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ARTICLE

## Interaction of a Symmetrical $\alpha,\alpha',\delta,\delta'$ -Tetramethyl-cucurbit[6]uril with $\text{Ln}^{3+}$ : Potential Applications for Isolation of Lanthanides

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The interaction of a symmetrical  $\alpha,\alpha',\delta,\delta'$ -tetramethyl-cucurbit[6]uril (TMeQ[6]) with a series of lanthanide cations ( $\text{Ln}^{3+}$ ) was investigated in neutral water and in acidic solution. Analysis by single crystal X-ray diffraction revealed that different isomorphous families formed under different synthetic conditions. Such differences in the interaction between TMeQ[6] and  $\text{Ln}^{3+}$  could potentially be used for isolating heavier  $\text{Ln}^{3+}$  from their lighter counterparts in neutral solution, and lighter lanthanide cations from their heavier counterparts in acidic solution.

### Introduction

The unique optical and magnetic properties of lanthanide cations ( $\text{Ln}^{3+}$ ) have led to their wide application in electronics, lasers and powerful magnets.<sup>1</sup> Due to the chemical similarities of the lanthanides, their elements typically coexist in nature. The cost-effective separation of lanthanide elements is critical for the application of lanthanides in modern technology. Solvent extraction and ion chromatography are currently the preferred methods for the separation of  $\text{Ln}^{3+}$ . These methods are based on the difference in formation constant ( $K_f$ ) of  $\text{Ln}^{3+}$  molecular complexes. However, the development of more environmentally-friendly and efficient separation methods remains an industry goal.<sup>2</sup>

Recent advances in solid-state coordination chemistry,<sup>3</sup> especially in the field of metal-organic frameworks (MOFs),<sup>4</sup> have made possible a unified MOF-based separation strategy capable of the efficient separation of  $\text{Ln}^{3+}$ . This new strategy is based on the difference in solubility of products ( $K_{sp}$ ) during fractional crystallization and the difference in the formation constant ( $K_f$ ) of metal complexes in solvent extraction or chromatography. MOFs can be viewed as 3D polymers of metal complexes, and therefore it is hypothesized that the effect of a small difference in  $K_f$  for a molecular  $\text{Ln}^{3+}$  complex might be amplified during MOF crystallization. This approach has the potential to outperform traditional fractional crystallization.

Cucurbit[ $n$ ]urils (Q[ $n$ ]s)<sup>5</sup> have been utilized to construct Q[ $n$ ]-based MOFs and other supramolecular architectures.<sup>6,7</sup> We previously reported the synthesis and characterization of symmetrical  $\alpha,\alpha',\delta,\delta'$ -tetramethyl-cucurbit[6]uril (TMeQ[6], Figure 1).<sup>8</sup> TMeQ[6] exhibited a greater solubility in water compared to unsubstituted Q[6]. The increased molecular polarity associated with the lower molecular symmetry of TMeQ[6] results in easier interactions with guest molecules in aqueous media. However, Q[ $n$ ]s have a high affinity for  $\text{Ln}^{3+}$ , forming various Q[ $n$ ]-based complexes, especially adducts, in the presence of structure directing agents, and can form novel coordination polymers and supramolecular assemblies.<sup>7e,7f</sup> For example, Fedin and coworkers<sup>9</sup> systematically investigated the coordination of Q[6] with  $\text{Ln}^{3+}$  in aqueous solution in the absence of additives and in the presence of structure directing agents. They later introduced 4-cyanopyridine into Q[6]- $\text{Ln}^{3+}$  systems, and obtained novel tetranuclear lanthanide aqua hydroxo complexes.<sup>10</sup> More recently, Thuéry<sup>11</sup> also focused on Q[ $n$ ]s- $\text{Ln}^{3+}$  coordination chemistry, and introduced a series of chiral amino-acids into Q[6]- $\text{Ln}^{3+}$  systems, resulting in the formation of a series of  $\text{Ln}^{3+}$  complexes and supramolecular assemblies. Our group investigated the coordination of a series of cucurbit[ $n$ ]urils (Q[ $n$ ]s) with a series of  $\text{Ln}^{3+}$  and their corresponding supramolecular assemblies, and found that cucurbit[ $n$ ]urils not only recognized the  $\text{Ln}^{3+}$ , but could also be used to isolate them.<sup>12</sup> For example, under the same synthetic conditions, Q[5]- $\text{Ln}^{3+}$  systems led to three distinct configurations for the coordination and supramolecular assemblies formed on increasing atomic number of the  $\text{Ln}^{3+}$ . Specifically, coordination of light  $\text{Ln}^{3+}$  cations with Q[5] formed one-dimensional coordination polymers, while intermediate  $\text{Ln}^{3+}$  cations such as Eu(III) or Gd(III) formed Q[5] pairs in which two Q[5] molecules are connected by cations. Coordination of heavy  $\text{Ln}^{3+}$  cations with Q[5] forms homochiral, one-dimensional helical coordination polymers.<sup>6p,7a</sup>

