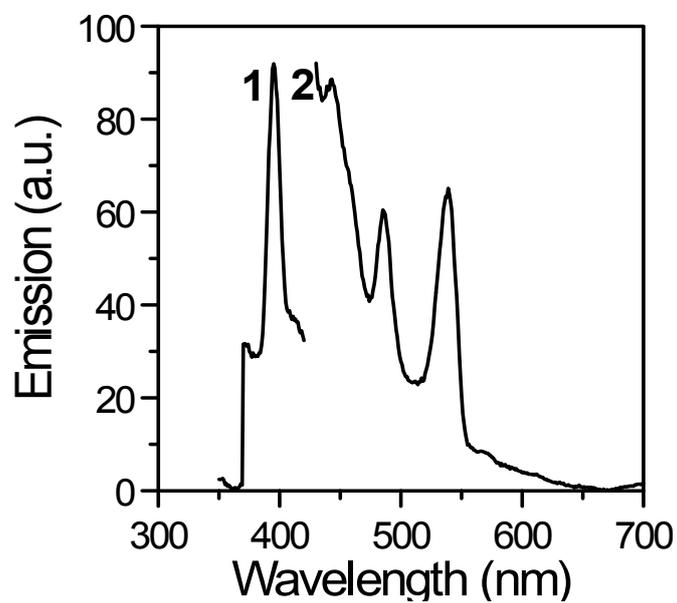


Fig. S6 Solid-state room temperature excitation (emission at 540 nm, curve 1) and emission (excitation at 400 nm, curve 2) for complex 3·2H₂O.

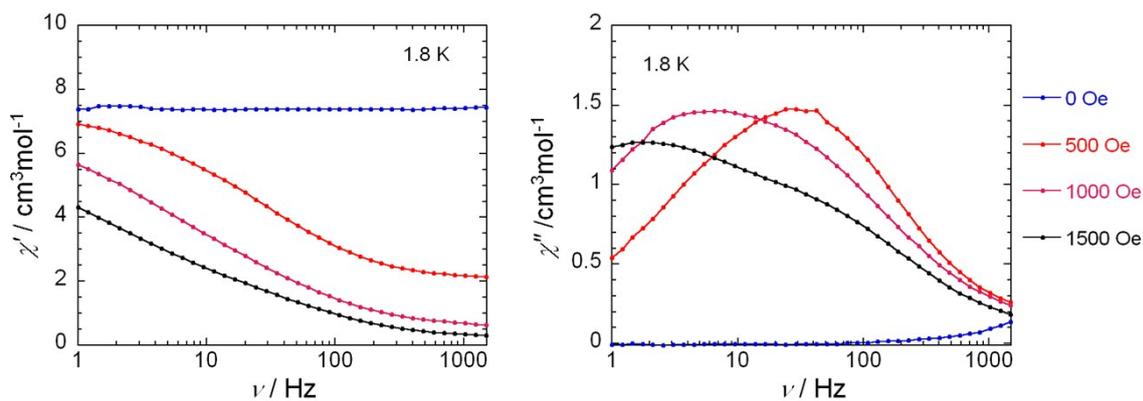


Fig. S7 Frequency dependence of the in-phase (χ' , left) and out-of-phase (χ'' , right) magnetic susceptibilities for **4** under different (0, 500, 1000 and 1500 Oe) dc fields at 1.8 K.

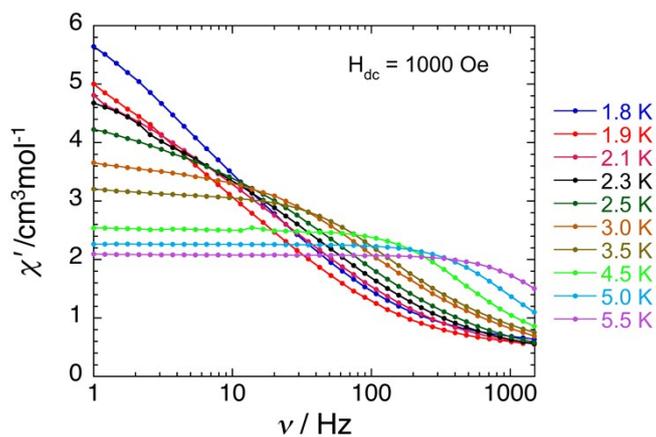


Fig. S8 Frequency dependence of the in-phase (χ') component of the ac susceptibility under an external dc field of 1000 Oe at the indicated temperatures for complex **4**.

Table S1 Continuous Shape Measures (CShM) values for the possible coordination polyhedra of the 9-coordinate Ln^{III} ions (Ln = Eu, Dy) in the molecular structures of **1**·2H₂O and **4**^{a,b}

Ideal polyhedron	Complex 1 ·2H ₂ O	Complex 4
Enneagon	32.18447	34.03600
Octagonal pyramid	24.48622	24.26826
Heptagonal bipyramid	17.54353	17.14165
Johnson triangular cupola J3	13.13307	13.90252
Capped cube J8	9.10721	8.75379
Spherical-relaxed capped cube	8.08157	7.87166
Capped square antiprism J10	2.26502	3.19278
Spherical capped square antiprism	1.80735	2.34820
Tricapped trigonal prism J51	2.02863	2.96985
Spherical tricapped trigonal prism	1.80967	2.36835
Tridiminished icosahedron J63	11.34007	11.24506
Hula-hoop	12.07364	10.50385
Muffin	2.26405	2.35765

^a The smallest value (in bold) defines the best polyhedron. ^b Chemically significant distortions give CShM values of 0.1 or higher, while values larger than 3 indicate important distortions.

REFERENCES FOR THE ESI

¹ M. Orama, H. Saarinen and J. Korvenranta, *J. Coord. Chem.*, 1990, **22**, 183.

² G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.