Electronic Supplementary Information (ESI)

Interaction of a symmetrical α,α',δ,δ'- tetramethylcucurbit[6]uril with Ln^{3+}: Potential for the Isolation of Lanthanides

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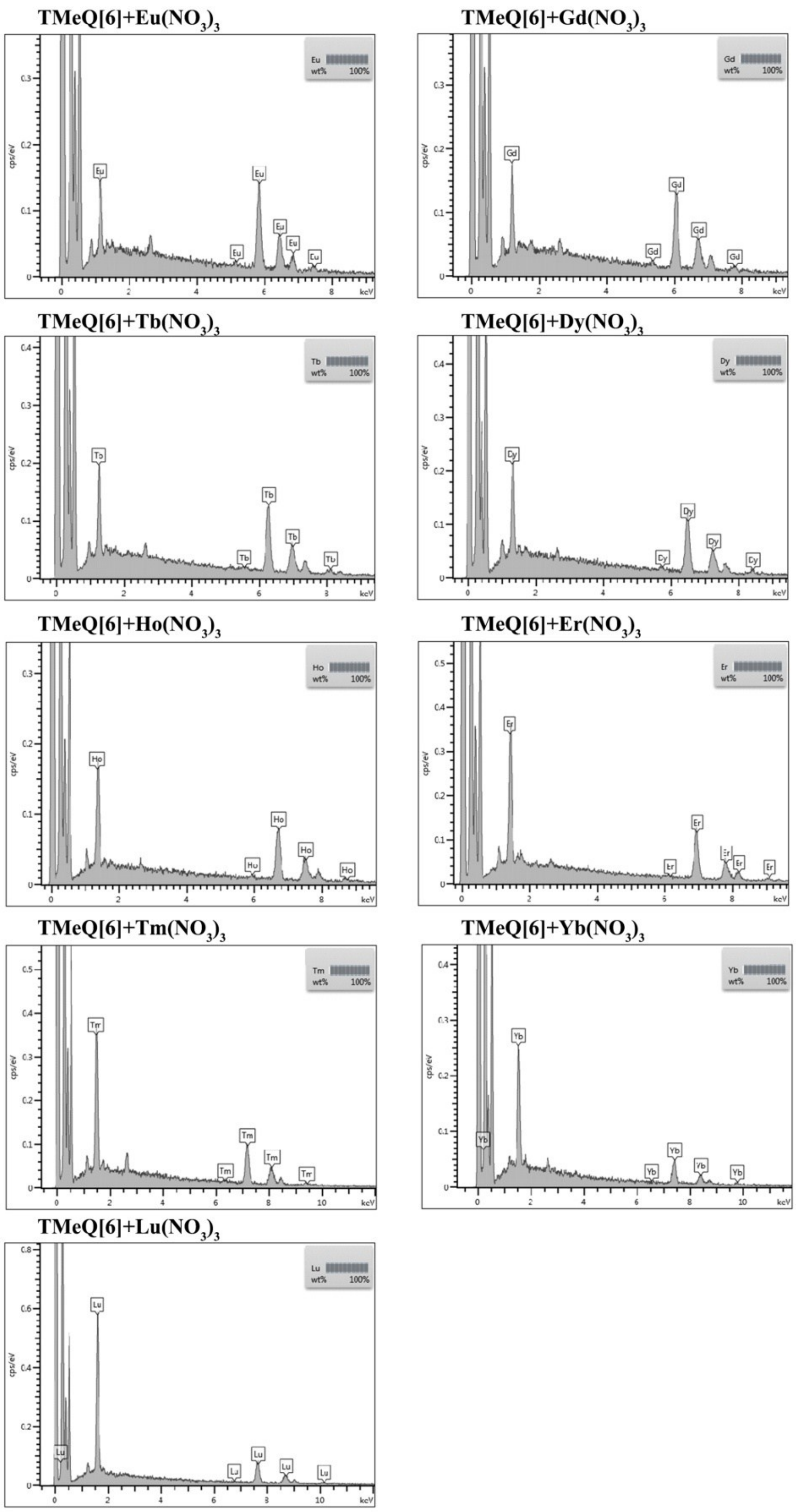

Figure S1 The energy dispersive spectroscopies of TMeQ[6]/Ln^{3+} systems using a 1:10 ratio of TMeQ[6] : lanthanides (Ln^{3+}=Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm3^{+}, Yb^{3+}, Lu^{3+}).

