Supplementary Information (SI) for the manuscript:

Magnetic order in a Cu^{II}-Dy^{III} oxamato-based two-dimensional coordination polymer

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Experimental Section

Preparation of $Li_2[Cu(Me_2pma)_2] \cdot 2H_2O$: A green polycrystalline solid was obtained from a metathesis from the previously reported tetrabutylammonium complex $(n\text{-}Bu_4N)_2[Cu(Me_2pma)_2] \cdot 2H_2O$ (4.8 g, 5 mmol), with $AgNO_3$ (1.70 g, 10 mmol) and (LiCl) (0.42 g, 10 mmol) in 25 mL of water. After eliminating AgCl by filtration, the solution was evaporated to dryness. The solid was collected and washed with a small amount of ethanol, acetone and diethyl ether and dried under vacuum. (2.31 g, 89 %). Elemental analysis calcd (%) for $C_{20}H_{22}N_2O_8Li_2Cu$ (495.8): C 48.45, H 4.47, N 5.65; found: C 48.32, H 4.21, N 5.66; IR (KBr): ν = 1653, 1621 cm^{-1} (C=O).

Theoretical calculations. The calculations were carried out with the version 4.0 of the ORCA programme,[1] using the TZVP basis set proposed by Ahlrichs[2] and the auxiliary TZV/C Coulomb fitting basis sets.[3] Relativistic effects were introduced from a zero-order regular approximation (ZORA).[4] Segmented all-electron relativistically contracted set for use with the ZORA Hamiltonian was employed for the dysprosium atom.[5] RIJCOSX method was used combining resolution of the identity (RI) and "chain of spheres" COSX approximations for the Coulomb and exchange terms, respectively.[6]

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[1] F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci*., 2012, **2**, 73

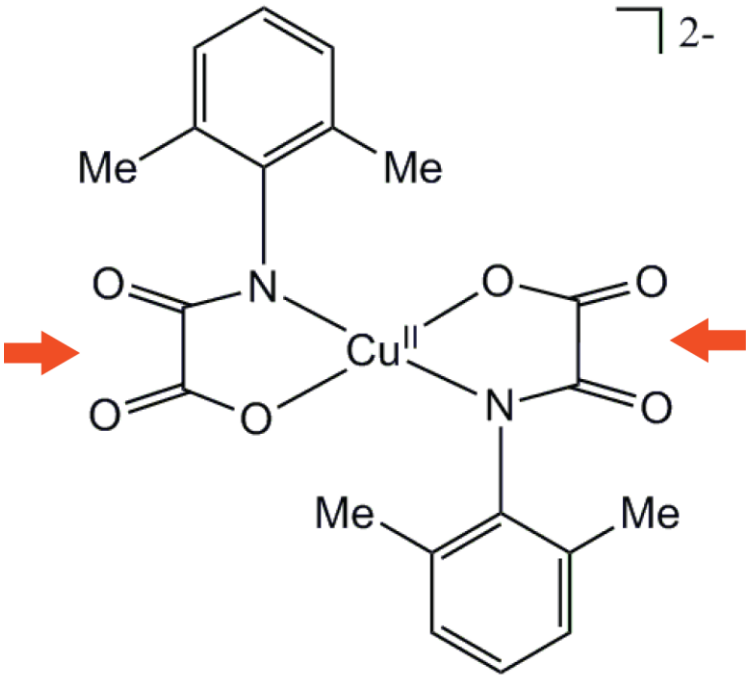
[2] (a) A. Schafer, H. Horn and R. Ahlrichs, *J. Chem. Phys*., 1992, **97**, 2571; (b) A. Schafer, C. Huber and R. Ahlrichs, *J. Chem. Phys.,* 1994, **100**, 5829

[3] (a) K. Eichkorn, O. Treutler, H. Ohm, M. Haser and R. Ahlrichs, *Chem. Phys. Lett*., 1995, **240**, 283; (b) K. Eichkorn, O. Treutler, H. Ohm, M. Haser and R. Ahlrichs, *Chem. Phys. Lett*., 1995, **242**, 652; (c) K. Eichkorn, F. Weigend, O. Treutler, H. Ohm and R. Ahlrichs, *Theor. Chem. Acc*., 1997, **97**, 19.

