

Supplementary Information

Polyoxometalates-based high spin cluster systems: A NMR relaxivity study up to 1.4 GHz/33 T

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Experimental

Materials and methods

The precursor salt $\text{Na}_{10}[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ was prepared according to the published procedure and characterized by IR spectroscopy.¹ All metal salts were purchased from Aldrich Chemicals. Elemental analyses were performed at the Institute for Applied Materials (IAM-AWP), Karlsruhe Institute of Technology. Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr discs. Elemental compositions were determined by an Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES) at the Institute for Applied Materials (IAM-AWP), Karlsruhe Institute of Technology. All reactions were carried out under aerobic conditions.

Synthesis of $\text{Cs}_{14}\text{Co}_6\text{Na}_{30}[\text{Dy}_{30}\text{Co}_8\text{Ge}_{12}\text{W}_{108}\text{O}_{408}(\text{OH})_{42}(\text{OH}_2)_{30}]\cdot \text{ca.}370\text{ H}_2\text{O}$ ($\text{Dy}_{30}\text{Co}_8$)²

$\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.106 g, 0.445 mmol) was dissolved in 20 mL H_2O . Then solid $\text{Na}_{10}[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ (0.60 g, 0.21 mmol) was added and stirred until a clear pink solution was obtained. Then 0.30 mL of 1M $\text{Dy}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (0.131 g, 0.299 mmol) was added to this solution in small portions. The resultant mixture was stirred for about 5 minutes, subsequently solid LiOH (0.008g, 0.334 mmol) was added. This mixture was heated and stirred at 80 °C for 1 hour, and then the precipitate was allowed to settle down, followed by filtration and addition of 0.05 mL of 1 M CsCl solution. Slow evaporation at room temperature led to the appearance of pink crystalline **CsNa-1** after about three weeks, which was filtered off and air-dried. Yield 70 mg (10 % based on W). IR (2% KBr pellet, ν/cm^{-1}): 938 (m), 800 (s), 669(s), 539 (m), 482 (m), 423 (w)

407(w). Elemental analysis (%) calc (found): Cs 4.28 (4.13), Na 1.58 (1.46), Co 1.90 (1.86), W 45.72 (45.80), Ge 2.01 (1.94), Dy 11.22 (11.50).

Synthesis of Cs₁₄Co₆Na₃₀[Gd₃₀Co₈Ge₁₂W₁₀₈O₄₀₈(OH)₄₂(OH₂)₃₀].ca.358H₂O (Gd₃₀Co₈)

CoCl₂·6H₂O (0.106 g, 0.445 mmol) was dissolved in 20 mL H₂O. Solid Na₁₀[A-α-GeW₉O₃₄].18H₂O (0.60 g, 0.21 mmol) was added and stirred until a clear pink solution was obtained. Then 0.30 mL of 1M Gd(NO₃)₃·5H₂O (0.130 g, 0.30 mmol) was added to this solution in small portions. The reaction mixture was stirred for about 10 minutes and then solid LiOH (0.006g, 0.25 mmol) was added which raised the pH from ca. 6.4 to ca. 7.5.

The resultant turbid solution was heated at 85 °C for one hour and filtered on cooling. Then 0.05 mL of 1 M CsCl was added to the pink filtrate. After three weeks, the crystalline pink product was isolated from the mother liquor by filtration and dried in air. Yield 0.11 g. IR (2% KBr pellet, ν/cm⁻¹): 944 (m), 798 (s), 673 (s), 533 (w), 481 (w), 410 (w). Elemental analysis (%) calc (found): Cs 0.63 (0.60), Na 2.25 (2.55), Co 1.69 (1.98), W 47.43 (47.50), Ge 2.08 (2.11), Gd 11.00 (11.27).