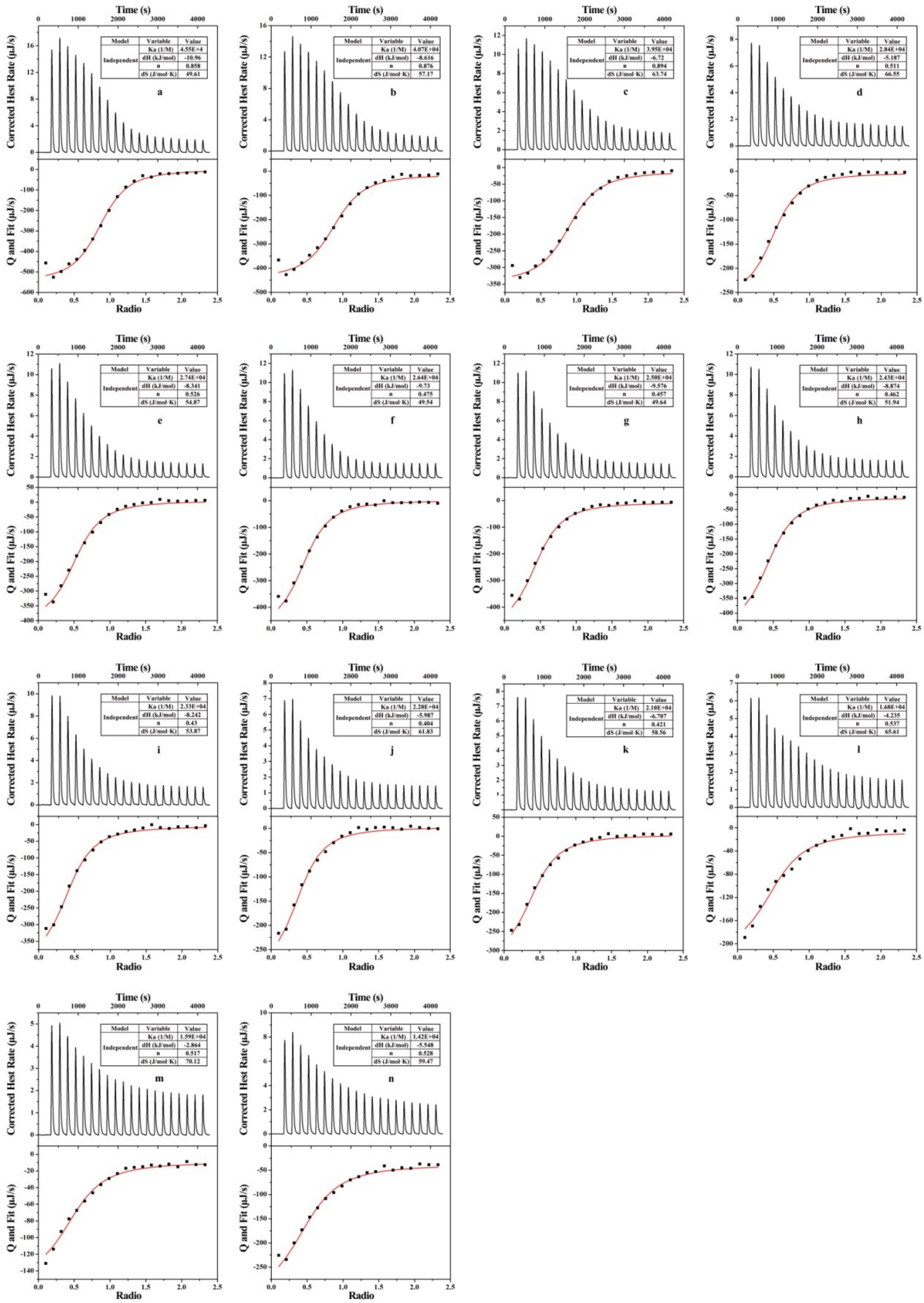

Figure S2 Isothermal titration calorimetry profiles of TMeQ[6] with $Ln(NO_3)_3$ in aqueous solution at 277.15 K. a) TMeQ[6]+$La(NO_3)_3$; b) TMeQ[6]+$Ce(NO_3)_3$; c) TMeQ[6]+$Pr(NO_3)_3$; d) TMeQ[6]+$Nd(NO_3)_3$; e) TMeQ[6]+$Sm(NO_3)_3$; f) TMeQ[6]+$Eu(NO_3)_3$; g) TMeQ[6]+$Gd(NO_3)_3$; h) TMeQ[6]+$Tb(NO_3)_3$; i) TMeQ[6]+$Dy(NO_3)_3$; j) TMeQ[6]+$Ho(NO_3)_3$; k) TMeQ[6]+$Er(NO_3)_3$; l) TMeQ[6]+$Tm(NO_3)_3$; m) TMeQ[6]+$Yb(NO_3)_3$; n) TMeQ[6]+$Lu(NO_3)_3$.

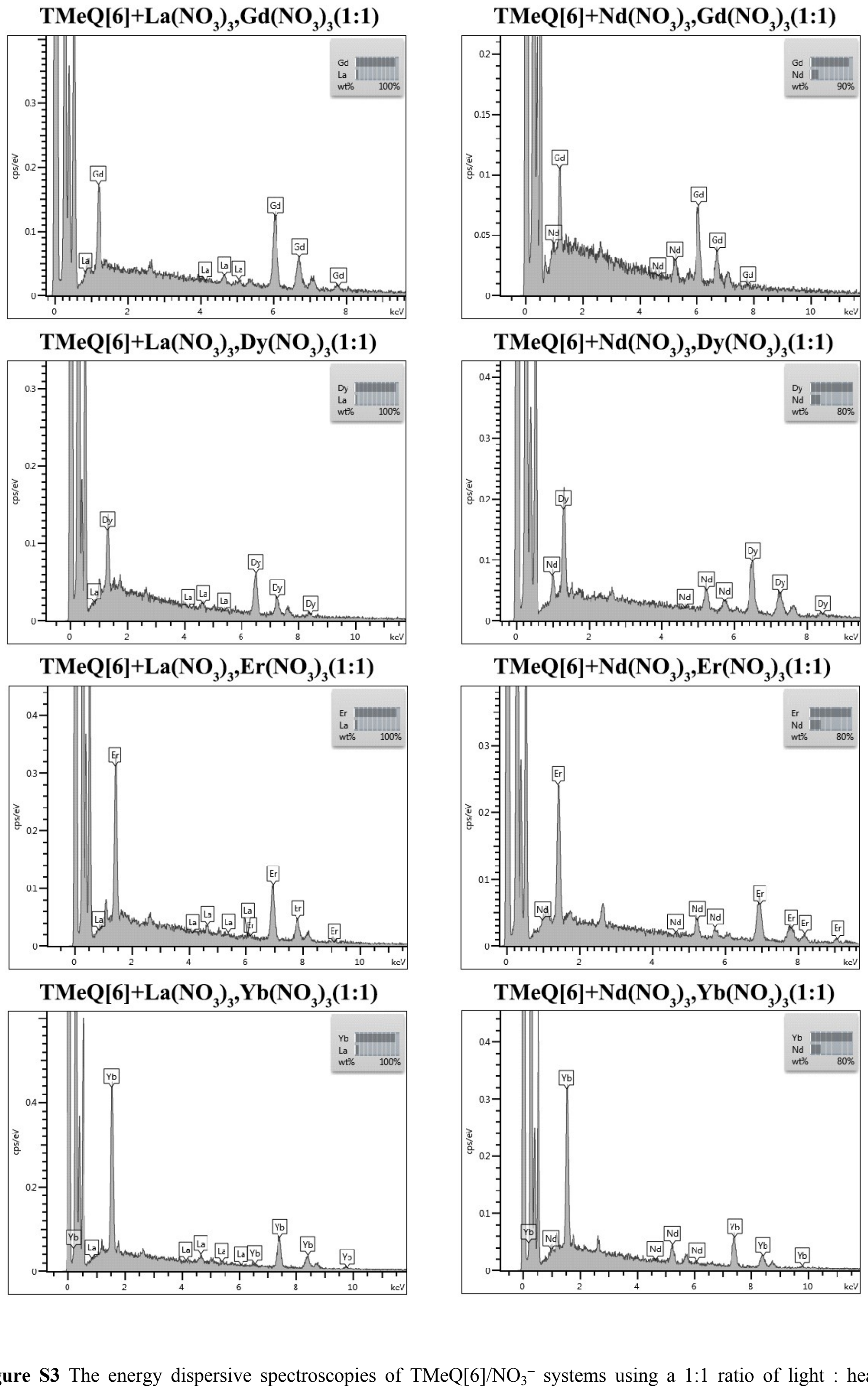

Figure S3 The energy dispersive spectroscopies of TMeQ[6]/NO_3^- systems using a 1:1 ratio of light : heavy lanthanides.

