

Electronic Supplementary Information (ESI)

A heteropentanuclear oxalato-bridged $[\text{Re}^{\text{IV}}_4\text{Gd}^{\text{III}}]$ complex: synthesis, crystal structure and magnetic properties

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Preparation of compound 1.

All starting chemicals and solvents were purchased from commercial sources and used without further purification. The mononuclear precursor $(\text{NBu}_4)_2[\text{ReBr}_4(\text{ox})]$ was prepared by following the procedure described for $(\text{PPh}_4)_2[\text{ReBr}_4(\text{ox})]$ (PPh_4^+ = tetraphenylphosphonium cation) by using NBu_4Cl instead of PPh_4Cl as the precipitating agent (*See Ref. 7c* from the main text). Compound **1** was prepared by pouring a solution of 107.9 mg (0.1 mmol) of $(\text{NBu}_4)_2[\text{ReBr}_4(\text{ox})]$ in a 2-propanol/MeCN (4:1, v/v, 25 mL) mixture into another one formed by 8.6 mg (0.025 mmol) of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 2-propanol (10 mL).

The resulting green–yellowish solution was allowed to evaporate at room temperature. X-ray suitable yellow crystals of **1** were grown after three weeks. They were filtered off and washed with diethyl ether. Yield: *ca.* 43%. Found: C, 28.2; H, 4.8; N, 1.9. Calc. for $\text{C}_{88}\text{H}_{184}\text{Br}_{16}\text{N}_5\text{O}_{18}\text{GdRe}_4$ (**1**): C, 28.0; H, 4.9; N, 1.9%. The 4:1 (Re:Gd) molar ratio in **1** was determined by X-ray microanalysis performed on a microcrystalline sample and by using a Philips XL-30 scanning electron microscope (SEM) equipped with an X-ray microanalysis system from the Central Service for the Support to Experimental Research (SCSIE) of the University of Valencia. IR (KBr pellet / cm^{-1}): bands associated to the oxalato ligand appear at 1700sh, 1682s, 1667vs (ν_{asCO}) and 807s (δ_{OCO}). Compound **1** is soluble at room temperature in common organic solvents such as acetone, acetonitrile and *N,N'*-dimethylformamide.

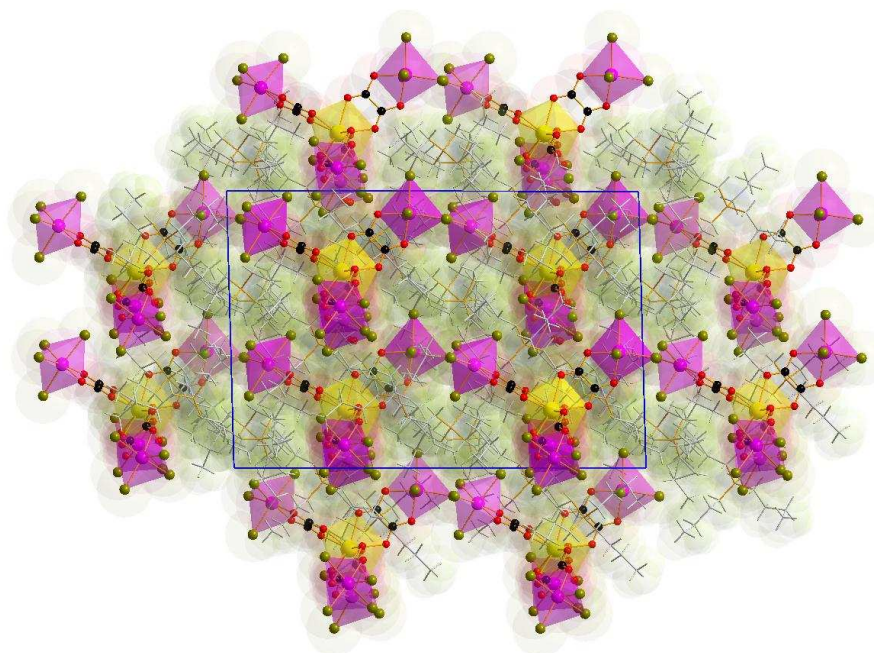
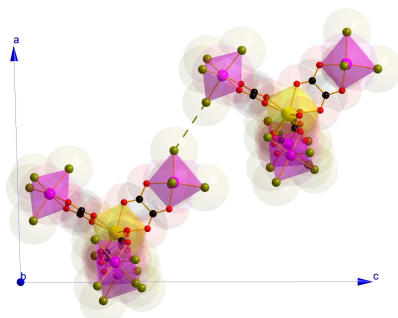


