Supporting Information

Molecular Amino-Phosphonate Cobalt-Lanthanide Clusters

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Experimental Details

Synthesis of starting materials

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification. \([\text{Co}_2(\mu-\text{OH})_2(O_2\text{C}^{\text{Bu}})_3\text{HO}_2\text{C}^{\text{Bu}})_4]^{6+}\) was prepared according to established methods. \([\text{Ln}_2(O_2\text{C}^{\text{Bu}})_6\text{HO}_2\text{C}^{\text{Bu}})_6]^{7+}\) (Ln = Gd, 7; Tb, 8, Dy, 9) were synthesized by refluxing \(\text{Ln}_2\text{O}_3\) (3.62 g, 10 mmol) and excess pivalic acid (30 g, 300 mmol) at 160 ºC for 5 hrs to form a clear solution. Followed by cooling the solution to room temperature and white precipitate came out. 50 ml toluene was added to dissolve the access pivalic acid and filtered in vacuum and 50 ml n-hexane were used to wash the product (yield ca. 13 g, 87 %).

Synthesis of (1-amino-1-cyclohexyl)phosphonic acid

1-amino-1-cyclohexylphosphonic acid: diethyl 1-amino-1-cyclohexylphosphonate (3 g, 13 mmol) and HCl 6M (45 mL) were heated in an ampule for 3 hours at 120 ºC. then the solution was evaporated until the odour of HCl
disappeared. The product was then dissolved in H$_2$O and precipitated with MeCN to give 1-aminocyclohexylphosphonic acid (2.0 g, 88%). The product contains one molecule of water of crystallization. Elemental analysis, calcd (%) for C$_{14}$H$_{14}$NPO$_3$ • H$_2$O: C 36.55, H 8.18, N 7.10, P 15.71; Found: C 36.53, H 7.92, N 7.05, P 15.57.

Synthesis of compound 1 to 2

1 was obtained by mixing 6 (0.036 g, 0.04 mmol), 7 (0.165 g, 0.1 mmol), Et$_3$N (0.1 ml, 1 mmol) and H$_2$O$_3$PC$_6$H$_{10}$NH$_2$ (0.036 g, 0.2 mmol) in MeCN (8 ml) were stirred at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 °C for 12 hrs. and then cooled to room temperature at a rate of 0.05 °C min$^{-1}$. Pink block-shape crystals were collected (yield 10 mg, 10 %, based on 7). EA for Co$_3$Gd$_{10}$PO$_3$C$_{12}$H$_{23}$, found (calc); C 28.96 (29.18), H 4.67 (4.66), Co 4.34 (4.62), Gd 29.65 (30.81), N 2.65 (2.74) and P 7.21 (7.28). 2 was obtained by mixing 6 (0.036 g, 0.04 mmol), 9 (0.165 g, 0.1 mmol), Et$_3$N (0.1 ml, 1 mmol) and H$_2$O$_3$PC$_6$H$_{10}$NH$_2$ (0.036 g, 0.2 mmol) in MeCN (8 ml) were stirred at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 °C for 12 hrs. and then cooled to room temperature at a rate of 0.05 °C min$^{-1}$. Pink block-shape crystals were collected (yield 10 mg, 10 %, based on 9). EA for Co$_3$Dy$_{10}$PO$_3$C$_{12}$H$_{23}$, found (calc); C 28.47 (28.89), H 4.53 (4.61), Co 4.48 (4.57), Dy 31.23 (31.52), N 2.65 (2.72) and P 7.18 (7.21).

Synthesis of compound 3 to 5

3 to 5 were synthesized from similar reaction, replacing the lanthanide source. 6 (0.095 g, 0.1 mmol), 7, 8 or 9 (0.075 mmol), Et$_3$N (0.1 ml, 0.7 mmol), Na$_3$PO$_3$ (0.05g, 0.3 mmol) and H$_2$O$_3$PC$_6$H$_{10}$NH$_2$ (0.018 g, 0.1 mmol) in MeCN (8 ml) were stirred at room temperature for a few minutes. The resulting slurry was transferred into a 10 mL Teflon-lined autoclave, which was heated at 150 °C for 12 hrs. and then cooled to room temperature at a rate of 0.05 °C min$^{-1}$. Block-shape purple crystals were collected. EA for 3 (yield 20 mg, 18.50 % based on 7) Co$_6$Gd$_{10}$Na$_2$O$_{46}$Na$_{16}$P$_8$C$_{96}$H$_{18}$, found (calc for 3 with loss of 2 MeCN and gain of 2 H$_2$O); C 32.52 (34.16), H 5.12 (5.55), Co 10.44 (10.48), Gd 17.90 (18.64), P 5.63 (5.51), N 3.12 (2.49) and Na 1.37 (1.36). EA for 4 (yield 18 mg, 16.6 % based on 8) Co$_6$Tb$_{10}$Na$_2$O$_{46}$Na$_{16}$P$_8$C$_{96}$H$_{18}$, found (calc for 4 with loss of 2 MeCN and gain of 2 H$_2$O); C 32.72 (34.09), H 5.35 (5.54), Co 10.85 (10.46), Tb 18.31 (18.79), P 5.21 (5.49), N 3.20 (2.5) and Na 1.23 (1.35). EA for 5 (yield 16 mg, 14.6% based on 9) Co$_6$Dy$_{10}$O$_{44}$Na$_{2}$P$_8$C$_{100}$H$_{18}$, found (calc); C 35.23 (34.89), H 5.28 (5.50), Co 10.98 (10.27), Dy 18.46 (18.88), P 5.71 (5.39), N 2.98 (3.25) and Na 1.41 (1.33).