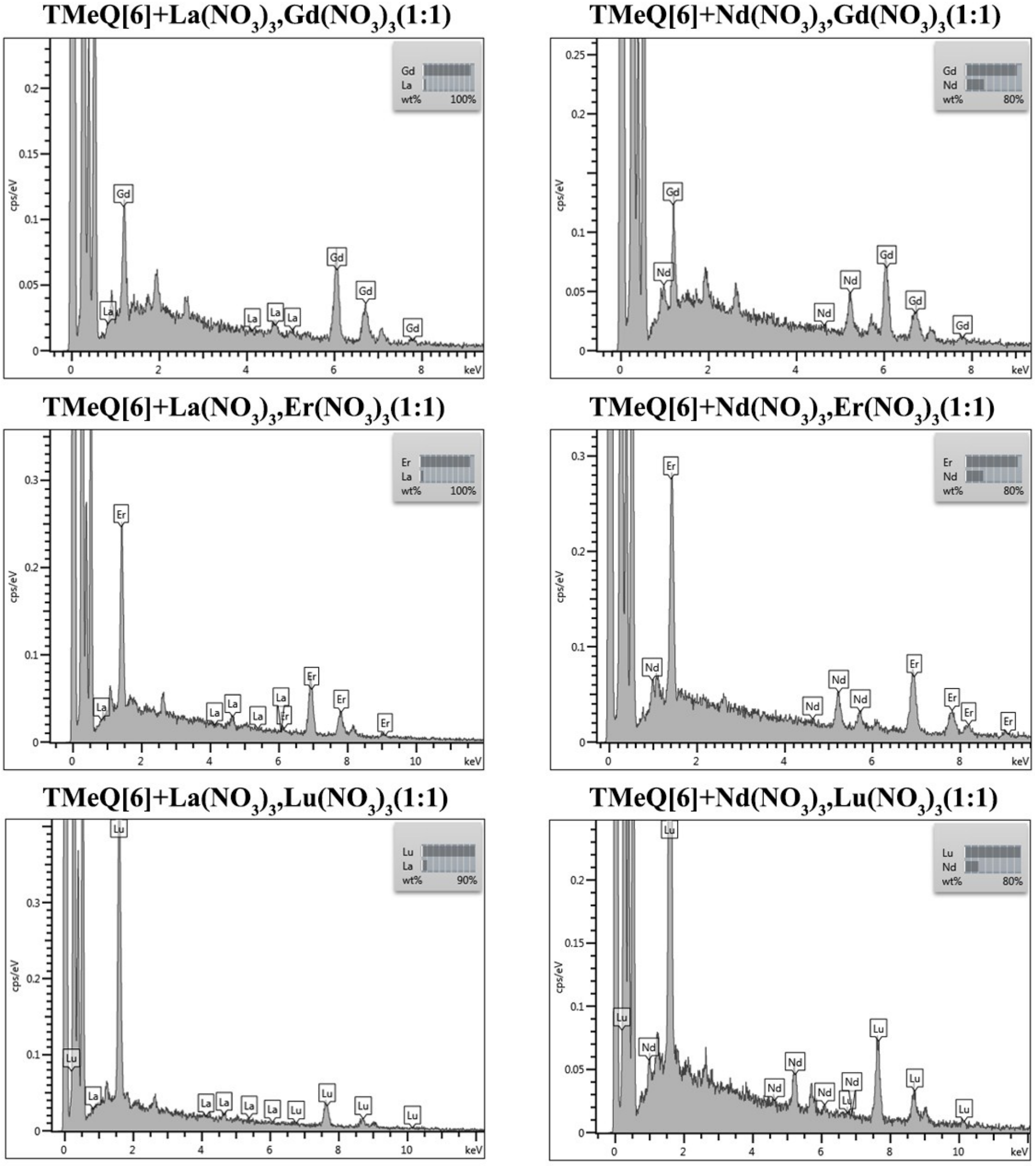

Figure S4 The energy dispersive spectroscopies of TMeQ[6]/NO_3^- systems using a 1:1 ratio of light : heavy lanthanides.