[4] C. Chang, M. Pelissier and Ph. Durand, *Phys. Scr.,* 1986, **34**, 394.

[5] (a) doi: 10.1021/ct800047t.; (b) **DOI:** 10.1021/ct800172j; (c) 10.1021/ct900090f;(d) 10.1021/ct100736b; (e) 10.1007/s00214-012-1292-x.

[6] (a) S. Kossmann and F. Neese, *J. Chem. Theory Comput*., 2010, **6**, 2325; (b) S. Kossmann and F. Neese, *Chem. Phys. Lett*., 2009, **481**, 240.



Scheme S1. Chemical structure of the mononuclear copper(II) anionic complex of formula $[Cu^{II}(Me_2pma)_2]^{2-}$, highlighting the free carbonyl groups acting as potential coordination sites (orange arrows).

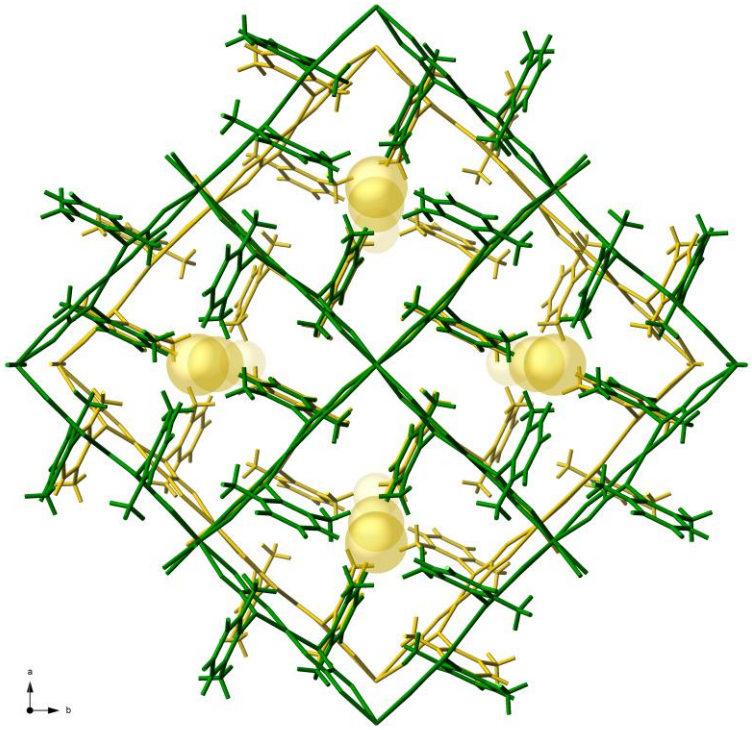


Figure S1. Crystal packing view of **1** along the *c* axis showing small hydrophobic voids. The coordination networks are represented with yellow and green sticks. The gold spheres represent the void space.

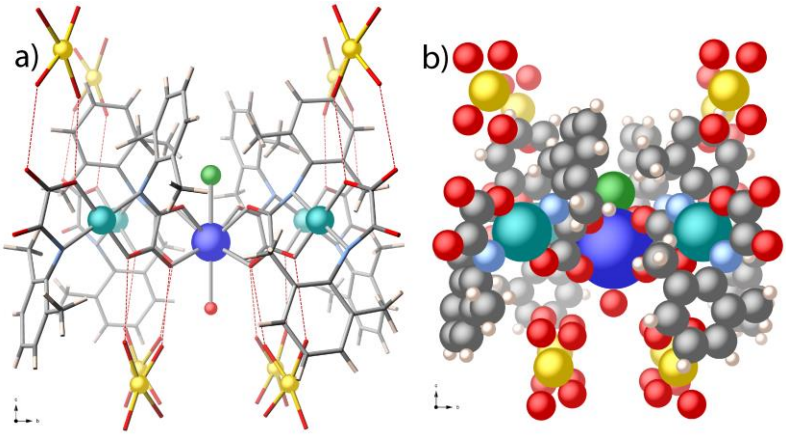


Figure S2. Perspective view, as balls and sticks and space filling model (a-b), of Dy(III) environment details in the $\{Dy^{III}[Cu(Me_2pma)_2]_2Cl(H_2O)\}^{2-}$ square-grids motif in **1**, interconnected by H-bonded $Li(H_2O)_4^+$ ions (red dashed lines) showing the basket-like cavity generated filled by water molecules and Chlorine atoms.