Crystallography

The data of 1 to 5 were collected on a Bruker SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The data of 5 were collected on a oxford SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F2 using SHELXTL. CCDC 922115-922117 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the
Crystal data for 1 \(\left[ \text{C}_{124}\text{H}_{214}\text{Co}_{4}\text{Gd}_{10}\text{N}_{10}\text{O}_{66}\text{P}_{12} \cdot 3(\text{C}_{2}\text{H}_{3}\text{N}) \right] \): \(M_r = 5226.25\), triclinic, space group \(P\bar{1}\), \(T = 100.15 \text{ K}\), \(a = 18.2190 (2)\), \(b = 22.4563 (3)\), \(c = 27.5752 (4)\) Å, \(\alpha = 70.1022 (12)\), \(\beta = 84.55267 (11)\), \(\gamma = 79.3776 (12)\)º, \(V = 10420.1 (2)\) Å³, \(Z = 2\), \(\rho = 1.666 \text{ g cm}^{-3}\), total data \(84001\), independent reflections \(42000\) \((R_{\text{int}} = 0.083)\), \(\mu = 3.61 \text{ mm}^{-1}\), 1975 parameters, \(R_I = 0.095\) for \(I \geq 2\sigma(I)\) and \(wR_2 = 0.218\). CCDC 922116

Crystal data for 2 \(\left[ \text{C}_{124}\text{H}_{228}\text{Co}_{4}\text{Dy}_{10}\text{N}_{10}\text{O}_{66}\text{P}_{12} \cdot \text{C}_{4}\text{N}_{2}\text{H}_{6} \right] \): \(M_r = 5229.68\), triclinic, space group \(P\bar{1}\), \(T = 100.15 \text{ K}\), \(a = 17.0917 (3)\), \(b = 20.9589 (3)\), \(c = 30.4298 (4)\) Å, \(\alpha = 108.0775 (13)\), \(\beta = 101.8103 (13)\), \(\gamma = 92.1947 (12)\)º, \(V = 10082.3 (3)\) Å³, \(Z = 2\), \(\rho = 1.725 \text{ g cm}^{-3}\), total data \(79235\), independent reflections \(40171\) \((R_{\text{int}} = 0.062)\), \(\mu = 4.14 \text{ mm}^{-1}\), 1877 parameters, \(R_I = 0.087\) for \(I \geq 2\sigma(I)\) and \(wR_2 = 0.194\). CCDC 922115

Crystal data for 3 \(\left[ \text{C}_{100}\text{H}_{186}\text{Co}_{6}\text{Gd}_{4}\text{N}_{8}\text{Na}_{2}\text{O}_{44}\text{P}_{6} \cdot 2(\text{C}_{2}\text{H}_{3}\text{N}) \right] \): \(M_r = 3501.06\), triclinic, space group \(P2_1/n\), \(T = 100.15 \text{ K}\), \(a = 15.8683 (5)\), \(b = 27.0973 (8)\), \(c = 19.4683 (6)\) Å, \(\beta = 112.274 (13)\)º, \(V = 7746.5 (4)\) Å³, \(Z = 2\), \(\rho = 1.501 \text{ g cm}^{-3}\), total data \(42633\), independent reflections \(15760\) \((R_{\text{int}} = 0.060)\), \(\mu = 2.45 \text{ mm}^{-1}\), 771 parameters, \(R_I = 0.055\) for \(I \geq 2\sigma(I)\) and \(wR_2 = 0.139\). CCDC 922117

Crystal data for 4 (unite cell) \(\left[ \text{Co}_{6}\text{Tb}_{4}\text{P}_{8}\text{N}_{8}\text{O}_{44}\text{C}_{100}\text{H}_{188} \right] \): monoclinic, space group \(P2_1/n\), \(T = 100.15 \text{ K}\), \(a = 15.8615(4)\), \(b = 27.2388(6)\), \(c = 19.440(5)\) Å, \(\gamma = 111.837(3)\)º, \(V = 7797.9(3)\) Å³.

Crystal data for 5 (unite cell) \(\left[ \text{Co}_{6}\text{Dy}_{4}\text{P}_{8}\text{N}_{10}\text{O}_{44}\text{C}_{104}\text{H}_{192} \right] \): monoclinic, space group \(P2_1/n\), \(T = 100.15 \text{ K}\), \(a = 15.810(3)\), \(b = 27.065(6)\), \(c = 19.386(4)\) Å, \(\beta = 111.888(5)\), \(V = 7697.12 \text{ Å}^3\).

Figure S1. Polyhedral representation of Co₄Dy₁₀P₁₂. Scheme: Dy, purple; Co, blue; P, green; O, orange; C, grey; N, cyan.
Figure S2. a) Full structure and polyhedral representation of Co$_6$Gd$_4$P$_6$ cluster; b) Polyhedral representation of Co$_6$Gd$_4$P$_6$. Scheme: Gd, purple; Co, blue; P, green; O, orange; C, grey; N, cyan; (H omitted for clarity).
Magnetic measurements

The magnetic properties of polycrystalline samples of 1-5 were performed with a Quantum Design MPMS-XL7 SQUID. The samples were ground, placed in a gel capsule and fixed with a small amount of eicosanoid acid to avoid movement during the measurement. The data were corrected for diamagnetism from the gel capsule, diamagnetic contribution from the eicosanoid acid and diamagnetic contribution calculated from Pascal constants.

Figure S3. a) Molar magnetic susceptibility ($\chi T$) vs. $T$ plot for 1-5 under 1 kG DC field.
Figure S4. a) M/N_{ββ} magnetization of 1 at different temperatures; b) Magnetic Entropy change of 1.
Figure S5. a) M/N_{μB} magnetization of 3 at different temperatures; b) Magnetic Entropy change of 3.