Coordination of Ln[3+] in Ortho-tetramethyl Substituted Cucurbituril Supramolecular Assemblies Formed in the Presence of Cadmium Nitrate: Potential Applications for Isolation of Heavier Lanthanides

Jia-Jia Zhou,[b] Xin Yu,[a] Ying-Chun Zhao,[a] Xin Xiao,[a] Yun-Qian Zhang,[a] Sai-Feng Xue,[a] Zhu Tao,[a] Jing-Xin Liu,*[b] and Qian-Jiang Zhu*[a]

[a] Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China
[b] College of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China.

ABSTRACT: Coordination in supramolecular assemblies was investigated by reacting a series of lanthanide cations (Ln[3+]) and a new alkyl-substituted cucurbituril, the ortho-tetramethyl substituted cucurbituril (*o*-TMeQ[6]), in the presence of cadmium nitrate as an inorganic structure inducer in neutral solution. X-ray diffraction analysis revealed that the coordination of lanthanide cations gives rise to two isomorphous groups bound to three and eight isomorphous compounds, respectively. One group is typical of the coordination of *o*-TMeQ[6] with light lanthanide cations such as Nd[3+], Sm[3+] and Eu^{3+}, while the other group is characteristic of the coordination of *o*-TMeQ[6] with heavy lanthanide cations such as Gd^{3+}, Tb[3+], Dy[3+], Ho[3+], Er[3+], Tm3^{+}, Yb[3+] and Lu[3+]. Most interestingly, no solid crystals were obtained for any compounds containing La, Ce, or Pr, suggesting that these compounds may be suitable for the separation of heavier lanthanide cations from their lighter counterparts.

KEYWORDS: Ortho-tetramethyl substituted cucurbituril, lanthanide cation, cadmium nitrate, coordination complexes, isolation, supramolecular assemblies

■INTRODUCTION

The chemistry of the lanthanides is a field of great interest to contemporary inorganic chemists, stimulated not only by their unique spectroscopic and magnetic properties, but also by their numerous applications in catalysts, magnets and luminescent materials.[1~9] Lanthanides generally present similar chemical properties due to the poor shielding of the nuclear charge by filling of the 4f electron shell, which makes isolating the lanthanides difficult. The extremely high rates of exchange of ligands at f-element centers also make the isolation of their coordination complexes difficult, particularly from aqueous solutions.

Cucurbit[n]urils are extensive macrocyclic ligands that form complexes with lanthanides, in which the lanthanide metal ion is coordinated in a multidentate manner with carbonyl oxygen donor ligands.[10] The first Ln^{3+}/Q[n] complex was a Sm^{3+}/Q[6] complex obtained by slowly evaporating an aqueous solution of $SmBr_3$ and cucurbituril, carried out by Fedin and co-workers in 2002.[11] They first systematically investigated Ln^{3+}-Q[6] coordination in aqueous solution, and found that the composition and structure of compounds formed from aqueous lanthanide salts and Q[6] was dependent on total metal concentration, metal salts, pH (by the addition of NaOH, KOH, or ammonia), and temperature.[12] Recent research revealed that the coordination selectivity exhibited by Q[n]s towards lanthanide cations and salts resulted in the formation of different Ln^{3+}/Q[n]-based complexes with different conformations that formed supramolecular assemblies. In particular, Ln^{3+}-Q[n]-based complexes obtained in the presence of third species that acts as a structure inducer showed significant differences in coordination features and properties, which could provide a way of separating lanthanides.[13~17] For example, the coordination of Ln^{3+} cations to Q[6] in the presence of $[M_{d\text{-block}}Cl_4]^{2-}$, $M_{d\text{-block}}$ = Cd, Zn, and so on) revealed that $[M_{d\text{-block}}Cl_4]^{2-}$ anions form honeycomb patterned supramolecular assemblies, in which the hexagonal cells are occupied by Ln^{3+}/Q[6] linear coordination polymers in the case of most lanthanides except La, Ce, Pr, Nd, and Pr, for which they instead rapidly precipitated. This phenomenon offers a means of isolating light lanthanide cations from their heavier counterparts.[14] While introducing Cd^{2+} into Q[8]-Ln^{3+}-HCl systems using $[CdCl_4]^{2-}$ anions, the coordination of heavy lanthanides with Q[8] and the resulting supramolecular assemblies showed significant differences from those containing the light lanthanide cations formed under the same synthetic conditions. Moreover, the Ln^{3+}_{light}-Q[8]-$[CdCl_4]^{2-}$ systems formed stick-like single crystals in a shorter time period, while the Ln^{3+}_{heavy}-Q[8]-$[CdCl_4]^{2-}$ systems gave diamond-like single crystals over a longer time period, which provides another potential strategy for separation.[17]

