Electronic Supplementary Information for Dalton Transactions

Caesium-templated lanthanoid-containing polyoxotungstates

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Supporting Information

Synthetic Details S1:Synthesis, FT-IR and elemental analysis of compounds Gd-1 – Er-1.

Synthesis of polyanion **Gd-1**: A sample of $Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]$ (0.493 g, 0.20 mmol was added with stirring to a solution of $Gd(NO_3)_3{\cdot}6H_2O$ (0.271 g, 0.60 mmol) in NaOAc/AcOH buffer (1.0 M, 25 mL) at pH 4.7. This solution was heated to 80 ºC for 60 minutes and then cooled to room temperature and was filtered off to remove small amounts of precipitate. 2 ml of 0.5 M CsCl solution was added to the filtrate and the solution was stirred for 5 minutes and the resulting solution was left to evaporate. Yield (18%), FTIR of **Gd-1:** 951 (s), 859 (s), 785 (s), 707 (s), 635 (sh), 478 (m) cm^{-1}. Elemental analysis (%); calcd. (found): Na 2.5 (2.8), Cs 3.4 (3.3), As 2.3 (2.3), W 60.0 (58.8), Gd 4.9 (4.6).

Synthesis of polyanion **Tb-1**: Experimental procedure cf. above, $Tb(NO_3)_3{\cdot}6H_2O$ (0.261 g, 0.60 mmol) was used instead of $Gd(NO_3)_3{\cdot}6H_2O$. Yield (15%), FTIR of **Tb-1:** 948 (s), 860 (s), 789 (s), 709 (s), 636 (sh), 480 (m) cm^{-1}. Elemental analysis (%); calcd (found): Na 2.5 (2.8), Cs 3.4 (3.4), As 2.3 (2.3), W 59.9 (58.6), Tb 4.9 (5.0).

Synthesis of polyanion **Dy-1**: Experimental procedure cf. above, $Dy(NO_3)_3{\cdot}6H_2O$ (0.263 g, 0.60 mmol) was used instead of $Gd(NO_3)_3{\cdot}6H_2O$. Yield (13%), FTIR of **Dy-1:** 948 (s), 860 (s), 789 (s), 714 (s), 637 (sh), 481 (m) cm^{-1}. Elemental analysis (%); calcd. (found): Na 2.7 (2.8), Cs 4.3 (5.0), As 2.4 (2.1), W 62.8 (63.4), Dy 5.3 (5.2).

Synthesis of polyanion **Ho-1**: Experimental procedure cf. above, $Ho(NO_3)_3{\cdot}6H_2O$ (0.265 g, 0.60 mmol) was used instead of $Gd(NO_3)_3{\cdot}6H_2O$. Yield (20%), FTIR of **Ho-1:** 948 (s), 861 (s), 789 (s), 713 (s), 636 (sh), 478 (m) cm^{-1}. Elemental analysis (%); calcd (found): Na 2.7 (2.7), Cs 4.3 (5.2), As 2.4 (2.1), W 62.8 (65.5), Ho 5.3 (5.2).

Synthesis of polyanion **Er-1**: Experimental procedure cf. above, $Er(NO_3)_3{\cdot}5H_2O$ (0.266 g, 0.60 mmol) was used instead of $Gd(NO_3)_3{\cdot}6H_2O$. Yield (20%), FTIR of **Er-1:** 949 (s), 861 (s), 787 (s), 710 (s), 634 (sh), 477 (m) cm^{-1}. Elemental analysis (%); calcd. (found) : Na 2.7 (3.8), Cs 4.3 (5.0), As 2.4 (2.0), W 62.7 (59.5), Er 5.4 (5.4).

Elemental analyses of **Eu-1**, **Gd-1** and **Tb-1** were performed by Mikroanalytisches Labor Pascher, Remagen Germany and for **Dy-1**, **Ho-1** and **Er-1** by Zentrale Chemische Analytik (ZCH), Forschungszentrum Jülich, Jülich, Germany.