Figure S1. A view along the crystallographic *b* axis of the packing in **1** showing the arrangement of the $[\text{Gd}\{\text{ReBr}_4(\mu\text{-ox})\}_4(\text{H}_2\text{O})]^{5-}$ anions (polyhedra) and NBu_4^+ cations (sticks). Solvent H_2O molecules have been omitted for clarity.

a)



b)

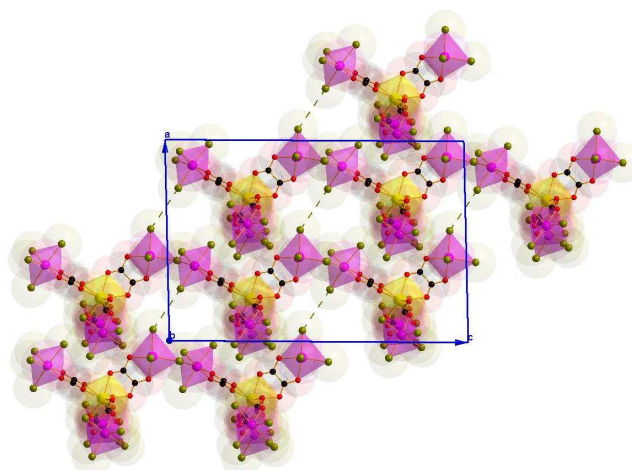


Figure S2. (a) Shortest intermolecular $\text{Br}\cdots\text{Br}$ separation between pentanuclear $[\text{Gd}\{\text{ReBr}_4(\mu\text{-ox})\}_4(\text{H}_2\text{O})]^{5-}$ units. (b) View of a fragment of packing in **1** showing the arrangement of three chains of anions through the shortest intermolecular $\text{Br}\cdots\text{Br}$ interaction (dashed lines).

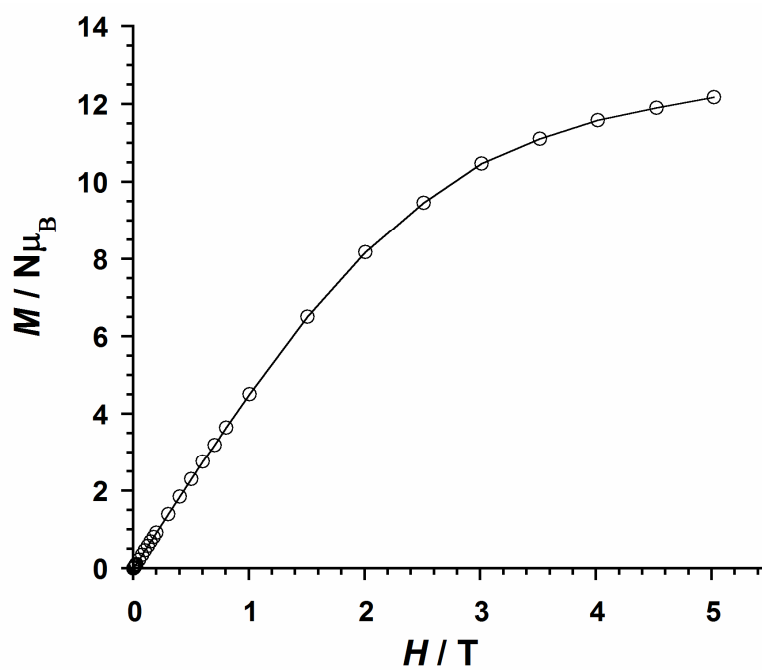


Figure S3. Field dependence of the magnetization at 2.0 K for **1** (the solid line is an eye guide).