In the present work, a alkyl-substituted cucurbituril, the ortho-tetramethyl substituted cucurbituril (o-TMeQ[6]),[18] was synthesized (Figure 1). Coordination with a series of lanthanide cations in the presence of $Cd(NO_3)_2$ gave rise to two isomorphous groups under identical synthetic conditions. One group was typical of the coordination of o-TMeQ[6] with light lanthanide cations such as Nd^{3+}, Sm^{3+}

and Eu^{3+}, while the other group was characteristic of the coordination of *o*-TMeQ[6] with heavy lanthanide cations such as Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, $Tm3^{+}$, Yb^{3+} and Lu^{3+}. Most interestingly, no solid crystals were obtained from compounds containing La, Ce, or Pr, which provides a possible method for separating heavy and light lanthanides.
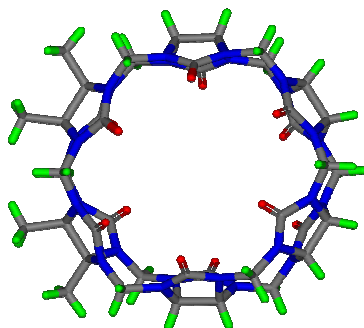

Figure 1 Structure of the ortho-tetramethyl substituted cucurbituril (*o*-TMeQ[6]).

EXPERIMENTAL SECTION

Synthesis: Chemicals, such as lanthanide nitrates and cadmium nitrate, were of reagent grade and were used without further purification. *o*-TMeQ[6] was prepared as reported elsewhere.[18] Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. A similar process was used to prepare crystals of related compounds: $Ln(NO_3)_3 \cdot xH_2O$ (0.09 mmol) and $Cd(NO_3)_2$ (5.2 mg, 0.02 mmol) were dissolved in 1.0 mL neutral water (solution A), *o*-TMeQ[6] (10 mg, 0.01 mmol) was dissolved in 1.0 mL neutral water (solution B), and was then added in the solution A with stirring. X-ray quality crystals were obtained from the solution over a period of 1-5 days. The color of crystals was dependent on the lanthanide ions. Summarizing the preparations, {$Nd(H_2O)_5(NO_3)(o$-TMeQ[6])}·$(NO_3)_2 \cdot 6H_2O$ (**4**) was obtained from $Nd(NO_3)_3 \cdot 6H_2O$ (0.038 g); {$Sm(H_2O)_5(NO_3)(o$-TMeQ[6])}·$(NO_3)_2 \cdot 6H_2O$ (**6**) was obtained from $Sm(NO_3)_3 \cdot 6H_2O$ (0.039 g); {$Eu(H_2O)_5(NO_3)(o$-TMeQ[6])}·$(NO_3)_2 \cdot 6H_2O$ (**7**) was obtained from $Eu(NO_3)_3 \cdot 6H_2O$ (0.039 g); {$Gd(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 16H_2O$ (**8**) was obtained from $Gd(NO_3)_3 \cdot 6H_2O$ (0.04 g); {$Tb(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 16H_2O$ (**9**) was obtained from $Tb(NO_3)_3 \cdot 6H_2O$ (0.04 g); {$Dy(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 16H_2O$ (**10**) was obtained from $Dy(NO_3)_3 \cdot 6H_2O$ (0.042 g); {$Ho(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 16H_2O$ (**11**) was obtained from $Ho(NO_3)_3 \cdot 5H_2O$ (0.039 g); {$Er(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 15H_2O$ (**12**) was obtained from $Er(NO_3)_3 \cdot 5H_2O$ (0.039 g); {$Tm(H_2O)_6(o$-TMeQ[6])}·$2 (NO_3) \cdot Cl \cdot 17H_2O$ (**13**) was obtained from $Tm(NO_3)_3 \cdot 5H_2O$ (0.039 g); {$Yb(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 14H_2O$ (**14**) was obtained from $Yb(NO_3)_3 \cdot 5H_2O$ (0.04 g); {$Lu(H_2O)_6(o$-TMeQ[6])}·$2(NO_3) \cdot Cl \cdot 15H_2O$ (**15**) was obtained from $Lu(NO_3)_3 \cdot 6H_2O$ (0.041 g); Elemental analysis