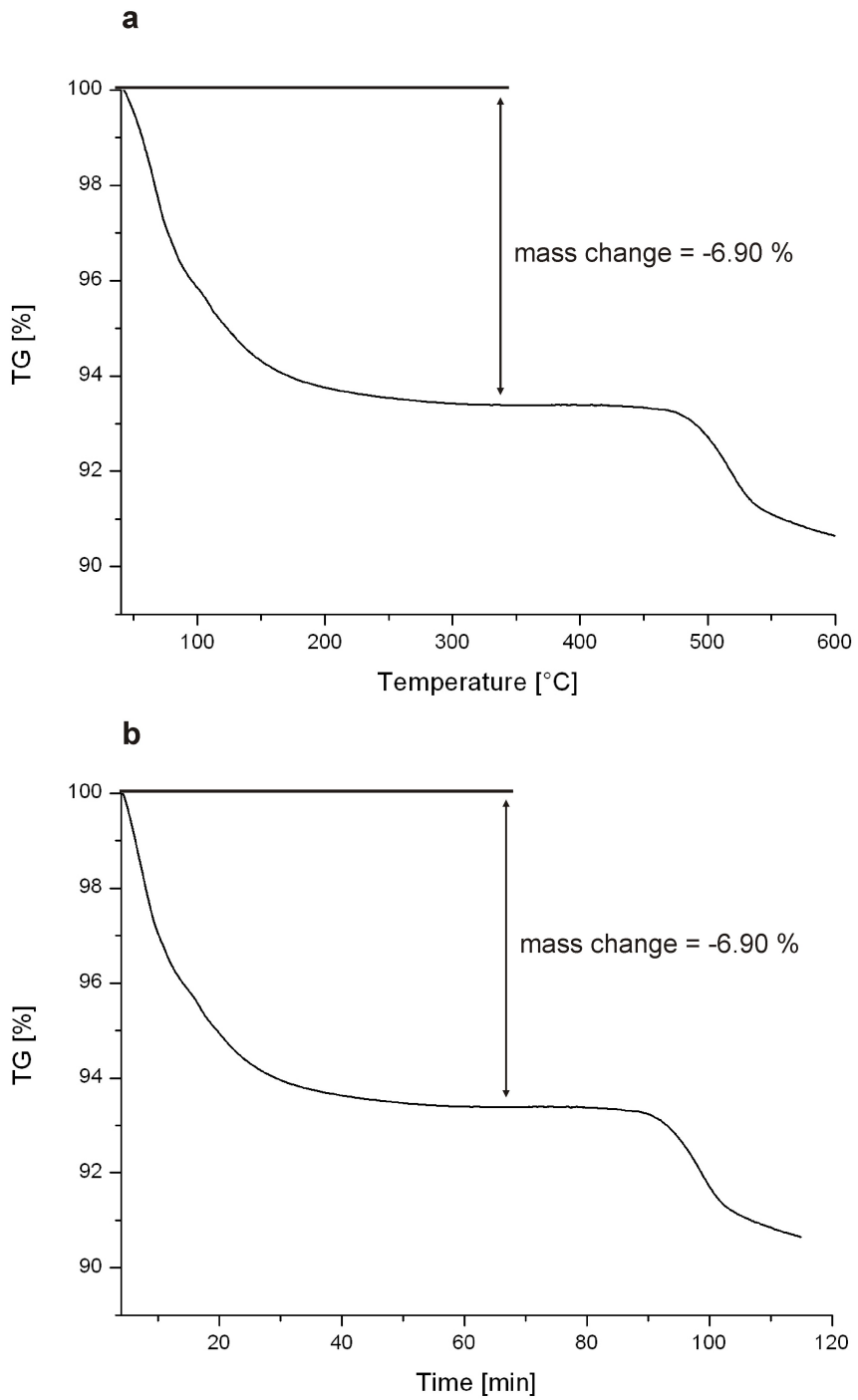

Figure S2. Representative thermogravimetric analysis of **Ho-1** displaying the mass loss corresponding to crystal water molecules (**Eu-1** = 7.22 %; **Gd-1** = 10.63 %; **Tb-1** = 5.78 %; **Dy-1** = 6.98 %; **Er-1** = 6.26 %).

