A heteropentanuclear oxalato-bridged \([\text{Re}^{IV}\text{Gd}^{III}]\) 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 (NBu4)2[ReBr4(ox)] was prepared by following the procedure described for (PPh4)2[ReBr4(ox)] (PPh4+ = tetraphenylphosphonium cation) by using NBu4Cl instead of PPh4Cl 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 (NBu4)2[ReBr4(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 Gd(NO3)3·6H2O 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 C88H184Br16N5O18GdRe4 (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 (\(\nu_{\text{asCO}}\)) and 807s (\(\delta_{\text{OCO}}\)). 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 $[\text{Gd} \{\text{ReBr}_4(\mu-\text{ox})\}_4(H_2O)]^5$ anions (polyhedra) and NBu$_4^+$ cations (sticks). Solvent H$_2$O molecules have been omitted for clarity.

**Figure S2.** (a) Shortest intermolecular Br···Br separation between pentanuclear $[\text{Gd} \{\text{ReBr}_4(\mu-\text{ox})\}_4(H_2O)]^5$ units. (b) View of a fragment of packing in 1 showing the arrangement of three chains of anions through the shortest intermolecular Br···Br interaction (dashed lines).
Figure S3. Field dependence of the magnetization at 2.0 K for 1 (the solid line is an eye guide).