results for the eleven compounds are given in Table 1. It should be noted that 1) the compounds (**1~3**, **5**) is corresponding to La, Ce, Pr and Pm, but we did not obtained crystals which still stay in solution state (except Pm); 2) although the chloride salts are not used in the crystal preparation processes, the crystal structure contains a chloride anion, which could come from the HCl, employed to synthesize *o*-TMeQ[6]; 3) In order to show the whole systems, the number of compounds are increased with increase of the atomic number of the lanthanide series.

Table 1. Elemental Analysis Results (%)

Results	4	6	7	8	9	10	11	12	13	14	15
C calcd.	30.41	30.26	30.23	27.21	27.18	27.12	27.09	27.33	26.76	27.52	27.21
found	30.98	30.80	30.79	27.27	27.24	27.21	27.14	27.43	26.86	27.59	27.29
H calcd.	4.21	4.19	4.19	5.02	5.02	5.01	5.00	4.93	5.05	4.85	4.91
found	4.21	4.19	4.16	4.92	5.00	4.96	4.91	4.87	5.00	4.80	4.86
N calcd.	23.95	23.82	23.80	20.62	20.60	20.56	20.53	20.72	20.28	20.86	20.62
found	23.48	23.39	23.37	20.67	20.69	20.65	20.50	20.67	20.20	20.81	20.58

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_α (λ = 0.71073 Å, μ = 0.828 mm^{-1}) radiation source operating in the ω-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.[19,20] 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 atom. Most of the water molecules in the compounds were omitted using the SQUEEZE option of the PLATON program. The squeezed water molecules are all 5 for the compounds **4**, **6**, **7**, and 15, 15, 15, 15, 14, 16, 13 and 14 for the compounds **8~15** respectively. 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 twenty five compounds are summarized in Table 2. In addition, the crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-997810 (**4**), 997811 (**6**), 997812(**7**), 997813 (**8**), 997814 (**9**), 997815 (**10**), 997816 (**11**), 997817 (**12**), 997818 (**13**), 997819 (**14**), 997820 (**15**).

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 2. Crystal Data and Structure Refinement Details for Compounds **4**, **6-15**

