Supporting Information

Nanospheric $[M_{20}(\text{OH})_{12}(\text{maleate})_{12}(\text{Me}_2\text{NH})_{12}]^{4+}$ clusters (M = Co, Ni) with O_h symmetry

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Synthesis

[Co₂₀(OH)₁₂(maleat)₁₂(Me₂NH)₁₂](BF₄)₃(OH)(H₂O)₁₄ (1): the mixture of Co(BF₄)₂·6H₂O (0.0681g, 0.2mmol) and fumaric acid (0.2mmol, 0.0232g) in a 1:5 (v:v) DMF / EtOH (total of 12 ml) was changed into a 25 ml Teflon-lined autoclave and kept at 160°C for 72 hours, and then slowly cooled to room temperature, cubically purple single crystals were received. Yield: 0.023g, 60% based on Co²⁺. Anal. Calcd for C₇₂H₁₄₉N₁₂O₇₅B₂F₁₂Co₂₀: C, 22.61; H, 3.90; N, 4.40; Found: C: 22.25; H: 3.742; N: 4.261. IR, 1064, 1084 cm⁻¹ (BF₄⁻).

[Ni₂₀(OH)₁₂(maleat)₁₂(Me₂NH)₁₂](BF₄)₃(OH)(H₂O)₁₀ (2): the synthesis method for **2** is similar to that for **1** except for Ni(BF₄)₂·6H₂O instead of Co(BF₄)₂·6H₂O. Cubically blue single crystals were received. Yield: 0.0076g, 20% based on Ni²⁺. Anal. Calcd for C₇₂H₁₄₅N₁₂O₇₃B₃F₁₂Ni₂₀: C, 22.85; H, 3.83; N, 4.44; Found: C, 23.08; H, 3.97; N: 4.48. IR, 1060, 1088 cm⁻¹ (BF₄⁻).

X-ray crystal structure analysis

Diffraction data for **1** and **2** were recorded on a Xcalibur, Sapphire3, Gemini ultra diffractometer. Data for **1** was collected with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at

room temperature, and data for **2** was collected with Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 150 K. The crystal structures were solved by means of direct methods and refined employing full-matrix least squares on F^2 (SHELXTL-97). All non-hydrogen atoms were refined anisotropically and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Hydrogen atoms are not fixed on the lattice water molecules. Due to badly thermally diffuse scattering and the high symmetric disorder, one anion OH $^-$ can't be determined directly by the X-ray crystallographic analysis, even if at the low temperature for complex **2**. We think the disordered anion is less possible to be regarded as one BF $_4^-$, since the anion located between cluster cations should have large residual peaks for BF $_4^-$ though the compounds are of high symmetry.

Fig. S1 the local coordination environment of metal ions (left) and the coordination mode of maleate (right) in **1**.

Fig. S2 the icosahedral shell consisting of 12 O atoms bound to Co atoms; cyan, Co.

Fig. S3 Field dependence of the magnetization (M) of **1** at 2 K.

Fig. S4 Field dependence of the magnetization (M) of **2** at 2 K

Fig. S5 FC and ZFC magnetization of **2** in the dc field of 10 Oe

Fig. S6 Plot of the in-phase (χ'_M) and out-of-phase (χ''_M) ac susceptibility signals for complex 2.

Fig. S7 Field dependence of the magnetization of 2.

Fig. S8 PXRD patterns of **1**: simulated (green), as-synthesized (red).

Fig. S9 PXRD patterns of **2**: simulated (green), as-synthesized (red).

Fig. S10 IR spectrum of **1**

Fig. S11 IR spectrum of **2**