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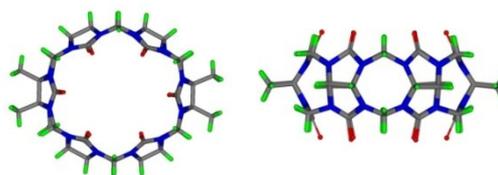
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This study also found that Q[6] on coordination with a series of  $\text{Ln}^{3+}$  cations formed linear coordination polymers in the presence of  $[\text{CdCl}_4]^{2-}$  and  $[\text{ZnCl}_4]^{2-}$  anions in acidic aqueous solutions containing HCl. The exceptions were  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  that immediately precipitated, and this could therefore offer a strategy for isolating lighter  $\text{Ln}^{3+}$  cations from their heavier counterparts.<sup>7c</sup> Similar phenomena can be observed in Q[7]/ $\text{Ln}^{3+}$  coordination and supramolecular assemblies in the presence of  $[\text{M}_{\text{d-block}}]^{2-}$  anions in HCl aqueous solutions. In particular,  $\text{Ln}^{3+}/\text{Q}[7]$ -based coordination polymers adopt a “zig-zag” conformation in aqueous solutions containing  $< 3 \text{ M}$  HCl.<sup>12f</sup> Moreover, in the presence of  $\text{Cd}(\text{NO}_3)_2$ , *o*-TMeQ[6] can coordinate with most lanthanide cations to form solid crystals, but complexes with the lightest  $\text{Ln}^{3+}$  (La, Ce, Pr) remain in solution. The *o*-TMeQ[6]- $\text{Ln}^{3+}$ - $\text{Cd}(\text{NO}_3)_2$  systems can separate heavier  $\text{Ln}^{3+}$  cations from lighter  $\text{Ln}^{3+}$  cations by forming solid crystals,<sup>[12e]</sup> as described in our recent review article.<sup>13</sup>

In the present work, a symmetrical TMeQ[6]<sup>8</sup> was selected as a ligand, and coordination of TMeQ[6] with a series of  $\text{Ln}^{3+}$  under different conditions was investigated using single X-ray diffraction and isothermal titration calorimetry (ITC). Interaction of TMeQ[6] with  $\text{Ln}^{3+}$  under neutral conditions and using two different interaction ratios gave rise to three isomorphous groups, in contrast to the use of acidic (HCl) conditions which yielded only two isomorphous groups. In neutral water using a 1:10 molar ratio of TMeQ[6] to  $\text{Ln}^{3+}$  cations, TMeQ[6] coordinated with  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  cations to form a simple 1:1 complex over an extended period (~40 days), whereas TMeQ[6] interacted with the remaining  $\text{Ln}^{3+}$  to form adducts of TMeQ[6] with aqua complexes of  $\text{Ln}^{3+}$  cations within 1 day; the exception was products containing either  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  which required 2 weeks. In neutral water with a 1:2 molar ratio of TMeQ[6] to  $\text{Ln}^{3+}$  cations, TMeQ[6] coordinated with  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ , and formed TMeQ[6]- $\text{Ln}^{3+}$  triple-decker sandwiches within 1 day, whereas products with the remaining  $\text{Ln}^{3+}$  ions were characteristic of TMeQ[6] adducts with aqua complexes of  $\text{Ln}^{3+}$  cations and formed within 6 h. In acidic solution (6 M HCl) at a 1:4 molar ratio of TMeQ[6] to  $\text{Ln}^{3+}$  cations, TMeQ[6] coordinated with  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ , and formed TMeQ[6]- $\text{Ln}^{3+}$  molecular capsules within 1 day, whereas products with the remaining heavier  $\text{Ln}^{3+}$  such as  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Lu}^{3+}$  were characteristic of TMeQ[6] adducts with aqua complexes of  $\text{Ln}^{3+}$  and formed over a longer period of time. It should be noted that the interaction of TMeQ[6] with  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  immediately gave rise to precipitation. Such differences in the interaction between TMeQ[6] and  $\text{Ln}^{3+}$  cations could be used for the isolation of heavier  $\text{Ln}^{3+}$  from their lighter counterparts in neutral solution, and lighter  $\text{Ln}^{3+}$  from their heavier counterparts in acidic solution, thereby providing a possible method for separating heavy and light  $\text{Ln}^{3+}$  cations. The three TMeQ[6]- $\text{Ln}^{3+}$  interaction systems described above are summarized in Table 1.



**Figure 1.** Structure of symmetrical TMeQ[6].

**Table 1.** The three TMeQ[6]- $\text{Ln}^{3+}$  systems characterized in this study.

TMeQ[6]: $\text{Ln}^{3+}$ ratio and conditions	$\text{Ln}^{3+}$ La.....Lu series and formation time		
1:10 in $\text{H}_2\text{O}$	1:1 complexes. La, Ce. 40 day	1:1 adducts. Pr, Nd, Sm. 7 day	Precipitation. Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. 1 day
1:2 in $\text{H}_2\text{O}$	3:2 triple-deckers. La, Ce, Pr, Nd. 1 day	1:1 adducts. Sm, Eu. 1 day	Precipitation Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. 4 hours
1:4 in HCl (6 M)	Precipitation. La, Ce. 4 hour	1:2 complexes. Pr, Nd, Sm, Eu. 1 day	1:1 adducts. Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. 15 day

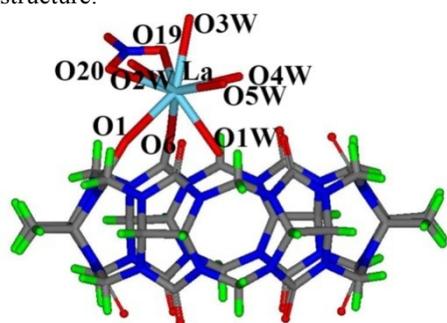
## Results and discussion

### Description of crystal structures

Cucurbit[*n*]uril (Q[*n*]) and alkyl-substituted cucurbit[*n*]urils (SQ[*n*]s) can interact with  $\text{Ln}^{3+}$  to form different adducts, simple coordination complexes, and coordination poly-dimensional polymers with supramolecular assemblies.<sup>6g-6p</sup> The interaction or coordination of Q[*n*] molecules with  $\text{Ln}^{3+}$  is strongly affected by synthetic conditions. TMeQ[6] is much more water-soluble than unsubstituted Q[6], and this allowed for the investigation of its coordination and supramolecular assemblies with  $\text{Ln}^{3+}$  in neutral aqueous solution. We also evaluated the coordination and supramolecular assemblies of TMeQ[6] with  $\text{Ln}^{3+}$  in 6 M HCl.