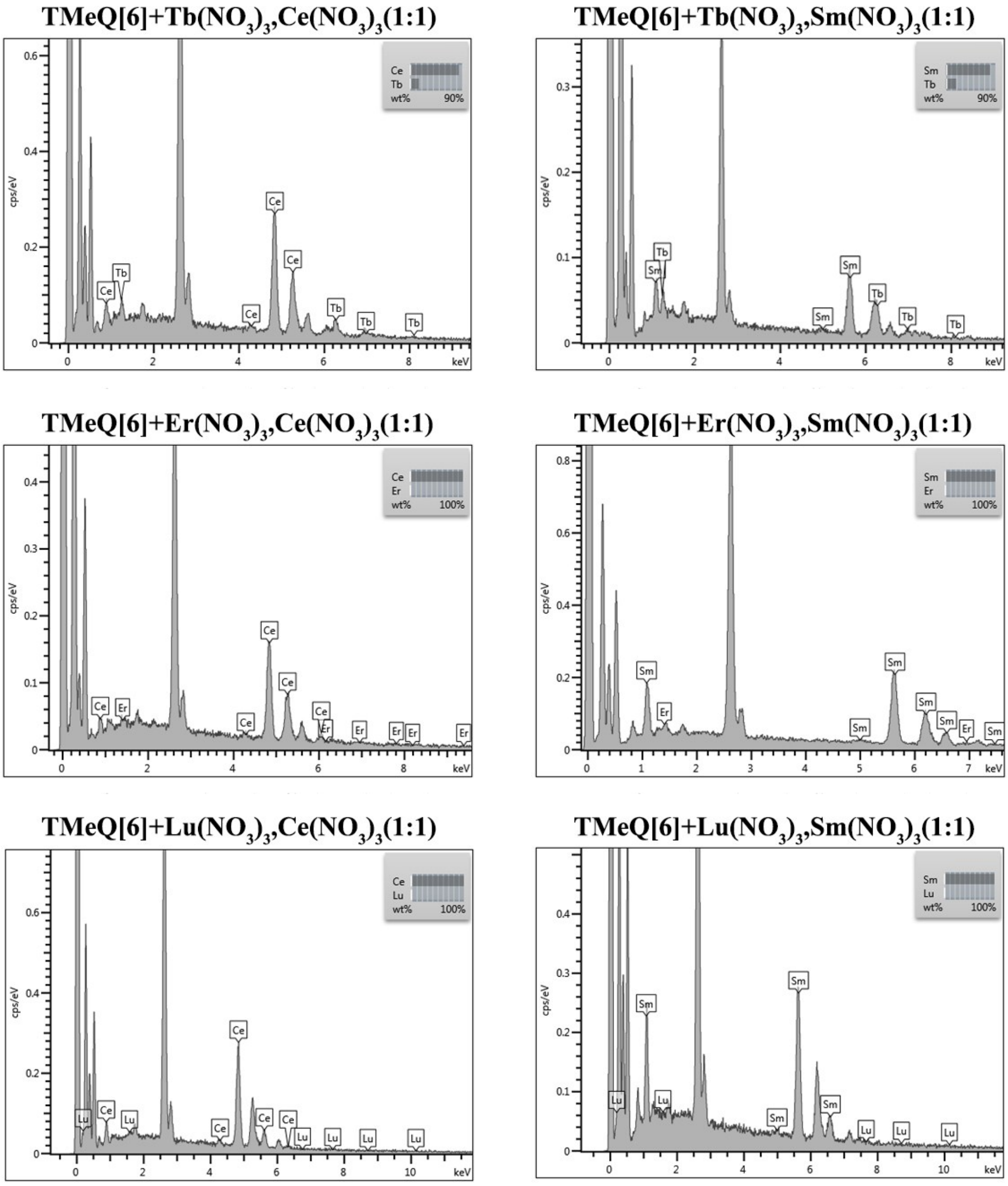

Figure S5 The electron spectroscopies of TMeQ[6]/NO_3^- systems using a 1:1 ratio of light : heavy lanthanides.

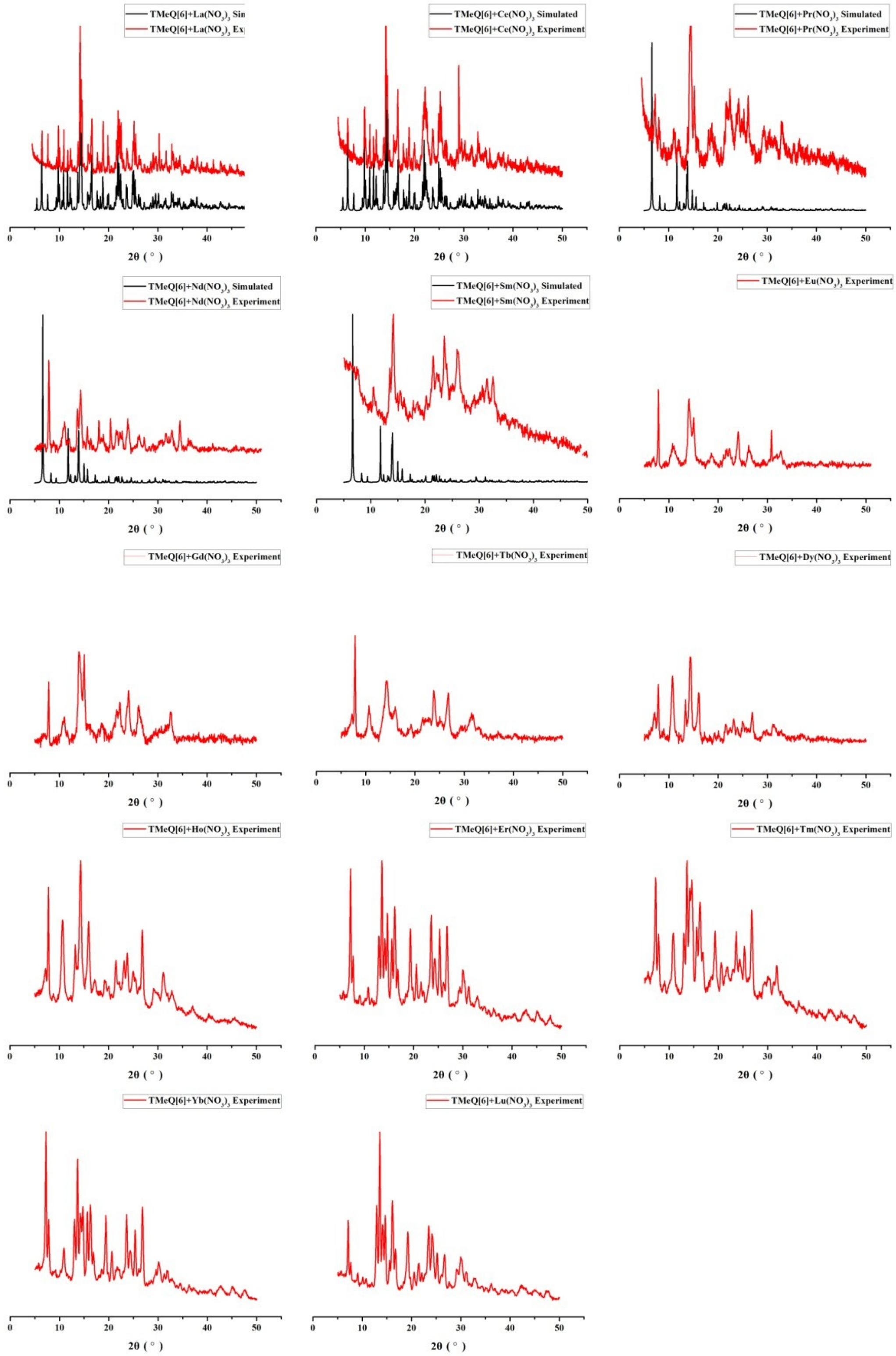

Figure S6 X-ray powder diffraction of representative crystals (the molar ratio of TMeQ[6] with lanthanide cations is 1:10 in neutral aqueous solution) .