Synthesis of Cs₁₀Co₆Na₃₄[Y₃₀Co₈Ge₁₂W₁₀₈O₄₀₈(OH)₄₂(OH₂)₃₀].ca.350H₂O (Y₃₀Co₈)

A sample of Na₁₀[A-α-GeW₉O₃₄].18H₂O (0.60 g, 0.21 mmol) was added with stirring to a solution of CoCl₂·6H₂O (0.106 g, 0.445 mmol) in 20 mL H₂O. Then 0.30 mL of 1M YCl₃·6H₂O (0.09 g, 0.30 mmol) were added to the clear pink solution, which was stirred for 10 minutes at room temperature. The pH was adjusted to 7.7 by using 0.01 g of LiOH. The reaction mixture was stirred and heated to 85°C for one hour. The precipitate formed was filtered off and 0.05 mL of 1 M CsCl

solution was added to the filtrate. Slow evaporation of the solvent at room temperature for about two weeks led to the formation of materials. Yield: 0.08 g. IR (2% KBr pellet, ν/cm^{-1}): 940 (m), 804 (s), 677 (s), 539 (w), 489 (m), 422 (m). Elemental analysis (%) calc (found): Cs 3.28 (3.44), Na 1.59 (1.77), Co 2.03 (2.27), W 48.95 (49.00), Ge 2.15 (2.23), Y 6.58 (6.62), C 0.17 (0.17).

Synthesis of $\text{Co}_6\text{Na}_{44}[\text{Eu}_{30}\text{Co}_8\text{Ge}_{12}\text{W}_{108}\text{O}_{408}(\text{OH})_{42}(\text{OH}_2)_{30}]\cdot\text{ca.}400\text{H}_2\text{O}$ ($\text{Eu}_{30}\text{Co}_8$)

A sample of $\text{Na}_{10}[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]\cdot 18\text{H}_2\text{O}$ (0.60 g, 0.21 mmol) was added to a solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.106 g, 0.445 mmol) in 20 mL H_2O while stirring. Then 0.30 mL of 1M $\text{EuCl}_3\cdot 6\text{H}_2\text{O}$ (0.11 g, 0.30 mmol) were added to the clear pink solution, which was stirred for 10 minutes at room temperature. The pH was adjusted to 7.7 by using 0.01 g of LiOH. The reaction mixture was stirred and heated to 85°C for one hour. The precipitate formed was filtered off and slow evaporation of the solvent at room temperature for about two week led to the formation of powder. Yield: 0.08 g. IR (2% KBr pellet, ν/cm^{-1}): 949 (m), 823 (s), 699 (s), 560 (w), 498 (m), 425 (m). Elemental analysis (%) calc (found): Na 2.11 (2.20), Co 2.03 (2.24), W 47.86 (47.3), Ge 2.10 (2.23), Eu 10.98 (10.9).

Characterization

The same synthetic approach as reported for $\text{Dy}_{30}\text{Co}_8$ was used for preparing the structural analogues labeled as $\text{Gd}_{30}\text{Co}_8$, $\text{Eu}_{30}\text{Co}_8$ and Y_{30}Co_8 . The obtained compounds were not determined by single crystal X-ray crystallography as no suitable single crystals were obtained. The

synthesized compounds were identified using elemental and thermogravimetric analysis, and FTIR spectroscopy.

Infrared spectroscopy is a frequently employed techniques for the characterization of polyoxometalates due to its characteristic peaks in the in the region ($1200 - 450 \text{ cm}^{-1}$) which is called the fingerprint region for the POM skeleton. The similarity in the FTIR Spectra of **Dy₃₀Co₈**, **Gd₃₀Co₈**, **Eu₃₀Co₈**, and **Y₃₀Co₈** exhibit the isostructural nature of the compounds (Figures S1). Thermogravimetric analyses were carried out to examine the total number of water molecules in the bulk material of **Dy₃₀Co₈**, **Gd₃₀Co₈**, **Eu₃₀Co₈**, and **Y₃₀Co₈** (Figure S2). The overall elemental composition of the bulk material were also determined by complete elemental analysis. The compounds were formulated based on elemental analysis and thermogravimetric analysis.

UV–Vis absorption spectra

UV-Vis spectroscopy was used to investigate the stability of POMs in solution. The comparison of the UV–Vis absorption spectra of **Dy₃₀Co₈**, **Gd₃₀Co₈**, **Eu₃₀Co₈**, and **Y₃₀Co₈** with ligand {GeW₉O₃₄} indicate that all the compounds were stable in solution (Fig. S3 and S4). Further, no change in the absorption profiles of the complexes were observed even after 17 hours. The absorption spectra of all the compounds present one prominent band centered around ca. 260 nm, which is the characteristic band of polyoxometalates, attributed to a ligand-to-metal charge-transfer (LMCT) transition ($O \rightarrow W$).