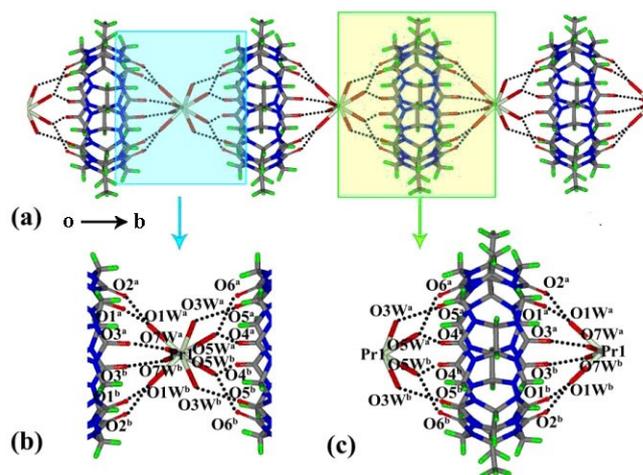
With a molar ratio of TMeQ[6] to  $\text{Ln}^{3+}$  of 1:10 in a neutral aqueous solution, a simple complex was formed through direct coordination of lighter  $\text{Ln}^{3+}$  ions with portal carbonyl oxygens of TMeQ[6]. Compound **1** (Figure 2) is a representative example of this isomorphous group. The crystal structure shows a TMeQ[6] molecule coordinated by a single  $\text{La}^{3+}$  cation at one of the two opening portals. The  $\text{La}^{3+}$  cation itself is coordinated with nine oxygens (two carbonyl oxygens [O1, O6], five water molecules [O1W, O2W, O3W, O4W, O5W], and two oxygens [O19, O20] from a nitrate anion). The bond distances between  $\text{La}^{3+}$  cations and the carbonyl oxygen atoms are in the range 2.49–2.54 Å, the distance between  $\text{La}^{3+}$  and the coordinated water oxygen atoms are 2.49–2.57 Å, and the bond distances between  $\text{La}^{3+}$  and oxygen atoms from the coordinated nitrate anion are 2.60–2.67 Å. Closer inspection revealed that the portal carbonyl oxygens coordinating the  $\text{La}^{3+}$  belonged to a dimethyl-substituted glycouril moiety and an unsubstituted glycouril moiety in the TMeQ[6] molecule. The rest of the

features of compound **2** in this isomorphous group had a similar structure.



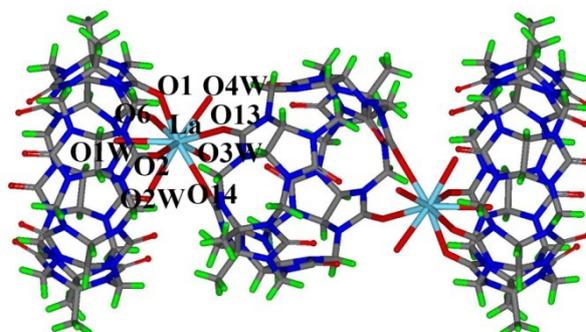
**Figure 2.** Crystal structure of compound **1** showing the coordination between TMeQ[6] molecules and  $\text{La}^{3+}$  cations. Solvate water molecules and nitrate anions are omitted for clarity.

TMeQ[6] interacted with the remaining  $\text{Ln}^{3+}$  cations to form powders containing TMeQ[6] and  $\text{Ln}^{3+}$  within 1 day, except for  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  which required 2 weeks. Compound **3** is an adduct formed through hydrogen bonding between portal carbonyl oxygens and coordinated water molecules of the  $[\text{Pr}(\text{H}_2\text{O})_8]^{3+}$  aqua complex and is a representative example of this isomorphous group. The crystal structure of the adduct revealed the formation of an alternative TMeQ[6] and  $[\text{Pr}(\text{H}_2\text{O})_8]^{3+}$  supramolecular chain (Figure 3a) in which each  $[\text{Pr}(\text{H}_2\text{O})_8]^{3+}$  complex interacts with two TMeQ[6] molecules, and in turn, each TMeQ[6] molecule is sandwiched between two  $[\text{Pr}(\text{H}_2\text{O})_8]^{3+}$  complexes through hydrogen bonding of the coordinated water molecules and six portal carbonyl oxygens ( $\text{O1W}^a$ ,  $\text{O3W}^a$ ,  $\text{O5W}^a$ ,  $\text{O7W}^a$  with  $\text{O1}^a$ ,  $\text{O2}^a$ ,  $\text{O3}^a$ ,  $\text{O4}^a$ ,  $\text{O5}^a$ ,  $\text{O6}^a$ ;  $\text{O1W}^b$ ,  $\text{O3W}^b$ ,  $\text{O5W}^b$ ,  $\text{O7W}^b$  with  $\text{O1}^b$ ,  $\text{O2}^b$ ,  $\text{O3}^b$ ,  $\text{O4}^b$ ,  $\text{O5}^b$  and  $\text{O6}^b$ ; Figure 3b, c). The distances between the  $\text{Pr}^{3+}$  cation and coordinated water oxygen atoms are in the range 2.50–2.62 Å, and the bond distances between the coordinated water oxygens with portal carbonyl oxygens of TMeQ[6] are in the range 2.40–2.76 Å. The remainder of the structural features of **4** and **6** were shared by the other structures in this isomorphous family. TMeQ[6] interacted with the heavier  $\text{Ln}^{3+}$  cations such as  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Lu}^{3+}$ , and formed powders within a short period of time that were not suitable for single crystal X-ray crystallography (Figure S1, see ESI†).