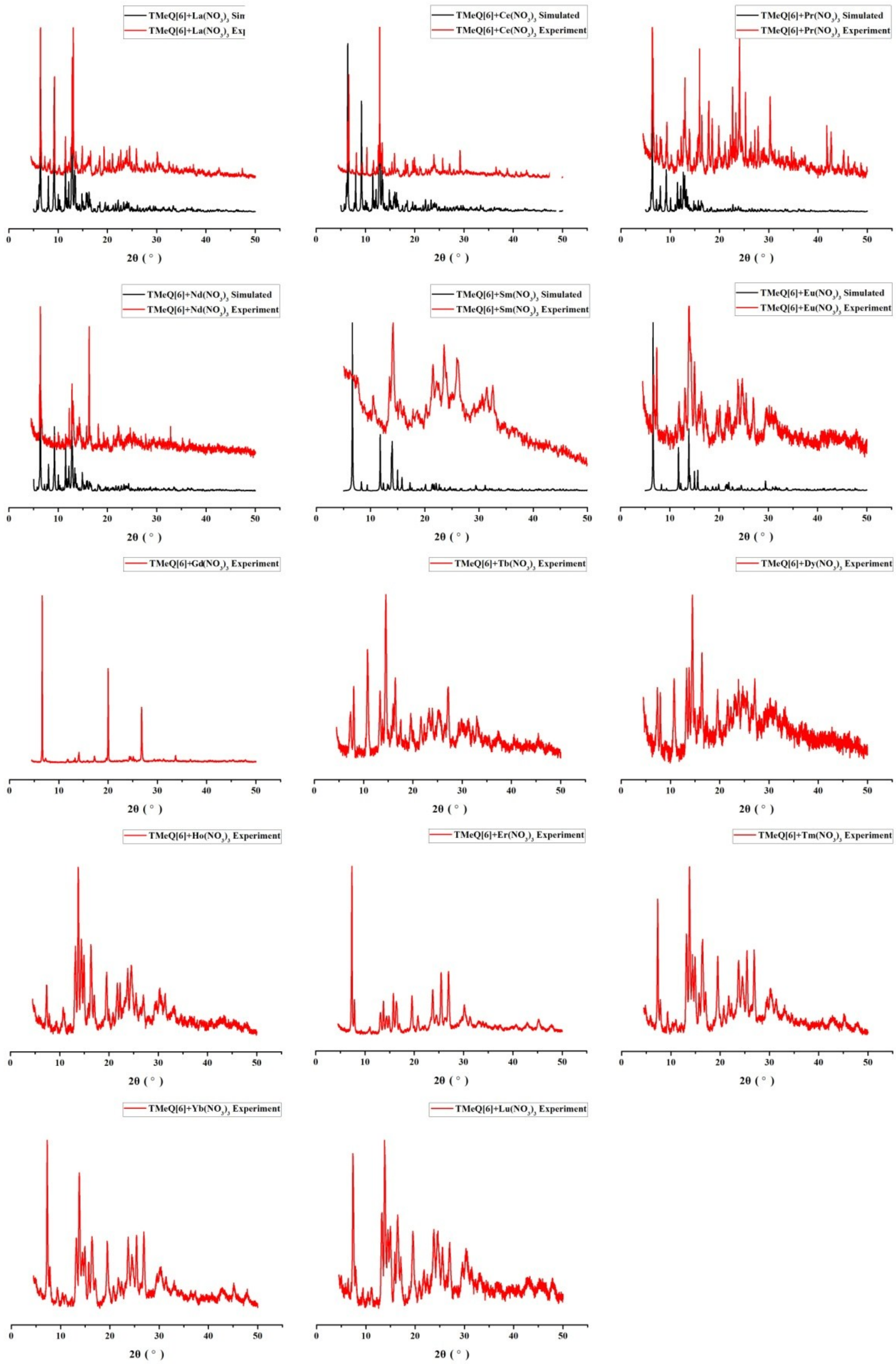

Figure S7 X-ray powder diffraction of representative crystals (the molar ratio of TMeQ[6] with lanthanide cations is 1:2 in neutral aqueous solution) .

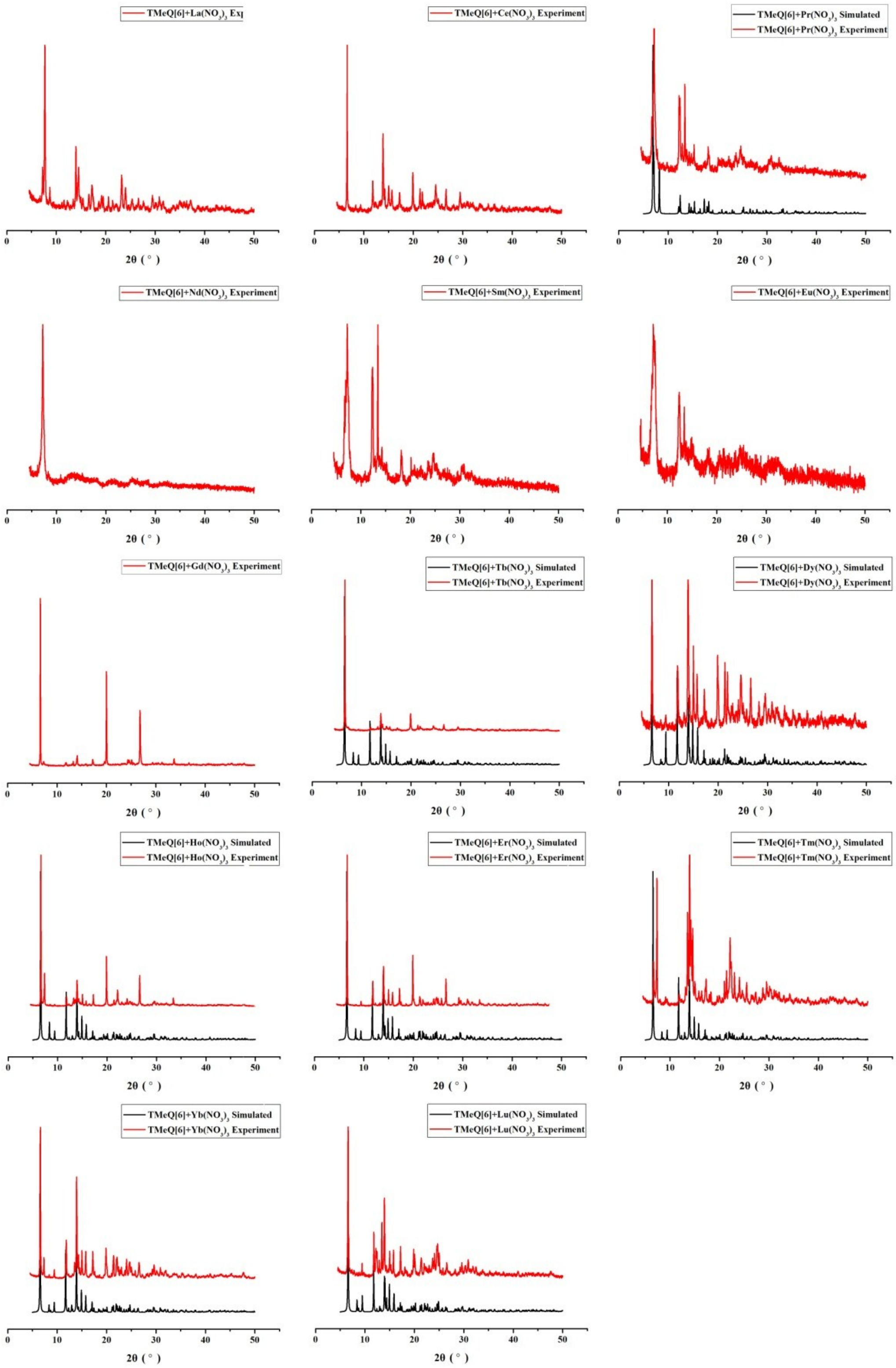

Figure S8 X-ray powder diffraction of representative crystals (the molar ratio of TMeQ[6] with lanthanide cations is 1:4 in 6M HCl).