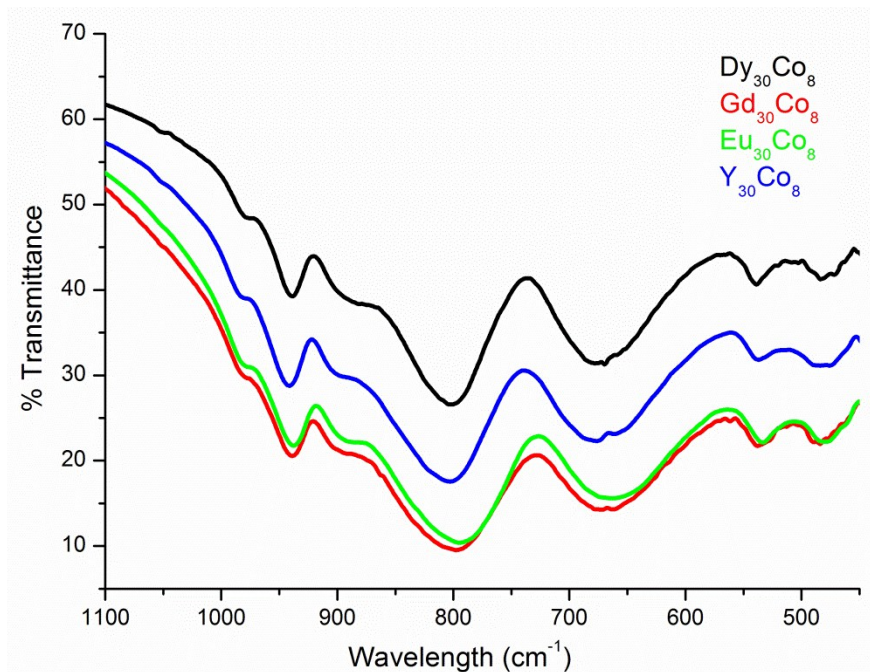


Figure S1. FTIR spectra of $\text{Dy}_{30}\text{Co}_8$, $\text{Gd}_{30}\text{Co}_8$, $\text{Eu}_{30}\text{Co}_8$, and Y_{30}Co_8 .

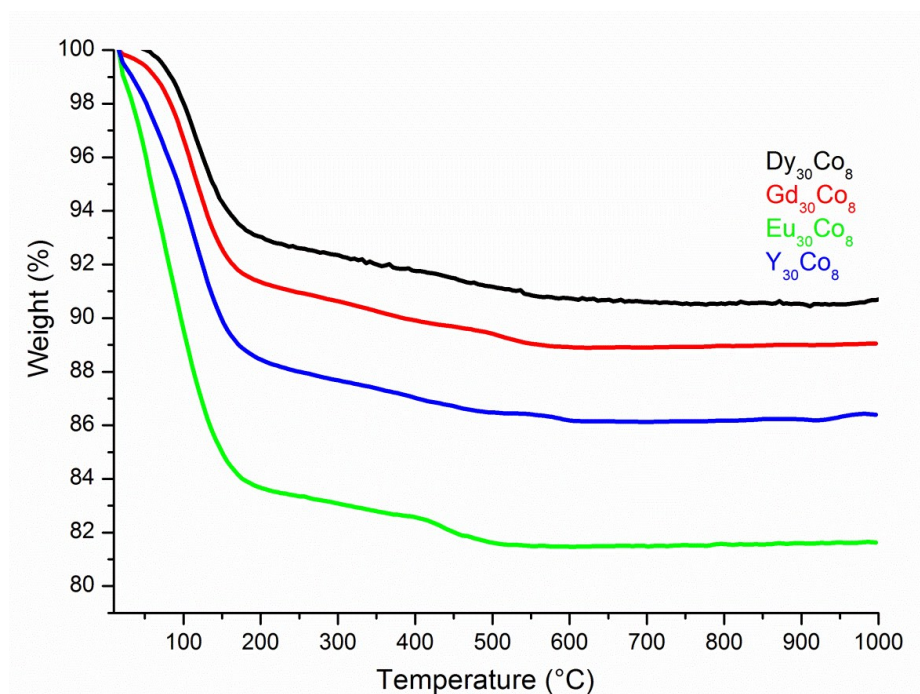


Figure S2. Thermograms of $\text{Dy}_{30}\text{Co}_8$, $\text{Gd}_{30}\text{Co}_8$, $\text{Eu}_{30}\text{Co}_8$, and Y_{30}Co_8 from 25 to 1000 °C under N_2 atmosphere.