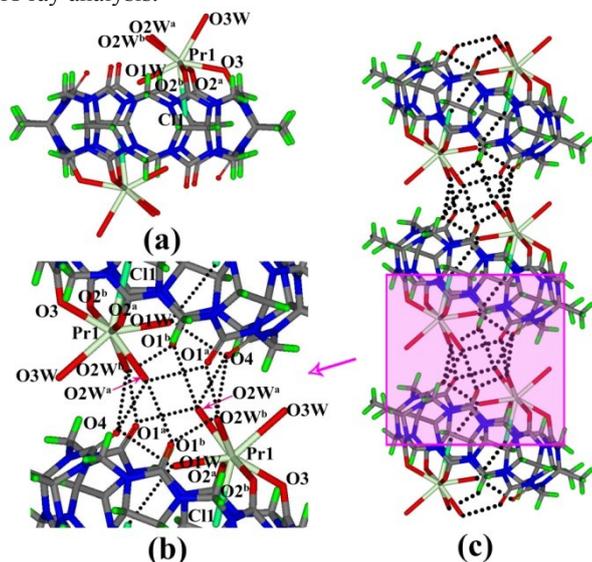
**Figure 3.** Crystal structure of compound **3**: (a) supramolecular chain of alternating  $[\text{Pr}(\text{H}_2\text{O})_8]^{3+}$  complexes and TMeQ[6] molecules; (b) adduct of TMeQ[6] molecules with a  $[\text{Pr}(\text{H}_2\text{O})_8]^{3+}$  complex; (c) interaction of TMeQ[6] complexes and  $\text{Pr}^{3+}$  cations. Solvate water molecules and chloride anions are omitted for clarity.

When the molar ratio of TMeQ[6] to  $\text{Ln}^{3+}$  in neutral aqueous solution was 1:2, four triple-decker sandwich complexes of TMeQ[6] were formed with the four lightest  $\text{Ln}^{3+}$  cations ( $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Nd}^{3+}$ ). Compound **1'** containing a  $\text{La}^{3+}$  cation is a representative example of this isomorphous group (Figure 4). The crystal structure shows three TMeQ[6] molecules linked by two  $\text{La}^{3+}$  cations, and each  $\text{La}^{3+}$  cation is itself coordinated by nine oxygens (five carbonyl oxygens  $\text{O1}$ ,  $\text{O2}$ ,  $\text{O6}$ ,  $\text{O13}$  and  $\text{O14}$  from neighboring TMeQ[6] molecules, and four coordinated water molecules  $\text{O1W}$ ,  $\text{O2W}$ ,  $\text{O3W}$  and  $\text{O4W}$ ). The bond distances between  $\text{La}^{3+}$  cations and carbonyl oxygen atoms are in the range 2.46–2.55 Å, and the distances between the  $\text{La}^{3+}$  cation and coordinated water oxygen atoms are 2.45–2.77 Å. Similarly, the  $\text{La}^{3+}$  cation preferred to coordinate with the portal carbonyl oxygen belonging to the dimethyl substituted glycouril moiety. The other three isomorphous compounds in this group (**2'**, **3'** and **4'**) possessed similar structural features. Moreover, compound **7'**, an adduct of TMeQ[6] with the aqua complex of  $\text{Ln}^{3+}$ , exhibited similar structural features to those in the first isomorphous group.



**Figure 4.** X-ray crystal structure of compound **1'**: (a) coordination between TMeQ[6] molecules and  $\text{La}^{3+}$  cations. Solvate water molecules and nitrate anions are omitted for clarity.

When the molar ratio of TMeQ[6] to  $\text{Ln}^{3+}$  was 1:4 in 6 M HCl the interaction of TMeQ[6] with  $\text{Ln}^{3+}$  resulted in the formation of molecular capsules when  $\text{Ln}^{3+}$  was  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  or  $\text{Sm}^{3+}$ . A complex of TMeQ[6] with a  $\text{Pr}^{3+}$  cation (compound **3''**; Figure 5a) is a representative example of this isomorphous group, and the crystal structure shows both portals of the TMeQ[6] molecule coordinated with one  $\text{Pr}^{3+}$  cation. The  $\text{Pr}^{3+}$  cation is coordinated by eight atoms (three carbonyl oxygens  $\text{O2}^a$ ,  $\text{O2}^b$  and  $\text{O3}$ , four water molecules  $\text{O1W}$ ,  $\text{O2W}^a$ ,  $\text{O2W}^b$  and  $\text{O3W}$ , and an included chloride anion  $\text{Cl1}$ ). The bond distances between the  $\text{Pr}^{3+}$  cation and the carbonyl oxygen atoms are in the range 2.45–2.47 Å, the distances between the  $\text{Pr}^{3+}$  cation and the coordinated water oxygen atoms are in the range 2.44–2.84 Å, and the bond distance between the  $\text{Pr}^{3+}$  cation and chlorine is 2.83 Å. TMeQ[6]/ $\text{Pr}^{3+}$  molecular capsules interacted with each other through hydrogen bonding between the coordinated water molecules ( $\text{O2W}^a$  and  $\text{O2W}^b$ ) and the portal carbonyl oxygens ( $\text{O1}^a$ ,  $\text{O1}^b$ ,  $\text{O4}$ ; Figure 5b and c). It is known that the  $\text{Pr}^{3+}$  cation coordinates with the portal carbonyl oxygen of the two dimethyl substituted glycouril moieties, due to the electron donating effect of the alkyl-substituted group, such as dimethyl.<sup>27</sup> The other three isomorphous compounds **4''** and **6''** exhibited similar conformations. TMeQ[6] interacted with the heavier  $\text{Ln}^{3+}$  and formed a series of adducts (**8''–15''**), which were isomorphous and shared similar structural features with the aforementioned compounds. It should be noted that TMeQ[6] interacted with  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  cations and rapidly formed solid powders that were not suitable for single crystal X-ray analysis.



**Figure 5.** Crystal structure of compound **3''**: (a) coordination between a TMeQ[6] molecule and  $\text{Pr}^{3+}$  cations; (b and c) interactions between TMeQ[6] molecular capsules through

hydrogen bonding. Solvate water molecules and chloride anions are omitted for clarity.