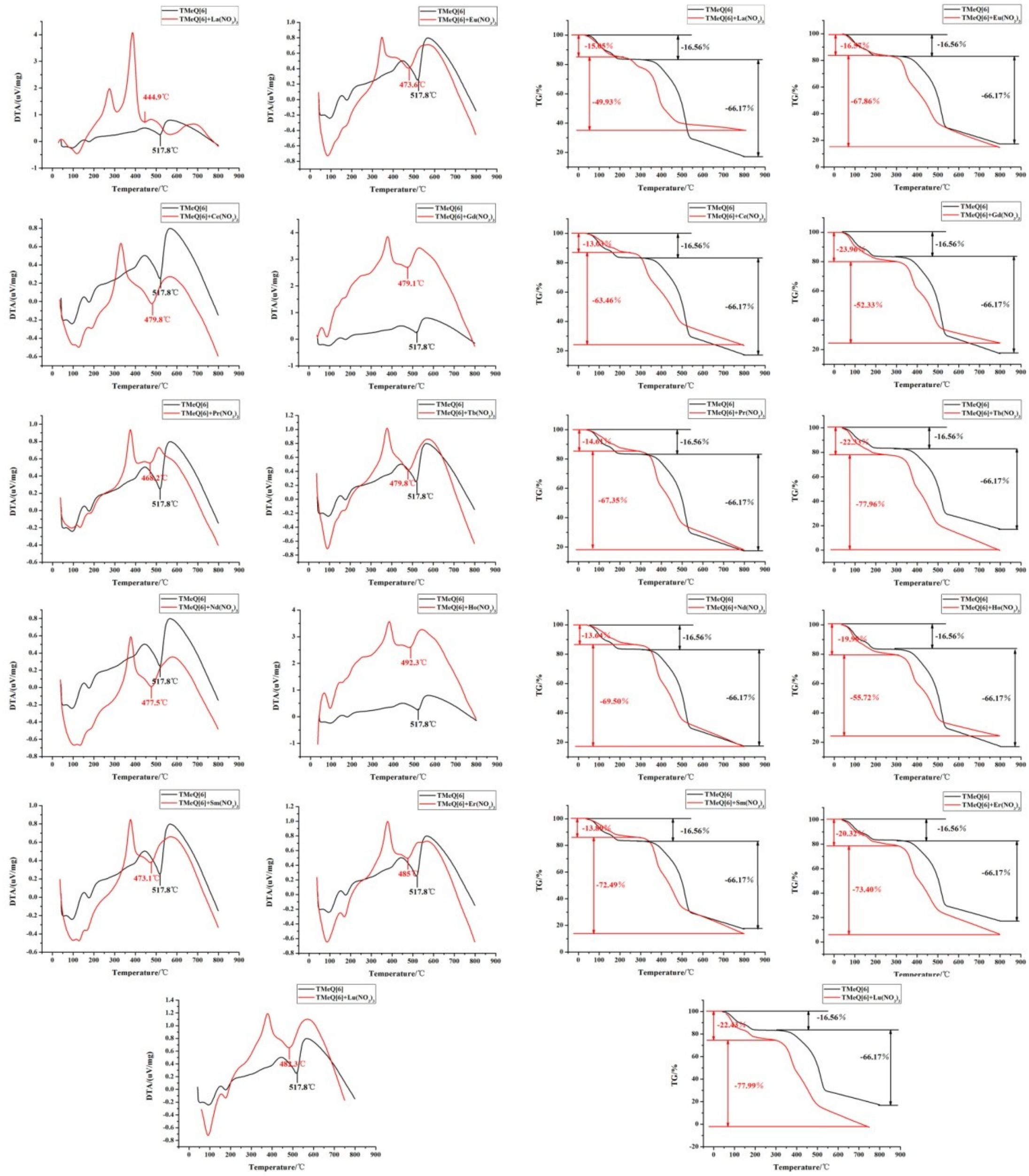

Figure S9 DTA (left) and TG (right) curves of representative crystals with a comparison TMeQ[6] in N_2 (the molar ratio of TMeQ[6] with lanthanide cations is 1:10 in neutral aqueous solution) .