TG measurements were performed on a Netzsch STA 449 C apparatus between 25 and 600 °C with a heating rate of 5 K/min in nitrogen atmosphere.

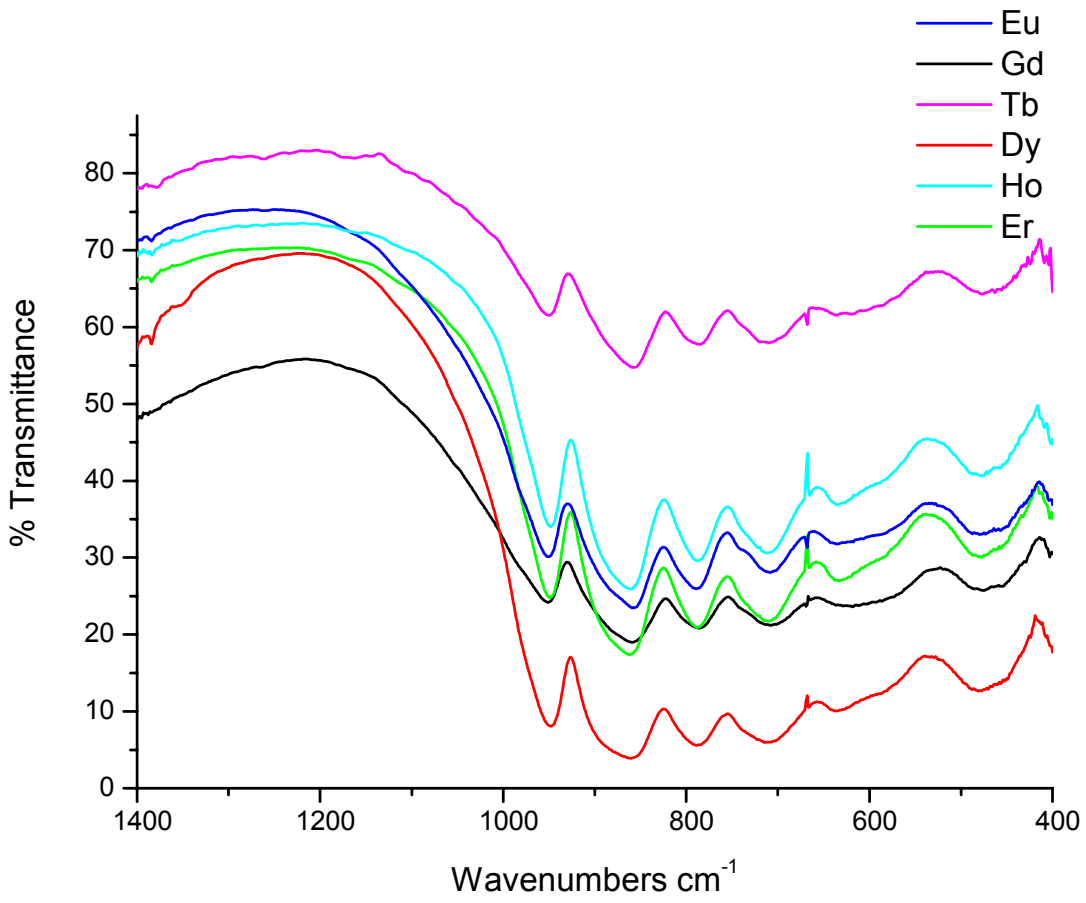

Figure S3. FT-IR spectra of compounds **Eu-1 – Er-1** (recorded in KBr, only the polyoxometalate "fingerprint region" is displayed).