#### Isothermal Titration Calorimetry (ITC)

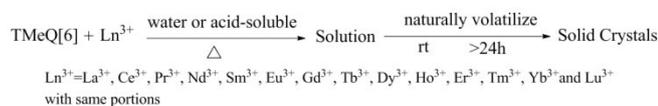
Single crystal X-ray diffraction can be performed to investigate the interactions occurring between TMeQ[6] molecules and  $\text{Ln}^{3+}$  ions in the solid state. Spectroscopy and spectral analysis are generally not suitable for examining the interactions of  $\text{Q}[n]$ s with metal ions or their complexes in solution. ITC is a quantitative technique for determining dynamic parameters such as association constants ( $K$ ), enthalpy changes ( $\Delta H$ ), and binding stoichiometry ( $n$ ) of interactions between two or more molecules in solution. In the present work, the results of ITC showed that the  $K$  values for the interactions between TMeQ[6] with  $\text{Ln}^{3+}$  gradually decreased with increasing atomic number, suggesting that lighter  $\text{Ln}^{3+}$  cations have a higher affinity for the portal carbonyl oxygens of TMeQ[6] than the heavier  $\text{Ln}^{3+}$  cations. In particular, the binding stoichiometry ( $n$ ) for the first three light  $\text{Ln}^{3+}$  cations ( $\text{La}$ ,  $\text{Ce}$ , and  $\text{Pr}$ ) was close to 1, whereas that of the remaining  $\text{Ln}^{3+}$  cations was close to 0.5, suggesting that TMeQ[6] and  $\text{Ln}^{3+}$  have different ‘interaction models’ in neutral water. Although we do not really know the detailed reasons, the 4f orbitals exhibit poor shielding of the nuclear charge leading to a small monotonic contraction of the ionic radii of the  $\text{Ln}^{3+}$  ions with increasing atomic number. The radii decrease from 1.03 Å for  $\text{La}^{3+}$  to 0.86 Å for  $\text{Lu}^{3+}$ . The differences in the interaction of the individual  $\text{Ln}^{3+}$  ions with a selected  $\text{Q}[n]$ , such as TMeQ[6] in this case could reflect the size differences between these ions. From the initial ITC measurements, changes in the Gibbs free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) may be determined using the following equation:  $\Delta G_{\text{standard}} = -RT \ln K = \Delta H_{\text{standard}} - T\Delta S_{\text{standard}}$ , where  $R$  is the gas constant and  $T$  is the absolute temperature. Generally,  $T\Delta S$  values are larger than  $\Delta H$ , suggesting that  $T\Delta S$  is the main driving force of the reaction between TMeQ[6] and  $\text{Ln}^{3+}$  that results in the formation of complexes or adducts (Table 2, Figure S2, see ESI†).

**Table 2.** Association constants of related  $\text{Ln}^{3+}$ –TMeQ[6] interaction products at 277.15 K.

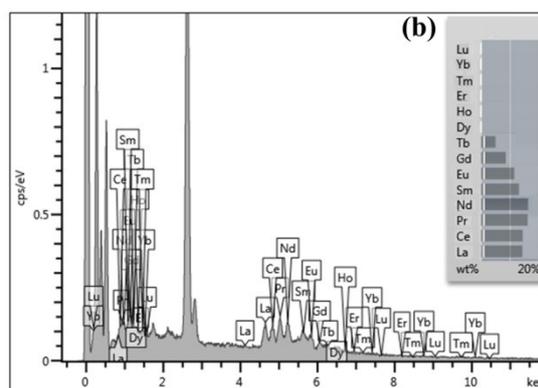
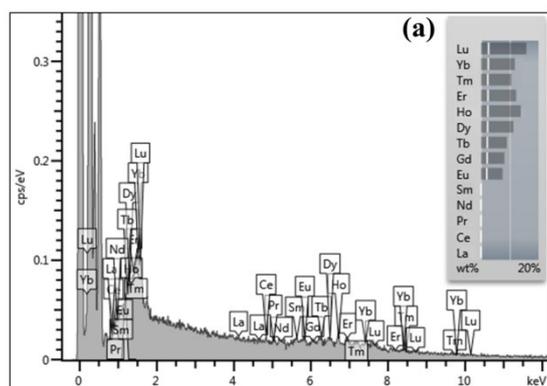
Experiment	$K$ (1/M)	$\Delta H$ (kJ/mol)	$n$	$T\Delta S$ (kJ/mol)
La	$(4.55 \pm 0.6) \times 10^4$	$-10.96 \pm 0.2$	$0.858 \pm 0.01$	13.75
Ce	$(4.07 \pm 0.8) \times 10^4$	$-8.616 \pm 0.3$	$0.876 \pm 0.02$	15.84
Pr	$(3.95 \pm 0.6) \times 10^4$	$-6.720 \pm 0.2$	$0.894 \pm 0.02$	17.67
Nd	$(2.84 \pm 0.7) \times 10^4$	$-5.187 \pm 0.5$	$0.511 \pm 0.04$	18.44
Sm	$(2.74 \pm 0.6) \times 10^4$	$-8.341 \pm 0.6$	$0.526 \pm 0.03$	15.21
Eu	$(2.64 \pm 0.4) \times 10^4$	$-9.730 \pm 0.6$	$0.475 \pm 0.02$	13.73
Gd	$(2.50 \pm 0.6) \times 10^4$	$-9.576 \pm 0.9$	$0.457 \pm 0.03$	13.76
Tb	$(2.43 \pm 0.5) \times 10^4$	$-8.874 \pm 0.8$	$0.462 \pm 0.03$	14.40
Dy	$(2.33 \pm 0.4) \times 10^4$	$-8.242 \pm 0.8$	$0.430 \pm 0.03$	14.93
Ho	$(2.28 \pm 0.4) \times 10^4$	$-5.987 \pm 0.6$	$0.404 \pm 0.03$	17.14
Er	$(2.10 \pm 0.6) \times 10^4$	$-6.707 \pm 0.9$	$0.421 \pm 0.04$	16.23
Tm	$(1.68 \pm 0.5) \times 10^4$	$-4.235 \pm 0.6$	$0.537 \pm 0.05$	18.18
Yb	$(1.59 \pm 0.4) \times 10^4$	$-2.864 \pm 0.3$	$0.517 \pm 0.04$	19.43