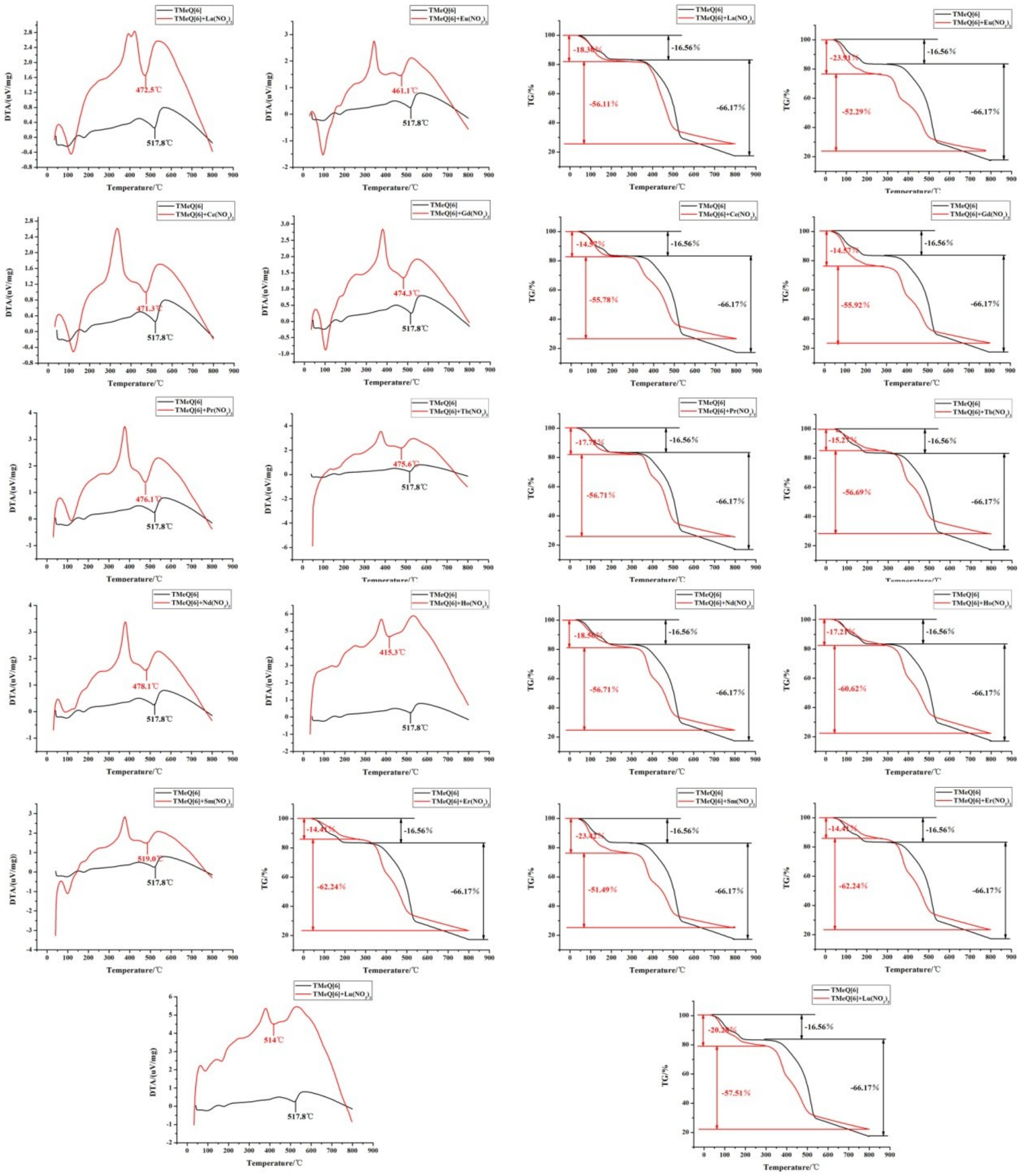

Figure S10 DTA (left) and TG (right) curves of representative crystals with a comparison TMeQ[6] in N_2 (the molar ratio of TMeQ[6] with lanthanide cations is 1:2 in neutral aqueous solution) .

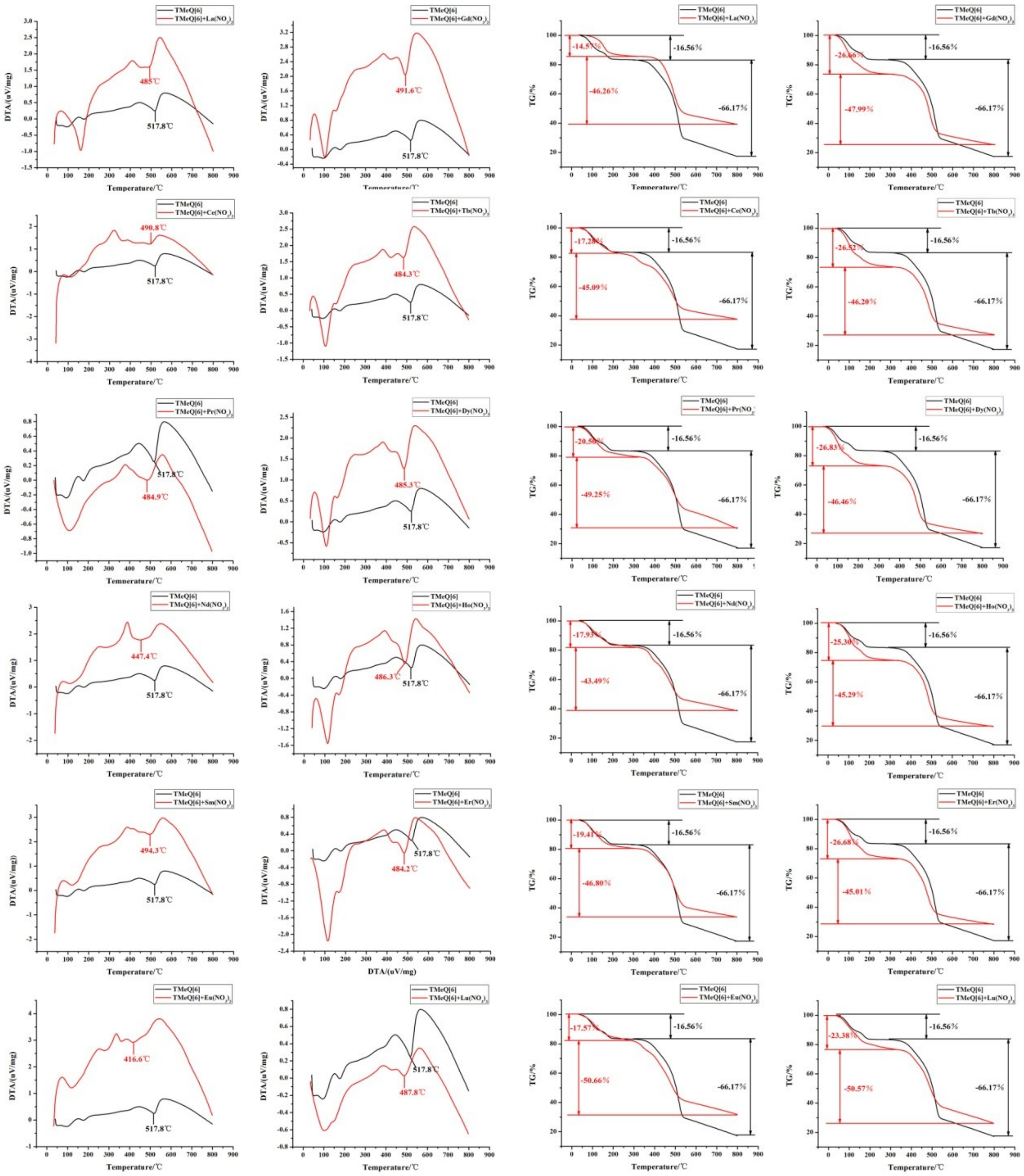

Figure S11 DTA (left) and TG (right) curves of representative crystals with a comparison TMeQ[6] in N_2 (the molar ratio of TMeQ[6] with lanthanide cations is 1:4 in 6M HCl) .