Magnetic Measurements

Magnetic susceptibility measurements were performed in a temperature range of 2 – 290 K for (**Gd-1**) at 0.1 – 5.0 T and for (**Er-1**) at 0.1 Tesla using a Quantum Design MPMS-5XL SQUID magnetometer. The experimental susceptibility values were corrected for the sample holder (Teflon tubes, the diamagnetic and temperature-independent paramagnetic (TIP) contributions of Gd^{3+} / Er^{3+} and the polyoxotungstate ligands ($\chi_{dia/TIP}$(**Gd-1**) = –35.0 × 10^{-9} m^3 mol^{-1}; ($\chi_{dia/TIP}$(**Er-1**) = –32.0 × 10^{-9} m^3 mol^{-1}).[1, 2]

Theoretical modeling: We consider a magnetically isolated f^N metal ion surrounded by ligands imposing a distinct point symmetry upon the magnetic center. In a static magnetic field **B** the Hamiltonian of the metal ion is then represented by

$$\begin{aligned}\hat{H} \;=\; & \underbrace{\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V(r_i)\right]}_{\hat{H}^{(0)}} + \underbrace{\sum_{i>j}^{N}\frac{e^2}{r_{ij}}}_{\hat{H}_{\mathrm{ee}}} + \underbrace{\sum_{i=1}^{N}\zeta(r_i)\,\kappa\;\hat{\boldsymbol{l}}_i\cdot\;\hat{\boldsymbol{s}}_i}_{\hat{H}_{\mathrm{so}}} + \\ & \underbrace{\sum_{i=1}^{N}\sum_{k=0}^{\infty}\left\{B_0^k C_0^k(i) + \sum_{q=2}^{k}\left[B_q^k\left(C_{-q}^k(i) + (-1)^q C_q^k(i)\right)\right]\right\}}_{\hat{H}_{\mathrm{LF}}} + \\ & \underbrace{\sum_{i=1}^{N}\mu_B(\kappa\;\hat{\boldsymbol{l}}_i + 2\;\hat{\boldsymbol{s}}_i)\cdot\;\boldsymbol{B}}_{\hat{H}_{\mathrm{mag}}}\end{aligned} \qquad (1)$$

While $H^{(0)}$ represents the energy in the central field approximation, H_{ee} and H_{so} account for interelectronic repulsion and spin-orbit coupling (modified by the orbital reduction factor κ), respectively. The former is taken into account by the Slater-Condon parameters F^2, F^4, F^6, the latter by the one-electron spin-orbit coupling parameter ζ. These sets of interelectronic repulsion parameters as well as ζ and κ are used as constants in the fitting calculations.

H_{lf} gives the electrostatic effect of the ligands in the framework of ligand field theory on the basis of the global parameters B_q^k. The spherical tensors C_q^k are directly related to the spherical harmonics $C_q^k = \sqrt{4\pi/(2k+1)}\,Y_q^k$ and the real ligand field parameters B_q^k (Wybourne notation[3, 4]) are given by $A_q^k\langle r^k\rangle$ where A_q^k is a numerical constant describing the charge distribution in the environment of the metal ion and $\langle r^k\rangle$ is the expectation value of $\langle r^k\rangle$ for the wave function.

For f electrons the terms in the expansion with k ≤ 6 are nonzero, whereas all terms with odd *k* values vanish since we consider only configurations containing equivalent electrons. The values of *k* and *q* are limited by the point symmetry of the metal ion site.

If the spherically symmetric term $B_0^0 C_0^0$ (which does not cause any splitting) is ignored, in cubic systems only spherical tensors with $k = 4$ and $k = 6$ are relevant and all B_q^k are zero. The ligand field operator with reference to the fourfold rotation axis for the angular part of the wave function reads.

$$H_{LF}^{tet} = B_0^2 \sum_{i=1}^{N} C_0^2(i) + B_0^4 \sum_{i=1}^{N} \left[C_0^4(i) + \sqrt{5/14}\left(C_4^4(i) + C_{-4}^4(i)\right)\right] + B_0^6 \sum_{i=1}^{N} \left[C_0^6(i) - \sqrt{7/2}\left(C_4^6(i) + C_{-4}^6(i)\right)\right]$$

For magnetochemical analyses, we developed the computer program CONDON.[5] For modeling the magnetic behaviour of the 4f-system (**Gd-1**) interelectronic repulsion (H_{ee}) and spin-orbit-coupling (H_{so}) and (**Er-1**) interelectronic repulsion (H_{ee}), spin-orbit-coupling (H_{so}) and lf effect (H_{LF}), has to be taken into account.

