Adducts of aqua complexes of Ln$^{3+}$ with a di-hydroxylated symmetrical octamethyl-substituted cucurbituril: potential applications for isolation of heavier lanthanides

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EXPERIMENTAL SECTION

Synthesis: Chemicals, such as lanthanide nitrates was of reagent grade and was used without further purification. \( \text{t(OH)}_2\text{OMeQ}[6] \) was prepared as reported elsewhere.\(^1\) Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. A similar process was used to prepare crystals of related compounds: \( \text{Ln(NO}_3)_3 \cdot x\text{H}_2\text{O} \) (0.0227 mmol) and \( \text{t(OH)}_2\text{OMeQ}[6] \) (10 mg, 0.0075 mmol) were dissolved in 3.0 mL neutral water with stirring. The solution was allowed to stand to allow slow evaporation of the volatiles in air at room temperature. X-ray quality crystals were obtained from the solution within a week. The color of crystals was dependent on the lanthanide ions. Summarizing the preparations, \{\text{t(OH)}_2\text{OMeQ}[6]\} \cdot \text{Eu(H}_2\text{O)}_8 \cdot 3\text{Cl} \cdot 18\text{H}_2\text{O} \) (1) was obtained from \( \text{Eu(NO}_3)_3 \cdot 6\text{H}_2\text{O} \) (10.14 mg), Anal. calcd for \( \text{C}_{44}\text{H}_{104}\text{N}_{24}\text{O}_{40}\text{EuCl}_3 \): H, 5.61; C, 28.29; N, 18.00; Found: H, 5.64; C, 28.23; N, 17.93; \{\text{t(OH)}_2\text{OMeQ}[6]\} \cdot \text{Gd(H}_2\text{O)}_8 \cdot 2\text{(NO}_3)_3 \cdot \text{Cl} \cdot 8\text{H}_2\text{O} \) (2) was obtained from \( \text{Gd(NO}_3)_3 \cdot 6\text{H}_2\text{O} \) (10.26 mg), Anal. calcd for \( \text{C}_{44}\text{H}_{84}\text{N}_{26}\text{O}_{36}\text{GdCl} \): H, 4.85; C, 30.27; N, 20.86; Found: H, 4.89; C, 30.19; N,
20.76; \(\{t(OH)_2OMeQ[6]\cdot[Tb(H_2O)_8]\}\cdot3Cl\cdot10H_2O \) (3) was obtained from \(\text{Tb(NO}_3)_3\cdot6H_2O \) (10.30 mg), Anal. calcd for \(\text{C}_{44}\text{H}_{88}\text{N}_{24}\text{O}_{32}\text{TbCl}_3\) (3): H, 5.13; C, 30.54; N, 19.42; Found: H, 5.16; C, 30.46; N, 19.33; \(\{t(OH)_2OMeQ[6]\cdot[Dy(H_2O)_8]\}\cdot3Cl\cdot11H_2O \) (4) was obtained from \(\text{Dy(NO}_3)_3\cdot6H_2O \) (11.00 mg), Anal. calcd for \(\text{C}_{44}\text{H}_{90}\text{N}_{24}\text{O}_{33}\text{DyCl}_3\) (4): H, 5.18; C, 30.16; N, 19.19; Found: H, 5.22; C, 30.09; N, 19.11; \(\{t(OH)_2OMeQ[6]\cdot[Ho(H_2O)_8]\}\cdot2(\text{NO}_3)_2\cdot\text{Cl}\cdot10H_2O \) (5) was obtained from \(\text{Ho(NO}_3)_3\cdot5H_2O \) (10.02 mg), Anal. calcd for \(\text{C}_{44}\text{H}_{88}\text{N}_{26}\text{O}_{38}\text{HoCl}_3\) (5): H, 4.96; C, 29.53; N, 20.35; Found: H, 4.99; C, 29.46; N, 20.26; \(\{t(OH)_2OMeQ[6]\cdot[Yb(H_2O)_8]\}\cdot3Cl\cdot19H_2O \) (7) was obtained from \(\text{Tm(NO}_3)_3\cdot5H_2O \) (10.11 mg), Anal. calcd for \(\text{C}_{44}\text{H}_{106}\text{N}_{26}\text{O}_{41}\text{TmCl}_3\) (7): H, 5.62; C, 27.77; N, 17.67; Found: H, 5.66; C, 27.68; N, 17.59; \(\{t(OH)_2OMeQ[6]\cdot[Lu(H_2O)_8]\}\cdot3Cl\cdot19H_2O \) (8) was obtained from \(\text{Yb(NO}_3)_3\cdot5H_2O \) (10.21 mg), Anal. calcd for \(\text{C}_{44}\text{H}_{106}\text{N}_{26}\text{O}_{41}\text{YbCl}_3\) (8): H, 5.60; C, 27.71; N, 17.63; Found: H, 5.66; C, 27.62; N, 17.52. 

