An unprecedented octahedral \{\text{Cd}_{30}\} nanocage supported by twelve pendant-armed tetraacetate macrocyclic ligands

Wei-Jie Gong,\textsuperscript{a} Ying-Ying Liu,*\textsuperscript{a} Jin Yang,\textsuperscript{a} Hua Wu,\textsuperscript{a} Jian-Fang Ma*\textsuperscript{a} and Teng-Feng Xie\textsuperscript{b}

\textsuperscript{a} Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People’s Republic of China
\textsuperscript{b} College of Chemistry, Jilin University, Changchun, 130021, People’s Republic of China

* Correspondence authors
E-mail: liuyy21@yahoo.com.cn (Y.-Y. Liu)
E-mail: jianfangma@yahoo.com.cn (J.-F. Ma)
Fax: +86-431-85098620 (J.-F. Ma)
Experimental section

Materials and methods

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. The inductively coupled plasma (ICP) analysis was performed on a Leeman Labs Prodigy inductively coupled plasma-optical atomic emission spectrometer (ICP-AES). The TG data was determined on a Perkin–Elmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C·min⁻¹. IR spectrum was recorded in the range of 400–4000 cm⁻¹ on an Alpha Centaurt FT/IR Spectrophotometer with pressed KBr pellets. The X-ray powder diffraction pattern (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer. The emission/excitation spectra and the lifetime were measured on an Edinburgh FLS-920 spectrophotometer equipped with a continuous Xe-900 xenon lamp, an nF900 nanosecond flash lamp. The surface photovoltage spectroscopy (SPS) and the field-induced surface photovoltage spectroscopy (FISPS) were measured with a solid junction photovoltaic cell ITO/sample/ITO by a light source-monochromator-lock-in detection technique. ITO glass was used as the transparent front and back electrodes. FISPS were obtained with a dc bias applied to the two sides of the sample cell. 1H-NMR spectra of H₂L¹ and H₂(CH₂CH₃)₄L were recorded at 25 °C on a Varian 500 MHz spectrometer.

Syntheses of H₂(CH₂CH₃)₄L and (NH₄)₁₂[Cd₃₀L₁₂(H₂O)₆]·68H₂O (1)

Synthesis of H₂(CH₂CH₃)₄L. Ethyl chloroacetate (1.47 g, 12 mmol) was added dropwise to a refluxing solution of the macrocyclic ligand H₂L¹ (1.32 g, 3 mmol) (Scheme 1), triethylamine (12.144 g, 120 mmol) and THF (150mL). The resulting pale yellow mixture was refluxed for 24 h and then filtered. The solvent was evaporated, and the H₂(CH₂CH₃)₄L was obtained. Yield: 78%. ¹H-NMR (D₂O) for H₂L¹: 7.21 (s, 4H, Ph), 4.20 (s, 8H, CH₂), 2.93 (s, 8H, CH₂), 2.21 (s, 6H, CH₃), 1.67 (s, 8H, CH₂); ¹H-NMR (CDCl₃) for H₂(CH₂CH₃)₄L: 9.91 (s, 2H, OH), 6.82 (s, 4H, Ph), 4.16 (q, J = 14.0, 7.0 Hz, 8H, CH₂), 3.77 (s, 8H, CH₂), 3.30 (s, 8H, CH₂), 2.58 (s, 8H, CH₂), 2.20 (s, 6H, CH₃), 1.52 (s, 8H, CH₂), 1.27 (t, J = 7.0 Hz, 12H, CH₃).
Synthesis of (NH₄)₁₂[Cd₃₀L₁₂(H₂O)₆]·6₈H₂O (1). A mixture of H₂(CH₂CH₃)₄L (0.073 g, 0.1 mmol) and Cd(OAc)₂·2H₂O (0.053 g, 0.2 mmol) in methanol (10 mL) and water (5 mL) was stirred for 30 min at room temperature. Then the mixture was placed in a Teflon reactor (15 mL) and heated at 130 °C for 3 days. After cooling to room temperature at a rate of 10 °C·h⁻¹, a white precipitate was obtained. Then a minimum amount of ammonia (14 M, 15 mL) was added to the solid. After stirring for about 1 h, the white solid was dissolved slowly. Colorless crystals of 1 suitable for X-ray crystallography was obtained by filtration and evaporating the filtrate at room temperature in a 31% yield. Elem and ICP anal. Calcd for C₄₀₈H₇₀₀Cd₃₀N₆₀O₁₉₄: C, 37.92; H, 5.46; N, 6.50; Cd, 26.10. Found: C, 37.71; H, 5.68; N, 6.33; Cd, 25.83. IR (cm⁻¹): 3421 (m), 2860 (w), 1607 (s), 1472 (m), 1404 (m), 1307 (w), 1088 (w), 795 (m), 738 (w), 416 (w).