In order to determine the magnetic behaviour of (**Gd-1**) we use only the Slater Condon Parameter (^2F = 91 800 cm^{-1}, ^4F = 64 425 cm^{-1}, ^6F = 49 258 cm^{-1}), the spin orbit-coupling constant (ζ = 1 470 cm^{-1}) and the applied magnetic field ($\boldsymbol{B_0}$ = 0.1, 0.5, 1, 2, 3, 4 , 5 T).[6, 7] The magnetochemical analyses show a g-value of 1.993 with the corresponding magnetic moment of 7.91. The reduce g-value is a result of the large spin-orbit interaction that mixes significant amounts of other terms into with J = 7/2 into the ground state. The major SL components of the ground state are ^{8}S (97 %) and ^{6}P (2.7 %) with the corresponding g_J factor 1.993.[8]

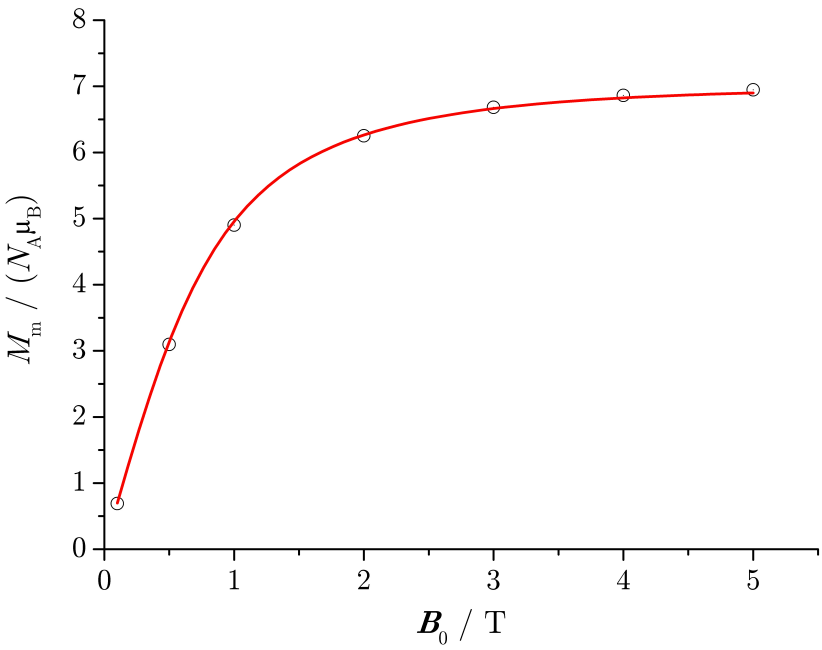

Figure S4. Magnetization as a function of external field at 2.0 K, showing a Brillouin-type behavior (experimental data: open circles, best fit: red graph). Parameters employed: S = 7/2, g_J = 1.993 and SQ = 0.18 %.