Compound	**4**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Empirical formula	$C_{40}H_{66}N_{27}O_{32}Nd$	$C_{40}H_{66}N_{27}O_{32}Sm$	$C_{40}H_{66}N_{27}O_{32}Eu$	$C_{40}H_{88}N_{26}O_{40}GdCl$	$C_{40}H_{88}N_{26}O_{40}TbCl$	$C_{40}H_{88}N_{26}O_{40}DyCl$	$C_{40}H_{88}N_{26}O_{40}HoCl$	$C_{40}H_{86}N_{26}O_{39}ErCl$	$C_{40}H_{90}N_{26}O_{41}TmCl$	$C_{40}H_{84}N_{26}O_{38}YbCl$	$C_{40}H_{86}N_{26}O_{39}LuCl$
Formula weight	1581.44	1587.55	1589.16	1766.06	1767.73	1771.31	1773.74	1758.06	1795.76	1745.82	1765.77
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pna*21	*Pna*21	*Pna*21	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a, Å	23.468(9)	23.369(3)	23.351(5)	35.306(5)	35.381(3)	35.375(4)	35.361(5)	35.370(2)	35.285(5)	35.396(4)	35.247(13)
b, Å	14.639(6)	14.6418(17)	14.641(3)	14.142(2)	14.2066(13)	14.1652(17)	14.168(2)	14.1610(17)	14.1423(19)	14.1853(18)	14.129(5)
c, Å	17.452(7)	17.407(2)	17.416(4)	13.4153(19)	13.4355(13)	13.4397(16)	13.4332(19)	13.4086(16)	13.3923(18)	13.4031(17)	13.384(5)
V, Å^3	5996(4)	5956.1(12)	5954(2)	6698.0(16)	6753.2(11)	6734.6(14)	6729.9(16)	6716.0(14)	6682.9(16)	6729.6(15)	6665(4)
Z	4	4	4	4	4	4	4	4	4	4	4
Dcalcd, g cm^{-1}	1.752	1.770	1.773	1.751	1.739	1.747	1.751	1.739	1.785	1.723	1.760
T, K	223	223	223	223	223	223	223	223	223	223	223
μ, mm^{-1}	0.985	1.106	1.174	1.153	1.208	1.271	1.337	1.410	1.493	1.547	1.642
Unique reflns	10238	10279	10588	6252	6302	6324	6754	6300	6715	6317	6235
Obsd reflns	7323	8715	8418	5129	4787	4504	4771	4915	4614	4559	3983
Params	861	861	861	445	445	445	445	442	448	445	445
Rint	0.0756	0.0482	0.0707	0.0583	0.0561	0.0687	0.0695	0.0646	0.0888	0.0593	0.0747
$R[I> 2\sigma(I)]^a$	0.0527	0.0412	0.0499	0.0631	0.0535	0.0503	0.0527	0.0552	0.0533	0.0445	0.0475
$wR[I> 2\sigma(I)]^b$	0.1138	0.1049	0.1212	0.1480	0.1411	0.1349	0.1438	0.1323	0.1440	0.1268	0.1387
R(all data)	0.0786	0.0492	0.0636	0.0760	0.0717	0.0729	0.0794	0.0720	0.0818	0.0665	0.0805
wR(all data)	0.1239	0.1098	0.1294	0.1542	0.1495	0.1441	0.1540	0.1396	0.1542	0.1366	0.1512
GOF on F^2	0.970	1.037	1.021	1.109	1.084	1.052	1.055	1.119	1.050	1.073	1.079
Flack params	0.321(14)	0.101(12)	0.55(3)								

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{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: Microcalorimetric experiments were performed using an isothermal titration calorimeter Nano ITC 2G (TA, USA). Each experiment consisted of 20 consecutive injections (10 μL) of a solution ($Ce(NO_3)_3 \cdot 6H_2O$ or $Eu(NO_3)_3 \cdot 6H_2O$ or $Yb(NO_3)_3 \cdot 5H_2O$

respectively: 1×10^{-3} M) into the microcalorimetric reaction cell (1mL) charged with a solution of *o*-TMeQ[6] (1×10^{-4} M) or *o*-TMeQ[6]-Cd(NO$_3$)$_2$·6H$_2$O (1×10^{-4} M，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.

∎RESULTS AND DISCUSSION

It is well known that cucurbituril (Q[6]) and alkyl-substituted cucurbiturils (SQ[6]s) can interact with lanthanide cations and form different adducts and coordination complexes of polymers with poly-dimensional supramolecular assemblies, as summarized in our recent review.[21] Coordination of lanthanide cations to Q[6] molecules is strongly affected by synthetic conditions, and different Q[6] molecules (interacting with lanthanide cations) form different coordination structures and supramolecular assemblies. Compared with the unsubstituted Q[6], *o*-TMeQ[6] has higher water solubility due to its unsymmetrical structure. This allows investigation of its coordination and supramolecular assemblies with lanthanide cations in neutral aqueous solution. The interaction of the series of lanthanide cations to *o*-TMeQ[6] in the presence of Cd(NO$_3$)$_2$ gives rise to two isomorphous groups under the same synthetic condition except with different lanthanide respectively. The first group with Pna21 space group is characteristic of coordination of *o*-TMeQ[6] molecule with Nd^{3+}, Sm^{3+}, Eu^{3+}; the second group with Pnma space group involves the coordination of *o*-TMeQ[6] molecule with Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+} cations respectively, which show m-symmetry in (x, -y+1/2, z). A complex of an *o*-TMeQ[6] with a neodymium cation (compound **4**; Figure 2a) is a representative example of the first isomorphous group. The crystal structure shows that an *o*-TMeQ[6] molecule is coordinated by a single Nd^{3+} cation at one opening of the two portals. The Nd^{3+} cation itself coordinates to nine oxygens (two carbonyl oxygens, five water molecules, and two oxygens from a nitrate anion). The bond distances between the Nd^{3+} cation and the carbonyl oxygen atoms are in the range of 2.45~2.48 Å, the distances between the Nd^{3+} cation and the coordinated water oxygen atoms are in the range of 2.45~2.50 Å, and the bond distances between the Nd^{3+} cation and oxygen atoms from the coordinated nitrate anion are in the range of 2.53~2.67 Å. A close inspection revealed that the portal carbonyl oxygens coordinated with the Nd^{3+} cation belong to two dimethyl substituted glycouril moieties in the *o*-TMeQ[6] molecule. Our recent series of novel coordination and supramolecular assemblies have proven that the electron donating effect of the alkyl-substituted groups leads to an increase in electron density on the portal carbonyl oxygen of the alkyl-substituted glycouril moiety in the cucurbit[*n*]uril, which results in formation of an unusual coordination of metal ions to alkyl-