X-ray crystallography: A suitable single crystal (~0.2 × 0.2 × 0.1 mm\(^3\)) was taken up in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo-\(K\alpha\) (\(\lambda = 0.71073 \ \text{Å}, \mu = 0.828 \ \text{mm}^{-1}\)) radiation source operating in the \(\omega\)-scan mode and a nitrogen cold stream (~50 C). Data were corrected for Lorentz and polarization effects (SAINT), and semi-empirical absorption corrections based on equivalent reflections were also applied (SADABS). The structure was elucidated by direct methods and refined by the full-matrix least-squares method on \(F^2\) with the SHELXS-97 and SHELXL-97 program packages, respectively. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent.
Most of the water molecules in the compounds were omitted using the SQUEEZE option of the PLATON program. The squeezed water molecules are 18, 8, 13, 10, 11, 10, 7, 19, 19 and 9 for compounds 1–9, respectively. Unfortunately, whatever how hard our crystallographer has tried, the A and B kind of alerts can not be get rid of at all in CIF check reports. Moreover, Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Details of the crystal parameters, data collection conditions, and refinement parameters for the nine compounds are summarized in Table SI-1. In addition, the crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1550305 (1), 1550306 (2), 1550307 (3), 1550308 (4), 1550309 (5), 1550310 (6), 1550311 (7), 1550312 (8), 1550313 (9). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table SI-1. Crystal Data and Structure Refinement Details for Compounds 1-9

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$^a R_1 = \Sigma |F_o| - |F_c|/\Sigma |F_o|, \quad ^b wR_2 = \Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w(|F_o|^2)^{1/2}$, where $w = 1/[(\sigma^2(F_o^2) + (aP)^2 + bP)], P = (F_o^2 + 2F_c^2)/3$.

### Isothermal titration calorimetry (ITC):
Microcalorimetric experiments were performed using an isothermal titration calorimeter Nano ITC 2G (TA, USA). Each consecutive injection (6 μL) of a solution (Ln(NO$_3$)$_3$·5 or 6H$_2$O respectively: 1×10$^{-3}$ M) into the microcalorimetric reaction cell (1mL) charged with a solution of t(OH)$_2$OMeQ[6] (1×10$^{-4}$ M). The heat of reaction was corrected for the heat of dilution of the guest solution determined in the separate experiments. All solutions were degassed prior to titration experiment by sonication. Computer simulations (curve fitting) were performed using the Nano ITC ananlyze software.

![Graphs showing normalized heat rate vs. ratio for La, Ce, Pr, and Nd](image-url)
Figure SI-1 ITC profile of $\text{t(OH)}_2\text{OMeQ}[6]$ with Ln(NO$_3$)$_3$ at 298.15 K: Ln = (a) La; (b) Ce; (c) Pr; (d) Nd; (e) Sm; (f) Eu; (g) Gd; (h) Tb; (i) Dy; (j) Ho; (k) Er; (l) Tm; (m) Yb; (n) Lu.
Figure SI-2 Powder X-ray diffraction (PXRD) of the adducts from nine isomorphous group respectively
Figure SI-3 the electron spectroscopy of the representative adducts with 1:1 ratios of Ln_{light}:Ln_{heavy}

References