Lu (1.42 ± 0.4) × 10<sup>4</sup> -5.548 ± 0.7 0.528 ± 0.05 16.48**Energy Dispersive spectroscopy (EDS)**

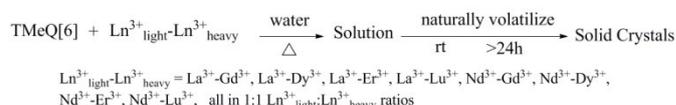
As previously mentioned, different Q[n]s can selectively interact with a series of Ln<sup>3+</sup> cations and form different products that are strongly dependent on the synthetic conditions employed. Using such differences, varying strategies for the isolation of Ln<sup>3+</sup> in solution can be established. For example, a previous study revealed that in the presence of [CdCl<sub>4</sub>]<sup>2-</sup> or [ZnCl<sub>4</sub>]<sup>2-</sup>, unsubstituted Q[6] could be used to isolate the first four light Ln<sup>3+</sup> ions (La, Ce, Pr, Nd) from their heavier counterparts. A recent study demonstrated that in the presence of Cd(NO<sub>3</sub>)<sub>3</sub>, *o*-TMeQ[6] can coordinate with most lanthanide cations to form solid crystals, but not with the lightest Ln<sup>3+</sup> ions (La, Ce, Pr), which remain in solution. Similarly, *o*-TMeQ[6]-Ln<sup>3+</sup>-Cd(NO<sub>3</sub>)<sub>3</sub> systems can separate heavier Ln<sup>3+</sup> cations from lighter Ln<sup>3+</sup> cations by forming solid crystals. The alkyl-substituted TMeQ[6] is both water- and acid-soluble, and interactions with lanthanide cations can be investigated in neutral or acidic (e.g., 6 M HCl) conditions (See Scheme 1). Co-precipitation experiments in which all Ln<sup>3+</sup> cations exist in the same proportions in water and in 6 M HCl revealed that TMeQ[6]-Ln<sup>3+</sup>-H<sub>2</sub>O systems can separate heavier Ln<sup>3+</sup> cations from lighter lanthanides by forming solid crystals regardless of whether the molar ratio of TMeQ[6] to Ln<sup>3+</sup> was 1:10 or 1:2 (see Figure 6a). Similarly, TMeQ[6]-Ln<sup>3+</sup>-HCl systems can separate lighter Ln<sup>3+</sup> cations from heavier lanthanides by forming solid crystals (see Figure 6b).



**Scheme 1.** TMeQ[6]-Ln<sup>3+</sup>-H<sub>2</sub>O systems with the same proportion of Ln<sup>3+</sup> and TMeQ[6]-Ln<sup>3+</sup>-HCl(6 M) systems with the same proportion of Ln<sup>3+</sup>.



**Figure 6.** EDS of co-precipitation from (a) a TMeQ[6]-Ln<sup>3+</sup>-H<sub>2</sub>O systems with the same proportion of Ln<sup>3+</sup>; (b) a TMeQ[6]-Ln<sup>3+</sup>-HCl(6 M) systems with the same proportion of Ln<sup>3+</sup>.



**Scheme 2.** TMeQ[6] to Ln<sup>3+</sup> was 1:10 in neutral aqueous solution.

Detailed experiments further confirmed our hypothesis. For example, when the molar ratio of TMeQ[6] to Ln<sup>3+</sup> was 1:10 in neutral aqueous solution (See Scheme 2), eight typical Ln<sup>3+</sup><sub>light</sub>-Ln<sup>3+</sup><sub>heavy</sub>-TMeQ[6] systems were selected as representatives (Ln<sup>3+</sup><sub>light</sub>-Ln<sup>3+</sup><sub>heavy</sub> = La<sup>3+</sup>-Gd<sup>3+</sup>, La<sup>3+</sup>-Dy<sup>3+</sup>, La<sup>3+</sup>-Er<sup>3+</sup>, La<sup>3+</sup>-Lu<sup>3+</sup>, Nd<sup>3+</sup>-Gd<sup>3+</sup>, Nd<sup>3+</sup>-Dy<sup>3+</sup>, Nd<sup>3+</sup>-Er<sup>3+</sup>, Nd<sup>3+</sup>-Lu<sup>3+</sup>), all in a 1:1 Ln<sup>3+</sup><sub>light</sub> : Ln<sup>3+</sup><sub>heavy</sub> ratio. EDS results revealed that the crystals from systems with 1:1 Ln<sup>3+</sup><sub>light</sub> : Ln<sup>3+</sup><sub>heavy</sub> ratios contained 80%–100% heavy Ln<sup>3+</sup> cations (Figure S3, see ESI†), whereas most lighter lanthanides remained in the mother liquor. We also tested a molar ratio of TMeQ[6] to Ln<sup>3+</sup> of 1:2 in neutral aqueous solution using six typical Ln<sup>3+</sup><sub>light</sub>-Ln<sup>3+</sup><sub>heavy</sub>-TMeQ[6] systems as representative examples (Ln<sup>3+</sup><sub>light</sub>-Ln<sup>3+</sup><sub>heavy</sub> = La<sup>3+</sup>-Gd<sup>3+</sup>, La<sup>3+</sup>-Er<sup>3+</sup>, La<sup>3+</sup>-Lu<sup>3+</sup>, Nd<sup>3+</sup>-Gd<sup>3+</sup>, Nd<sup>3+</sup>-Er<sup>3+</sup>, Nd<sup>3+</sup>-Lu<sup>3+</sup>), all at a 1:1 ratio. EDS showed that these crystals contained 80%–90% heavy lanthanides (Figure S4, see ESI†), whereas the majority of the lighter lanthanides remained in solution. In addition, six typical Ln<sup>3+</sup><sub>heavy</sub>-Ln<sup>3+</sup><sub>light</sub>-TMeQ[6]-HCl systems were selected as representative examples (Ln<sup>3+</sup><sub>heavy</sub>-Ln<sup>3+</sup><sub>light</sub> = Tb<sup>3+</sup>-Ce<sup>3+</sup>, Tb<sup>3+</sup>-Sm<sup>3+</sup>, Er<sup>3+</sup>-Ce<sup>3+</sup>, Er<sup>3+</sup>-Sm<sup>3+</sup>, Lu<sup>3+</sup>-Ce<sup>3+</sup>, Lu<sup>3+</sup>-Sm<sup>3+</sup>), all at a 1:1 ratio. EDS showed that these crystals contained 90%–100% light Ln<sup>3+</sup> cations (Figure S5, see ESI†), while heavy Ln<sup>3+</sup> cations remained in the mother liquor. These results suggest that these systems could be effectively used to separate heavy and light Ln<sup>3+</sup> cations in neutral aqueous solution, and to isolate lighter Ln<sup>3+</sup> cations from their heavier counterparts under acidic conditions.