substituted Q[*n*] molecules and novel SQ[*n*]s-based supramolecular assemblies.[22~24] Thus, it is evident that Ln^{3+} cation selectively influences the coordination of the portal carbonyl oxygens of dimethyl substituted glycouril moieties on the *o*-TMeQ[6] molecule. This turned out to be common among the coordination complexes of the *o*-TMeQ[6] molecules with other lanthanide cations in this isomorphous group.
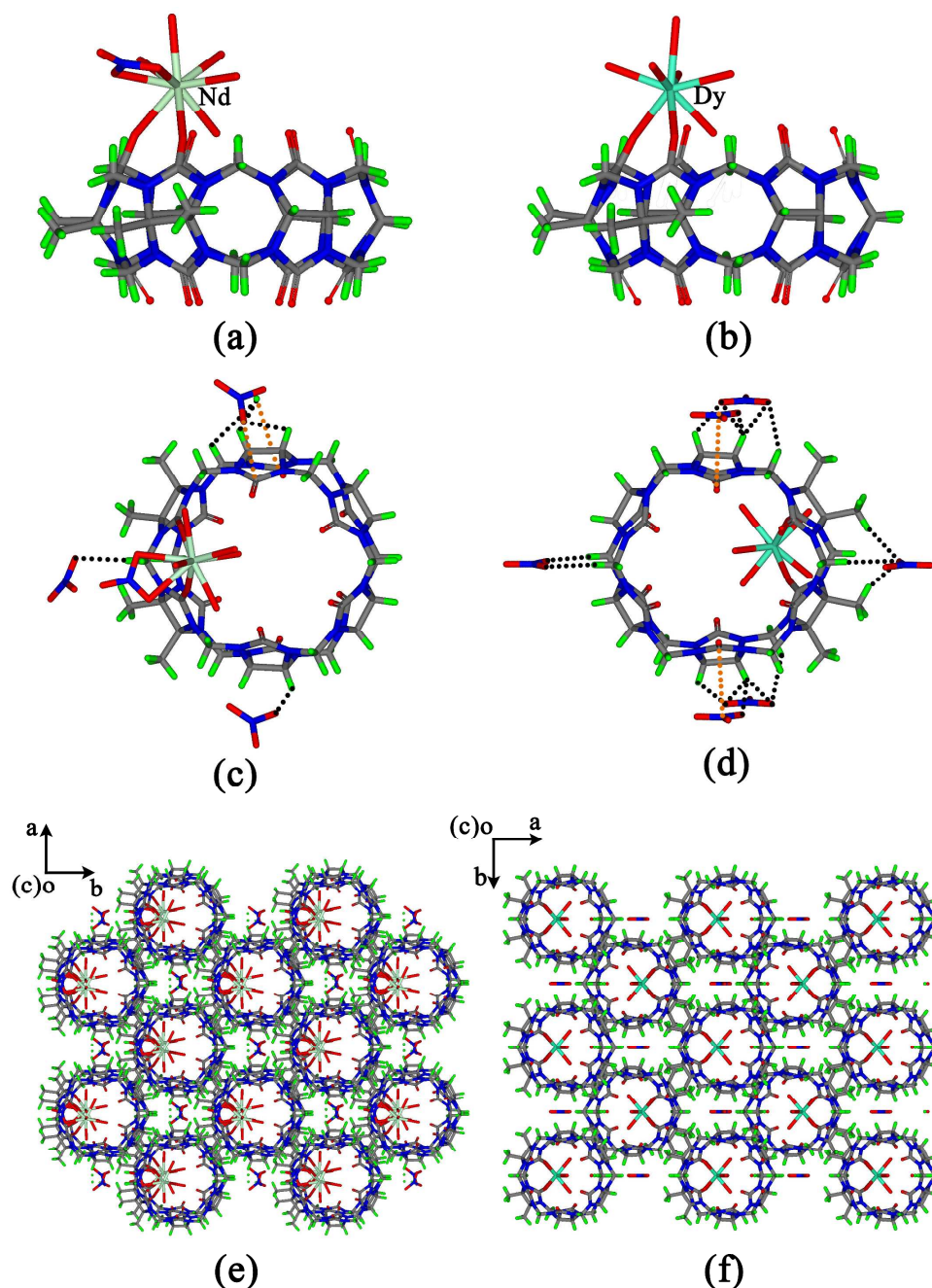

