Experimental Details

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Synthesis.

HL. To a solution of isonicotinic hydrazide N-oxide (1.019 g, 6.49 mmol) in ethanol (30 cm^3) was added 2-pyridylaldehyde (0.725 g, 6.77 mmol). After addition of a few drops of glacial acetic acid the solution was refluxed for 6 h. The solid was separated and dried to give HL as a light yellow solid. Yield: 1.308 g, 82%.

Compound 1. To a solution of HL (0.047 g, 0.175 mmol) in DMF (10 cm^3) was added $Ni(ClO_4)_2 \cdot 6H_2O$ (0.046 g, 0.126 mmol). Diffusion of benzene into the resulting brownish red solution over two weeks gave brownish red crystals of **1** in 63% yield.

Compound 2. To the brownish red solution of HL (0.0464 g, 0.172 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.0478 g, 0.126 mmol) in DMF (10 cm^3) was added $Gd(ClO_4)_3 \cdot 6H_2O$ (0.0796 g, 0.141 mmol). Diffusion of benzene/acetonitrile into the resulting brownish red solution over three weeks gave brownish red crystals of **2** in 50% yield.

Compound 3. To the brownish red solution of HL (0.0468 g, 0.174 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.0473 g, 0.129 mmol) in DMF (10 cm^3) was added $Tb(ClO_4)_3 \cdot 6H_2O$ (0.0911 g, 0.161 mmol). Diffusion of benzene/acetonitrile into the resulting brownish red solution over two weeks gave brownish red crystals of **3** in 41% yield.

Compound 4. To the brownish red solution of HL (0.0473 g, 0.176 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.0480 g, 0.131 mmol) in DMF (10 cm^3) was added $Dy(ClO_4)_3 \cdot 6H_2O$ (0.0802 g, 0.141 mmol). Diffusion of benzene/acetonitrile into the resulting brownish red solution over two weeks gave brownish red crystals of **4** in 16% yield.

Anal. Calcd. For $C_{24}H_{26}N_8O_7$ (**HL**): C, 53.53; H, 4.87; N, 20.81. Found: C, 53.78; H, 4.793; N, 20.91%.

Anal. Calcd. For $NiC_{24}H_{23}N_8O_{10}Cl$ (**1**): C, 42.54; H, 3.42; N, 16.54. Found: C, 42.81; H, 3.72; N, 16.73%.

Anal. Calcd. For $GdNi_2C_{60}H_{75}N_{20}O_{33}Cl_4$ (**2**): C, 35.66; H, 3.74; N, 13.86. Found: C, 35.69; H, 4.20; N, 13.93%.

Anal. Calcd. For $TbNi_2C_{60}H_{65}N_{20}O_{28}Cl_4$ (**3**): C, 37.29; H, 3.39; N, 14.50. Found: C, 37.41; H, 3.86; N, 14.42%.

Anal. Calcd. For $DyNi_2C_{60}H_{70}N_{20}O_{27}Cl_3$ (**4**): C, 38.14; H, 3.73; N, 14.83. Found: C, 38.06; H, 4.13; N, 14.68%.

Crystallographic Studies. Diffraction intensity data for single crystals of **1**, **2, 3** and **4** were collected at 180K on a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the Sortav program. [1] The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. [2] Hydrogen atoms were located geometrically and refined isotropically. See the CIF file for details.

Physical measurements. Elemental analyses (C, H, N) were performed on an Elementar Varia EL analyzer. Variable-temperature magnetic susceptibilities were measured on a MagLab 2000 magnetometer.

(1) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.
(2) (a) Sheldrick, G. M. SHELXTL Version 5.1. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1998**. (b) Sheldrick, G. M. SHELXL-97, PC Version. University of Göttingen, Germany, **1997**.