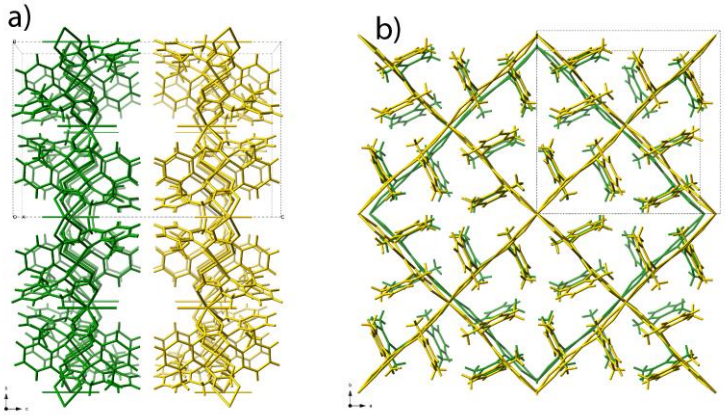


Figure S3. Perspective views of the eclipsed packing of the adjacent layers of **1** along the *c* (a) and *c* (b) axis, respectively. The two adjacent planes are depicted in yellow and green colors. The countercations and the solvent molecules have been omitted for clarity.

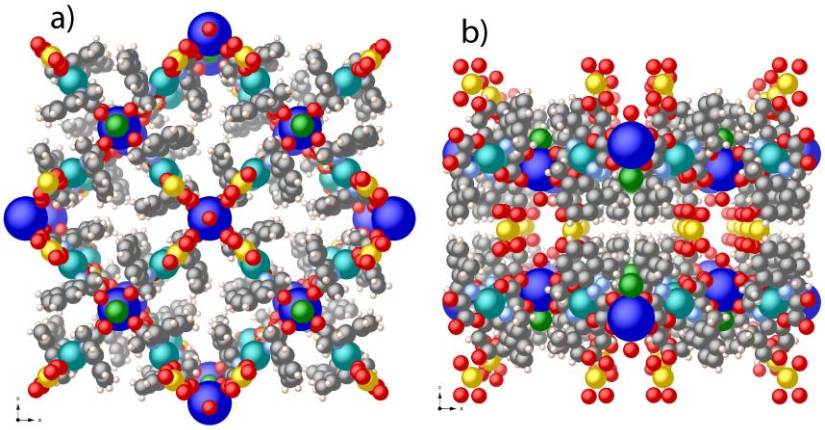


Figure S4. Space filling views along *c* and *b* directions of $\{Dy^{III}[Cu(Me_2pma)_2]_2Cl(H_2O)\}^{2-}$ square-grids interconnected by $Li(H_2O)_4^+$ ions (a-b). Cu, Dy, Li, O, N, C and H atoms are depicted as green, blue, gold, red, sky blue, gray and white spheres, respectively.

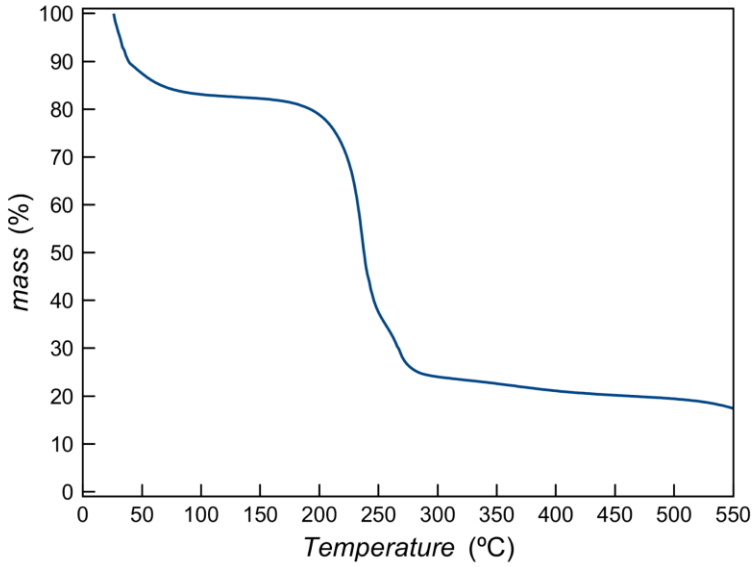


Figure S5. Thermogravimetric Analysis of **1** under dry N_2 atmosphere in the 25-550 ºC range.