(a)   (b)

(c)   (d)

(e)   (f)

Figure 2. (a, b) X-ray crystal structure of a complex of *o*-TMeQ[6] with Nd^{3+} and Dy^{3+} cations of compound **4** and **10**, respectively; (c, d) detailed interactions of a Nd^{3+}/*o*-TMeQ[6] and Dy^{3+}/*o*-TMeQ[6] complex with the surrounding NO$_3^-$ anions in compound **4** and **10** respectively; (e, f) an

overall view of the supramolecular assemblies of Nd^{3+}/ o-TMeQ[6] complexes and NO_3^- anions of compound **4** and **10**, respectively.

A complex of o-TMeQ[6] with a dysprosium cation (compound **10**) (Figure 2b) is a representative example of the second isomorphous group. The crystal structure of the Dy^{3+}/o-TMeQ[6] complex shows a similar structure to molecules in the first group; o-TMeQ[6] coordinates to a single Dy^{3+} cation at one of the two portals. The Dy^{3+} cation coordinates to eight oxygens (two carbonyl oxygens and six water molecules). The bond distances between the Dy^{3+} cation and the carbonyl oxygen atoms are roughly the same (2.318 Å), and the distances between the Nd^{3+} cation and the coordinated water oxygen atoms are in the range of 2.34~2.46 Å. It should be noted that the Dy^{3+} cation also selectively coordinates to the portal carbonyl oxygens of two dimethyl substituted glycouril moieties in the o-TMeQ[6] molecule. This further confirms the electron donating effect of the alkyl-substituted groups on the SQ[n] molecules.

We recently focused on the outer-surface interactions of cucurbit[n]urils which appear to play an important role in the formation of novel Q[n]-based supramolecular assemblies.[25] These outer-surface interactions include (1) unusual hydrogen bonding of the waist methine ($\equiv$CH) or bridge methylene ($=CH_2$) groups on the back of Q[n] molecules with electron-sufficient species, such as the oxygen ends of inorganic anions or chloride ends of polychloridometallate anions;[26,27] (2) dipole–dipole interactions between the electron-sufficient ends and the electron-deficient portal carbonyl carbon of Q[n] moieties. Such interactions can be observed between the Ln^{3+}/o-TMeQ[6] complexes and the adjacent anions in compounds in the present work, such as nitrate and chloride anions. These interactions can be clearly seen in Figures 2c and 2d (black and orange dashed lines, respectively). The distances between $C_{methine\ or\ methylene}$–$O_{nitrate}$ or $C_{methine\ or\ methylene}$–Cl in the unusual hydrogen bonds are in the range of 3.04~3.41 Å, and the distances between $C_{carbonyl}$–$O_{nitrate}$ or $C_{carbonyl}$–Cl in the ion–dipole interaction are in the range of 3.08~3.28 Å for compound **4**. The corresponding distances are in the range of 3.16~3.47 Å and 3.32~3.38 Å for compound **10**. The combination of these outer-surface interactions between o-TMeQ[6] and the counter anions results in the formation of Ln^{3+}/o-TMeQ[6]-based supramolecular assemblies as shown in Figure 2e and 2f. The nitrate anions are surrounded by four Ln^{3+}/o-TMeQ[6] complexes along the c axis in the supramolecular assemblies in both representative examples, and it appears that the counter anions attract the o-TMeQ[6] molecules through these outer-surface interactions. The main difference between the two assemblies is the orientation of the four substituted ortho-methyl groups, which are all on the left in the Ln^{3+}/o-TMeQ[6]-based supramolecular assemblies in the first isomorphous group (Figure 2e), and spread evenly on the left and right in the second isomorphous group (Figure 2f). Although we can not conclude directly the structure directing effect of