Crystallographic study of (NH₄)₁₂[Cd₃₀L₁₂(H₂O)₆]·6₈H₂O (1). Single-crystal X-ray diffraction data for cage 1 was recorded at a temperature of 200(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with CuKα radiation (λ = 1.54184 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms of the complex were easily found from the Fourier difference maps and refined with anisotropic atomic displacement parameters. The hydrogen atoms attached to carbons were generated geometrically. The solvent molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine. Thermogravimetric and elemental analyses indicate the presence of ca. 74 water molecules and 12 NH₄⁺ cations in the structure of cage 1. All H atoms on NH₄⁺ cations and water molecules were directly included in the molecular formula. Crystal data of 1: Mr = 12922.28, Tetragonal, P4/nnc, a = 28.3550(2), c = 33.1880(5) Å, V = 26683.3(5) Å³, Z = 2, ρ = 1.608 g cm⁻³, μ = 10.130 mm⁻¹, F(000) = 13120, GOF = 1.198, A total of 67365 reflections were collected in the range of 3.46° ≤ θ ≤ 63.68°, 11003 of which were unique (Rint = 0.1232
after SQUEEZE). $R_1(wR2) = 0.1157(0.2394)$ for 701 parameters and 7868 reflections ($I > 2\sigma(I)$). CCDC 817538 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References


![Fig. S1. The asymmetric unit of cage 1.](image)
Fig. S2. The coordination mode of L ligand in cage 1.

Fig. S3. (a) View of the (Cd₂L)-a unit; (b) view of the propeller-like \{Cd[(Cd₂L)-a]₄\} species; (c) Schematic representative of the propeller-like \{Cd[(Cd₂L)-a]₄\} species constructed by one Cd₃ atom and four (Cd₂L)-a units. Square: Cd₃; circle: (Cd₂L)-a.
**Fig. S4.** (a) View of the (Cd$_2$L)-b unit; (b) view of the wheel-like \( \{\text{Cd}_4[(\text{Cd}_2L)-\text{b}]_4\} \) fragment; (c) Schematic representative of the wheel-like \( \{\text{Cd}_4[(\text{Cd}_2L)-\text{b}]_4\} \) fragment constructed by four Cd$_5$ atoms and four (Cd$_2$L)-b units. Square: Cd$_5$; circle: (Cd$_2$L)-b.

**Fig. S5.** The space-filling wheel-like \( \{\text{Cd}_4[(\text{Cd}_2L)-\text{b}]_4\} \) fragment of cage 1.
**Fig. S6.** The space-filling arrangement of cage 1.

**Fig. S7.** The packing arrangement of cage 1.

**Fig. S8.** The packing arrangement of cage 1.
**Fig. S9.** Emission and excitation spectra cage 1.

**Fig. S10.** Luminescent decay curve for cage 1 ($\lambda_{\text{em}} = 446$ nm).

**Fig. S11.** IR spectrum for cage 1.
**Fig. S12.** Simulated and experimental XRPD patterns of cage 1.

**Fig. S13.** The TG curve of cage 1. The weight loss, corresponding to the water molecules and ammonia, is observed over the wide temperature range from 43 to 220 °C (Found: 11.88%, calcd: 11.90%).
**Fig. S14.** $^1$H-NMR (D$_2$O) for H$_2$L$^1$.

![NMR spectrum](image)

**Fig. S15.** $^1$H-NMR (CDCl$_3$) for H$_2$(CH$_2$CH$_3$)$_4$L