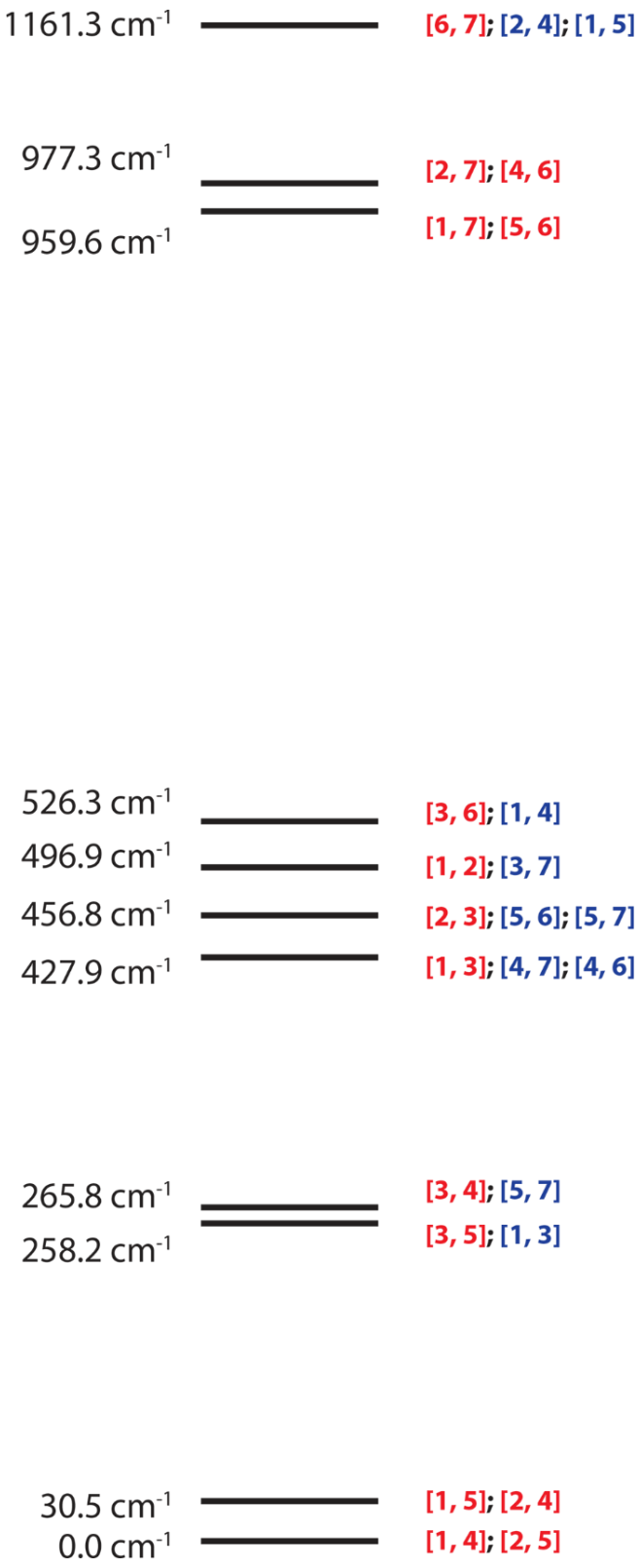


Fig. S6. Schematic energy diagram of the splitting of the ^{6}H term by crystal filed in **1**. Values correspond to the energies in cm^{-1}. Labels shows the electronic configurations that mainly contribute to a particular state. Red and blue colors are used for strong and moderate contributions. Each electronic configuration is noted indicating the electrons occupy an f orbital following the energetic order displayed in Fig. 7: {f_{-1}, f_{+1}, f_{-2}, f_{+3}, f_{-3}, f_{0}, f_{+2}}. In the shown electronic configurations, one electron is placed in each one of these f orbital and only a second electron is in *i* and *j* orbitals, being [*i*, *j*] a simplified notation of an electronic configuration. Thus, [1,3] refers to the {2,1,2,1,1,1,1} electronic configuration.