the cadmium nitrate, ITC experiments showed that Cd^{2+} could affect the coordination of heavier lanthanide cations to *o*-TMeQ[6]. In the absence of cadmium nitrate, the Ce^{3+} cation has a stronger ability to coordinate *o*-TMeQ[6], whereas when cadmium nitrate is present, the selected heavier lanthanide cations Eu^{3+} and Yb^{3+} have the stronger coordination ability (Table 3). Detailed information needs to be further investigated.

Table 3 Association constants of selected Ln^{3+}−*o*-TMeQ[6] complexes.

Interaction systems	$K_{Ce(NO_3)_3}$	$K_{Eu(NO_3)_3}$	$K_{Yb(NO_3)_3}$
o-TMeQ[6] +	3.1×10^6	9.9×10^5	5.5×10^5
o-TMeQ[6]+Cd(NO_3)_2 +	1.4×10^6	2.9×10^6	7.8×10^5

The variation in bond lengths of the Ln^{3+}–$O_{carbonyl}$ with the atomic number of the lanthanide generally reflects the subtle differences arising from lanthanide contraction with increasing atomic number.[14,15] Figure 3 shows such a profile for the Ln^{3+}–*o*-TMeQ[6] systems in this study. Interestingly, one can see that the average bond lengths can be catalogued into two groups corresponding with the two isomorphous groups. In the first group they slowly decrease with increasing atomic number from Nd to Sm to Eu. There is then a sharp drop in bond length to the second group which then also slowly decreases with increasing atomic number. This result suggests that the correlation of Ln^{3+}–$O_{carbonyl}$ bond length and the atomic number of the lanthanide reflects not only the subtle differences arising from lanthanide contraction, but also the structural differences between the isomorphous groups. Further experiments are needed to determine if this is a common phenomenon and to understand the driving forces involved.
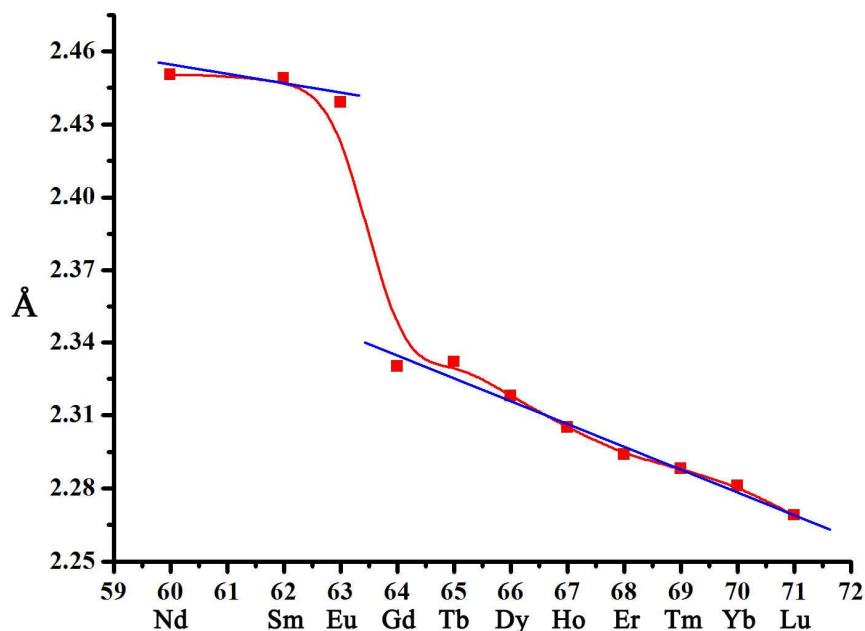
Figure 3 Profile of the average bond lengths between the Ln^{3+} and the portal carbonyl oxygen atoms of *o*-TMeQ[6] vs. the atomic number of the lanthanides.