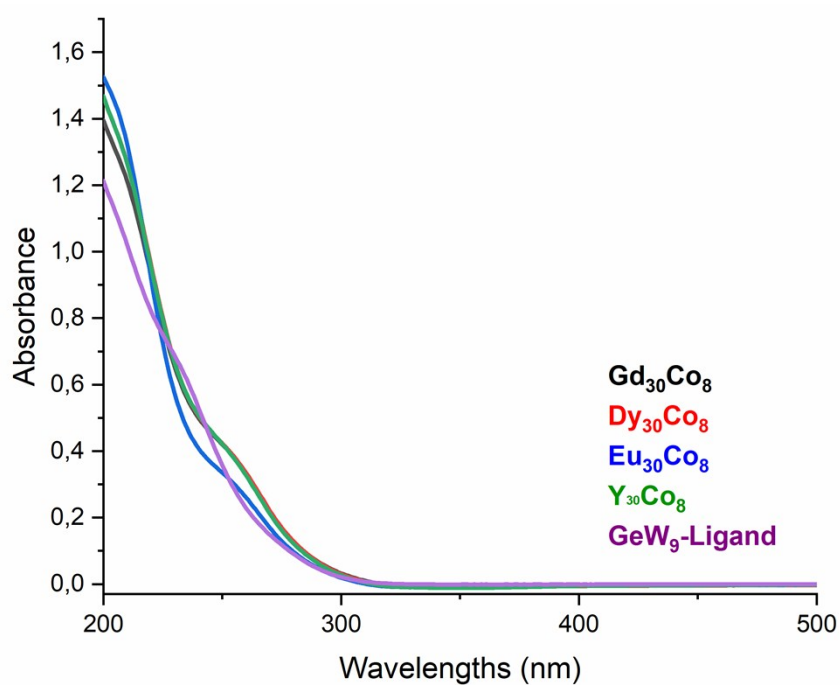


Figure S3. Overlay UV-Vis absorption spectra of RE₃₀Co₈ upon dissolution in water

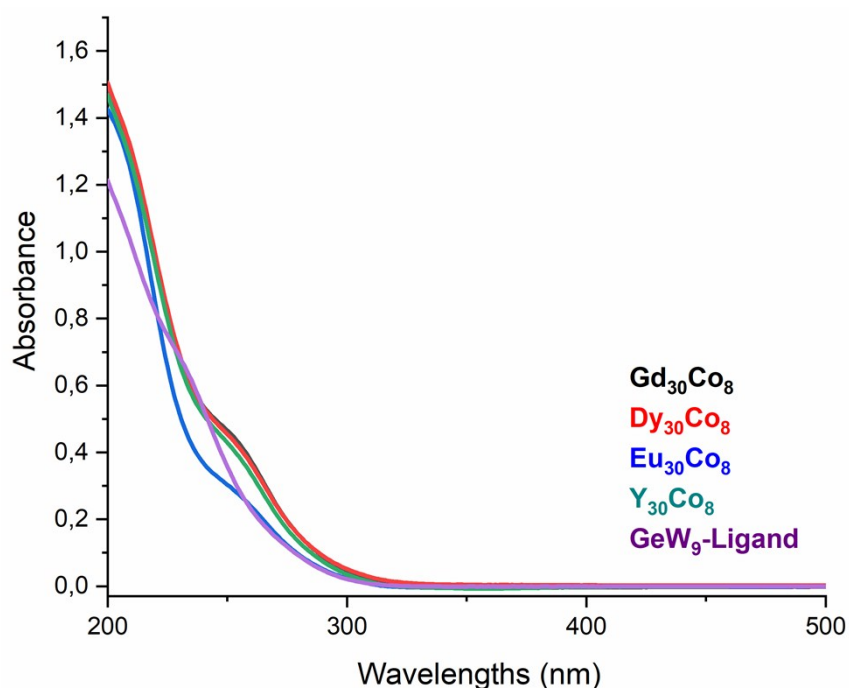


Figure S4. Overlay UV-Vis absorption spectra of RE₃₀Co₈ after 17 hours.

References:

- [1] G. Hervé, A. Tézé, *Inorg. Chem.* **1977**, **16**, 2115–2117.
- [2] M. Ibrahim, V. Mereacre, N. Leblanc, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Angew. Chem. Int. Ed.*, 2015, **54**, 15574-15578.