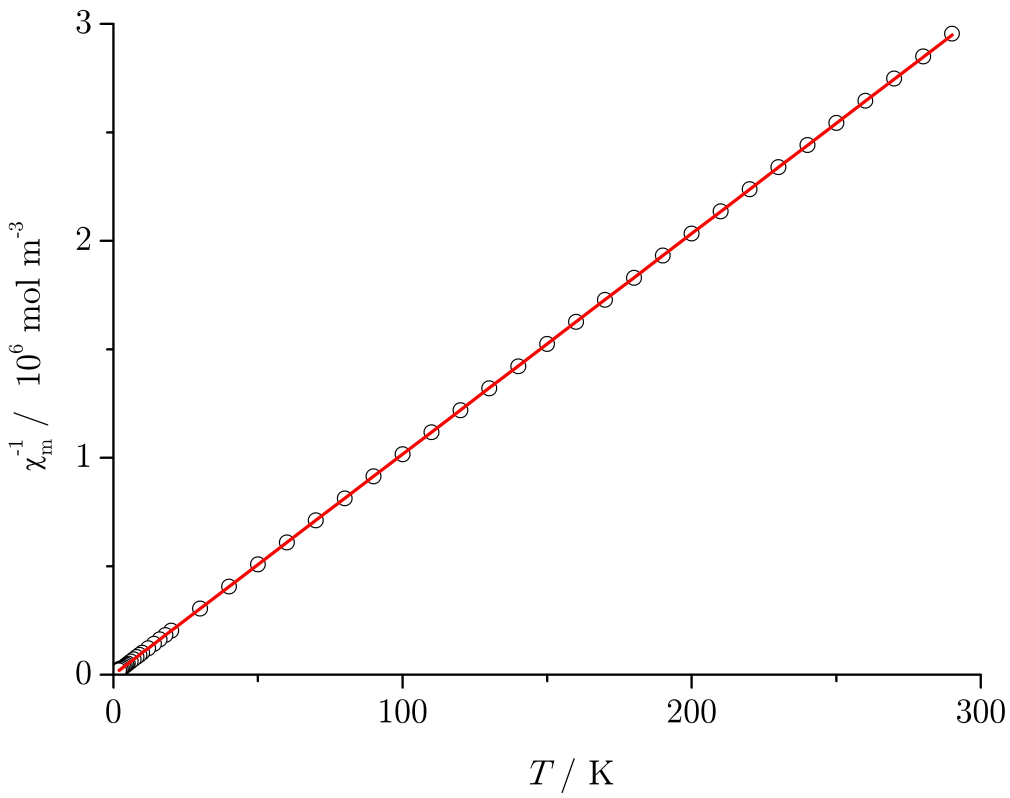

Figure S5. Temperature dependence of the reciprocal susceptibility (χ_m^{-1}) of (**Gd-1**) at 0.1 Tesla emphasizing the near perfect Curie paramagnetism (experimental data: open circles, best fit: red graph); see text for parameters.

In the case of Er (III), the consideration of the ligand field effect (H_{lf}) is especially important. To reduce the number of lf parameters, the local point symmetry C_s; (15 independent lf parameters) was idealised to D_{4h} (3 independent lf parameters). The intial set of B_q^k parameter values was taken from spectroscopically determined energy levels for Er(III) in cubic elpasolite crystals.[10]

In order to determine the corresponding ligand field parameters B_q^k the assumption of D_{4h} symmetry was sufficient to yield an excellent fit (Figure 3; SQ 0.4%) B_0^2 = 240 cm^{-1}, B_0^4 = 1550 cm^{-1}, B_0^6 = 230 cm^{-1} and a spin-orbit coupling parameter ζ = 2369 cm^{-1}.

The following fitting procedure was employed:

(1) Starting parameters for a cubic Er (III) system (B_0^4 and B_0^6); the corresponding compound is listed in ref. 10.

(2) The ratios between the parameters B_0^4 and B_4^4 as well as B_0^4 and B_4^4 were set as constant, reflecting cubic ligand field symmetry ($B_4^4 = \sqrt{5/14}\, B_0^4$ and $B_4^6 = \sqrt{7/2}\, B_0^6$).[10] Note that the quality of the fit does not increase significantly upon removing these constraints.

(3) To accommodate the assumed near-tetragonal symmetry of the Er (III) ligand field, a third free parameter B_0^2 was introduced.

(4) The (fixed) spin-orbit coupling parameter was chosen as $\zeta = 2369\ \mathrm{cm}^{-1}$ according to ref. 10.

References

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