As shown in our previous work, normal cucurbiturils in which Q[6] is unsubstituted can interact with a series of lanthanide cations in acidic (HCl) aqueous solutions due to the poor solubility of Q[6] in neutral water.[14] Lighter lanthanide cations such as La^{3+}, Ce^{3+}, and Pr^{3+} interact with Q[6] to form compounds that precipitate rapidly and almost quantitatively, suggesting that Q[6] can be used to separate light and heavy lanthanide cations, while the *o*-TMeQ[6] molecule can coordinate with most lanthanide cations to form solid crystals, apart from the lightest lanthanides (La, Ce and Pr), which remain in solution. The *o*-TMeQ[6]-Cd(NO$_3$)$_3$ system therefore has the ability to separate heavy lanthanide cations from light lanthanide cations by forming solid crystals, providing another isolation strategy. In order to investigate this further, nine typical $Ln^{3+}_{light}–Ln^{3+}_{heavy}–o$-TMeQ[6]$–$Cd(NO$_3$)$_3$ systems were selected as representative examples ($Ln^{3+}_{light}–Ln^{3+}_{heavy}$ and $La^{3+}–Ho^{3+}$, $La^{3+}–Tm^{3+}$, $La^{3+}−Yb^{3+}$, $Ce^{3+}−Ho^{3+}$, $Ce^{3+}−Tm^{3+}$, $Ce^{3+}−Yb^{3+}$, $Pr^{3+}−Ho^{3+}$, $Pr^{3+}−Tm^{3+}$ and $Pr^{3+}−Yb^{3+}$), all in 1:1 ratios. Electron spectroscopy showed that the crystals obtained only heavy lanthanides (SI-Figure 2 and SI-Figure 3 in the Supplementary Information), while the Ln^{3+}_{light} lanthanides remained in the mother liquor. Considering the practical possibilities of this strategy, further experiments were performed on selected *o*-TMeQ[6]/NO$_3^-$ systems with 10:1, 5:1, 1:5, and 1:10 ratios of heavy:light (La, Ce, Pr) lanthanides. Again, crystals were only formed with the higher heavy:light ratios. For the two isomorphous groups, a series of $Eu^{3+}_{light}−Yb^{3+}_{heavy}−o$-TMeQ[6]$−$Cd(NO$_3$)$_3$ systems with 10:1, 5:1, 1:1, 1:5, 1:10 ratios of Eu^{3+}:Yb^{3+} were selected as representative examples. Electron spectroscopy gave values of 1:23, 1:9, 1:2, 8:3, 9:1 for the corresponding systems, suggesting that these systems could not

effectively isolate heavy lanthanides from their lighter counterparts (SI-Figure 4 in the Supplementary Information).

Powder X-ray diffraction (PXRD) of the representative crystals from the two isomorphous groups, and comparison with simulations, showed that the samples essentially consisted of pure crystalline phases (referring to SI-Figure 5 in the Supplementary Information). Thermal analysis was used to generate DSC and TG curves of representative crystals from the two isomorphous groups. There were no significant differences between crystals, but they were different from the o-TMeQ[6] complexes (SI-Figure 6 in the Supplementary Information). Furthermore, FT-IR spectra showed that the absorption band of the portal carbonyl high-wavelength number is different in the two isomorphous groups (SI-Figure 7 in the Supplementary Information).

CONCLUSION

In summary, we have investigated the coordination of o-TMeQ[6] molecules with a series of Ln^{3+} cations in the presence of cadmium nitrate $(Cd(NO_3)_3)$. The experimental results based on X-ray diffraction analysis revealed that the Ln^{3+}/o-TMeQ[6] complexes formed can be catalogued into two isomorphous groups with slightly different coordination and supramolecular assemblies. The groups could be separated simply by the correlation of $Ln^{3+}–O_{carbonyl}$ bond length and the atomic number of the lanthanide. ITC experiments demonstrated the effects of cadmium nitrate for coordination of Ln^{3+} to o-TMeQ[6]. Importantly, the light lanthanide cations $(La^{3+}, Ce^{3+}, Pr^{3+})$ never formed solid crystals under the conditions tested and remained in solution, which offers a possible means of isolating heavy lanthanide cations from their lighter counterparts. Further detailed investigations aimed at developing this separation technique are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information Available: An X-ray crystallographic file in CIF format for this article is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gzutao@263.net (Q.J.Z.), Tel: +86-851-3620906 (Q.J.Z.), Fax:+86-851-3620906 (Q.J.Z.),

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