Other characteristics of the adducts determined using PXRD, thermal analysis and Fourier transform infrared spectroscopy (FT-IR) are shown in the Electronic supplementary information. PXRD measurements of representative crystals from the four isomorphous groups were compared with simulations, which confirmed that the samples were essentially of a pure

crystalline phase (Figure S6–S8, see ESI†). Thermal analysis was performed to generate DSC and TG curves of representative crystals of two isomorphous groups, and this revealed no marked differences between crystals, although they were different from TMeQ[6] complexes (Figure S9–S11, see ESI†). Furthermore, FT-IR spectra showed that the absorption bands of the portal carbonyl of the four isomorphous groups at high-wavelength numbers were different (Figure S12–S14, see ESI†).

## Conclusions

In summary, we have investigated the coordination and interaction of TMeQ[6] molecules with a series of Ln<sup>3+</sup> cations under neutral and acidic solutions with different proportions of TMeQ[6] and Ln<sup>3+</sup> cations. X-ray diffraction analysis revealed that the structures and properties (e.g., solubility) of the TMeQ[6]/Ln<sup>3+</sup> complexes and adducts were strongly dependent on the structural features of the lanthanides and on the experimental conditions (e.g., ion dimension, pH, proportion of components in systems) employed. Generally, lighter lanthanides formed complexes with TMeQ[6], presumably due to the larger ionic diameters. In contrast, heavier lanthanides tended to form aqua complexes which formed adducts with TMeQ[6], and this was likely due to the shorter ionic diameters. Generally, the poor shielding of 4f orbitals results in the increase of the nuclear charge and the Ln<sup>3+</sup> ions have an increased hydrolysis tendency and the hydrolyzed products have a decreased solubility with increasing atomic number. Moreover, the acidic medium prohibited hydrolysis of the lanthanides and subsequent formation of aqua complexes in aqueous solutions, therefore most lanthanide cations formed complexes with TMeQ[6]. Generally, the more acidic the medium, the faster the formation of crystals of complexes or adducts. Importantly, these differences could be used to separate heavier Ln<sup>3+</sup> cations from their lighter counterparts in neutral solution, and to isolate lighter Ln<sup>3+</sup> cations from heavier lanthanides in acidic conditions. Further studies aimed towards developing such separation techniques are ongoing in our laboratory.

## Experimental

**Synthesis:** Chemicals including lanthanide nitrates were of reagent grade and were used without further purification. TMeQ[6] was prepared as previously reported.<sup>37</sup> Elemental analyses were carried out using a EURO EA-3000 elemental analyzer. A similar process was used to prepare crystals of related compounds as follows:

(1) Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (0.081 mmol) was dissolved in 2.5 mL neutral water (solution A); TMeQ[6] (10 mg, 0.008 mmol) was dissolved in 2.5 mL neutral water (solution B), added to solution A and stirred. X-ray diffraction-quality crystals were obtained from the solution over a period of hours to months depending on the lanthanide cation present. Crystal colour was also dependent on the lanthanide. To summarize the

preparations, [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)La(H<sub>2</sub>O)<sub>5</sub>(NO<sub>3</sub>)<sub>3</sub>]·4(NO<sub>3</sub>)·13(H<sub>2</sub>O) (**1**) was obtained from La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.035 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Ce(H<sub>2</sub>O)<sub>5</sub>]·3(NO<sub>3</sub>)·7(H<sub>2</sub>O) (**2**) was obtained from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.035 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Pr(H<sub>2</sub>O)<sub>8</sub>]·3(OH)·20(H<sub>2</sub>O) (**3**) was obtained from Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.035 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Nd(H<sub>2</sub>O)<sub>8</sub>]·3(OH)·10(H<sub>2</sub>O) (**4**) was obtained from Nd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.036 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Sm(H<sub>2</sub>O)<sub>8</sub>]·3(OH)·9(H<sub>2</sub>O) (**6**) was obtained from Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.036 g).

(2) Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (0.040 mmol) was dissolved in 1.25 mL neutral water (solution A), TMeQ[6] (25 mg, 0.020 mmol) was dissolved in 1.25 mL neutral water (solution B), and these were mixed and stirred. Crystal colour was again dependent on the lanthanide. To summarize the preparations, [(C<sub>120</sub>H<sub>132</sub>N<sub>72</sub>O<sub>36</sub>)La<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>]·6(NO<sub>3</sub>)·58(H<sub>2</sub>O) (**1'**) was obtained from La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.018 g); [(C<sub>120</sub>H<sub>132</sub>N<sub>72</sub>O<sub>36</sub>)Ce<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>]·6(NO<sub>3</sub>)·10(H<sub>2</sub>O) (**2'**) was obtained from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.018 g); [(C<sub>120</sub>H<sub>132</sub>N<sub>72</sub>O<sub>36</sub>)Pr<sub>2</sub>]·6(NO<sub>3</sub>)·18(H<sub>2</sub>O) (**3'**) was obtained from Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.018 g); [(C<sub>120</sub>H<sub>132</sub>N<sub>72</sub>O<sub>36</sub>)Nd<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub>]·6(NO<sub>3</sub>)·40(H<sub>2</sub>O) (**4'**) was obtained from Nd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.018 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Eu(H<sub>2</sub>O)<sub>8</sub>]·3(OH)·13(H<sub>2</sub>O) (**7'**) was obtained from Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.018 g).

(3) Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (0.080 mmol) was dissolved in 1.25 mL 6 M HCl (solution A), TMeQ[6] (25 mg, 0.020 mmol) was dissolved in 1.25 mL 6 M HCl (solution B), and these were mixed and stirred. Crystal colour was again dependent on the lanthanide. To summarize the preparations, [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Pr<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·3Cl·17(H<sub>2</sub>O)·3NO<sub>3</sub> (**3''**) was obtained from Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.035 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Nd<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·2Cl·20(H<sub>2</sub>O)·2NO<sub>3</sub> (**4''**) was obtained from Nd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.036 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Sm<sub>2</sub>Cl<sub>2</sub>]·16(H<sub>2</sub>O)·4NO<sub>3</sub> (**6''**) was obtained from Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.036 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Gd(H<sub>2</sub>O)<sub>9</sub>]·3Cl·9(H<sub>2</sub>O) (**8''**) was obtained from Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.037 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Tb(H<sub>2</sub>O)<sub>8</sub>]·3Cl·4.5(H<sub>2</sub>O) (**9''**) was obtained from Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.037 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Dy(H<sub>2</sub>O)<sub>8</sub>]·3Cl·8(H<sub>2</sub>O) (**10''**) was obtained from Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.037 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Ho(H<sub>2</sub>O)<sub>8</sub>Cl<sub>2</sub>]·3Cl·10(H<sub>2</sub>O) (**11''**) was obtained from Ho(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.036 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Er(H<sub>2</sub>O)<sub>8</sub>]·3Cl·17(H<sub>2</sub>O) (**12''**) was obtained from Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.037 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Tm(H<sub>2</sub>O)<sub>8</sub>]·3Cl·11(H<sub>2</sub>O) (**13''**) was obtained from Tm(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.036 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Yb(H<sub>2</sub>O)<sub>8</sub>]·3Cl·11(H<sub>2</sub>O) (**14''**) was obtained from Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.036 g); [(C<sub>40</sub>H<sub>44</sub>N<sub>24</sub>O<sub>12</sub>)Lu(H<sub>2</sub>O)<sub>8</sub>]·3Cl·14(H<sub>2</sub>O) (**15''**) was obtained from Lu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.038 g).

In order to investigate the whole system, the number of compounds increased with increasing atomic number of the Ln<sup>3+</sup> series. Thus, compounds **1–4** and **6–15** corresponded to La–Nd and Sm–Lu, respectively.

**X-ray crystallography:** A suitable single crystal (~0.2 × 0.2 × 0.1 mm<sup>3</sup>) was taken up in paraffin oil and mounted on a Bruker

SMART Apex II CCD diffractometer equipped with a graphite monochromator Mo- $K_{\alpha}$  ( $\lambda = 0.71073 \text{ \AA}$ ,  $\mu = 0.828 \text{ mm}^{-1}$ ) radiation source operating in the  $\omega$ -scan mode with a nitrogen cold stream at  $-50^{\circ}\text{C}$ . Data were corrected for Lorentz and polarization effects using SAINT, and semi-empirical absorption corrections based on equivalent reflections were also applied using SADABS. The structures were elucidated by direct methods, and were refined using the full-matrix least-squares method using  $F^2$  and SHELXS-97. 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. 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 21 compounds are summarized in Table S1, see ESI†. In addition, the crystallographic data for the reported structures were deposited at the Cambridge Crystallographic Data Centre with the following supplementary publication numbers: CCDC-1038158 (1), 1038166 (2), 1038169 (3), 1038172 (4), 1038174 (6); CCDC-1038157 (1'), 1038165 (2'), 1038168 (3'), 1038171 (4'); 1038175 (7'); CCDC-1038167 (3''), 1038170 (4''), 1038173 (6''), 1038176 (8''), 1038177 (9''), 1038159 (10''), 1038160 (11''), 1038161 (12''), 1038162 (13''), 1038163 (14''), 1038164 (15''). Data can be obtained free of charge at [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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).

**Isothermal titration calorimetry:** Microcalorimetric experiments were performed using a Nano ITC 2G isothermal titration calorimeter (TA, USA). Each experiment consisted of 25 consecutive injections (10  $\mu\text{L}$ ) of 1 mM  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  into a microcalorimetric reaction cell containing 1.3 mL of 0.1 mM TMeQ[6] at 277.15 K. The heat of reaction was corrected for the heat of dilution of the cell solution which was determined in separate experiments. All solutions were degassed by sonication prior to the titration experiment. Computer simulations (curve fitting) were performed using the Nano ITC Analyze Software.

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## Notes and references

† Electronic supplementary information (ESI) available: crystallographic data, PXRD, thermal analysis and Fourier

transform infrared spectroscopy (FT-IR). For the ESI and crystallographic data in CIF See DOI: 10.1039/x0xx00000x

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