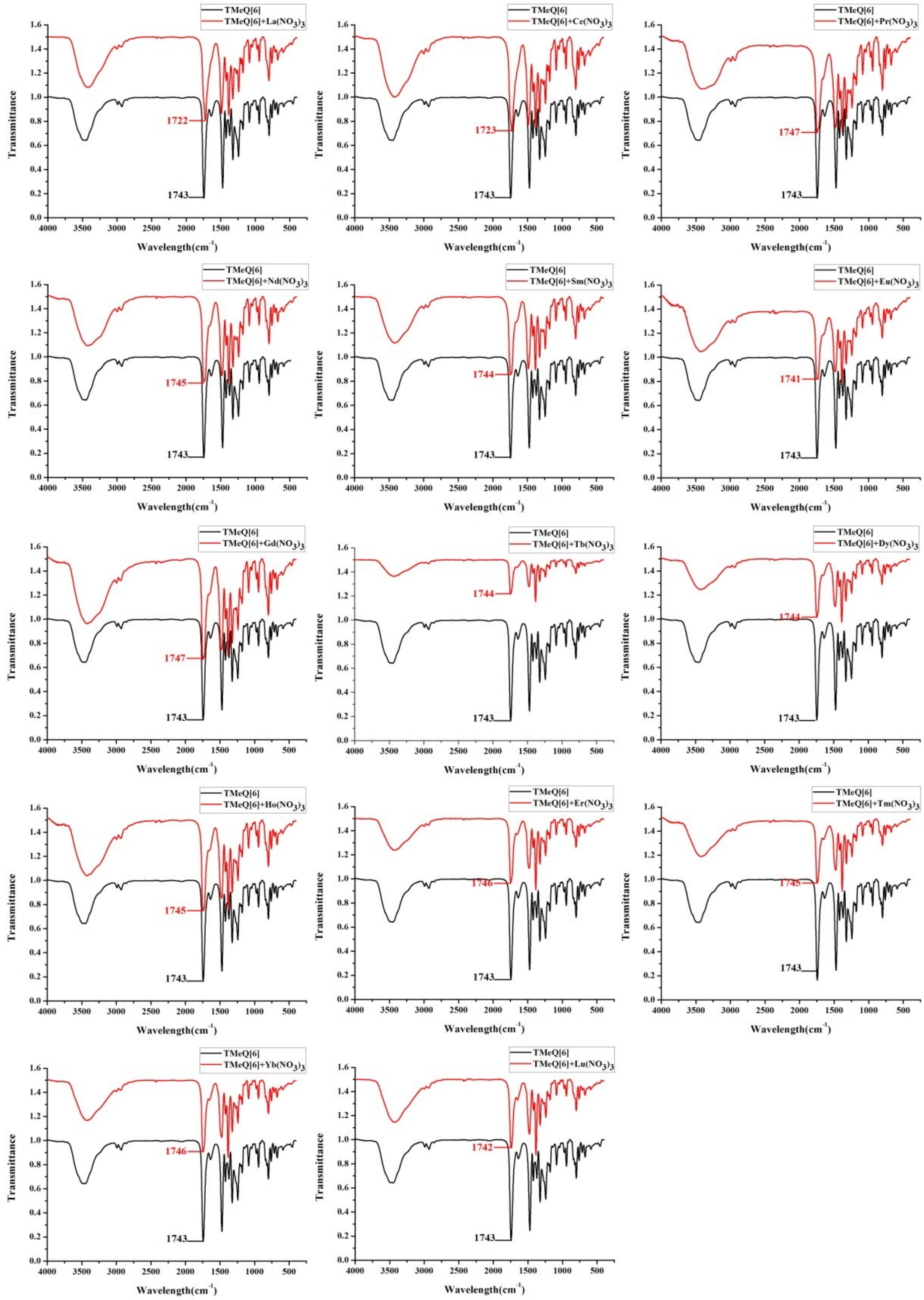

Figure S12 FT-IR spectra of representative crystals with a comparison of TMeQ[6] powders respectively (the molar ratio of TMeQ[6] with lanthanide cations is 1:10 in neutral aqueous solution).

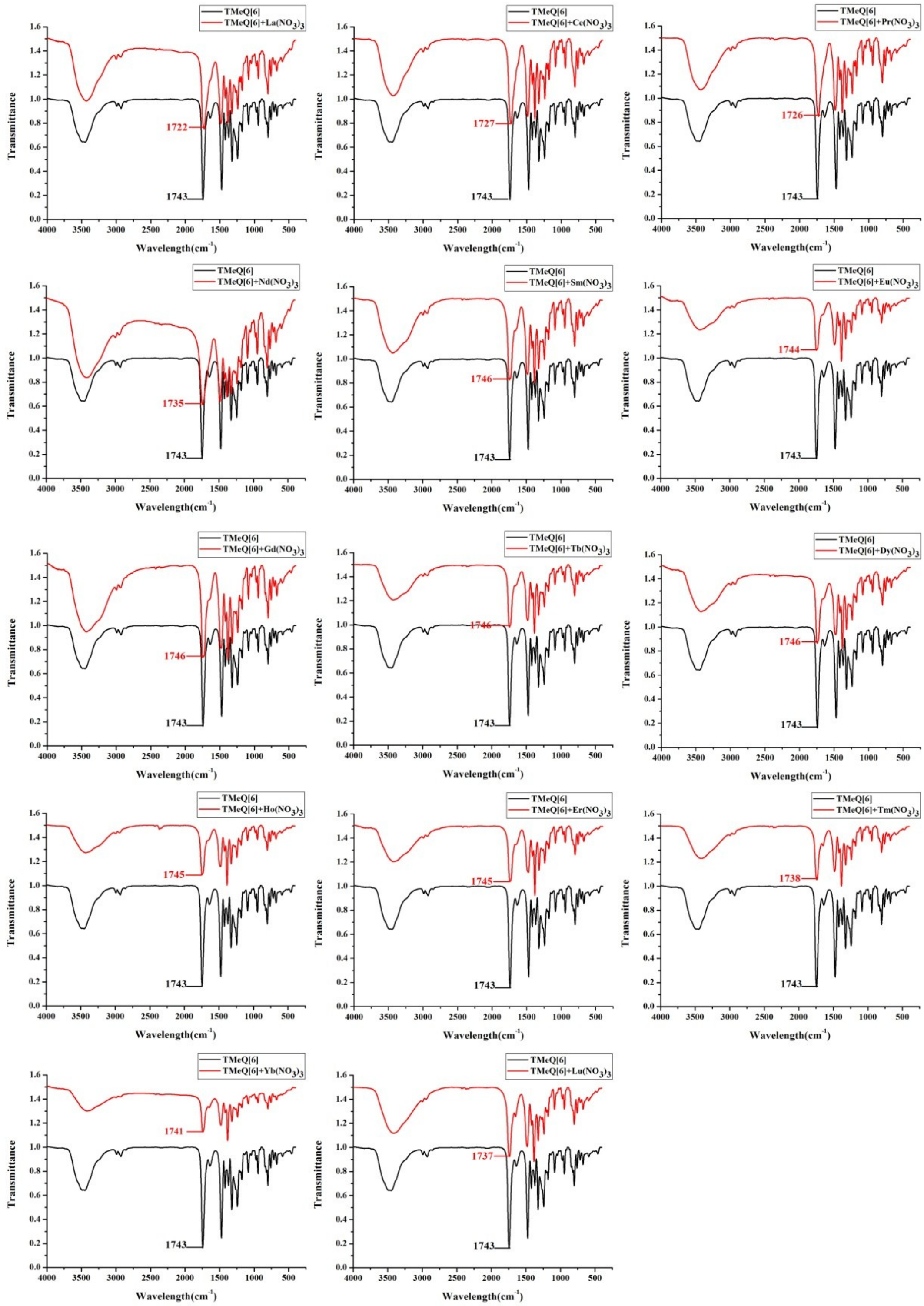

Figure S13 FT-IR spectra of representative crystals from with a comparison of TMeQ[6] powders respectively (the molar ratio of TMeQ[6] with lanthanide cations is 1:2 in neutral aqueous solution).

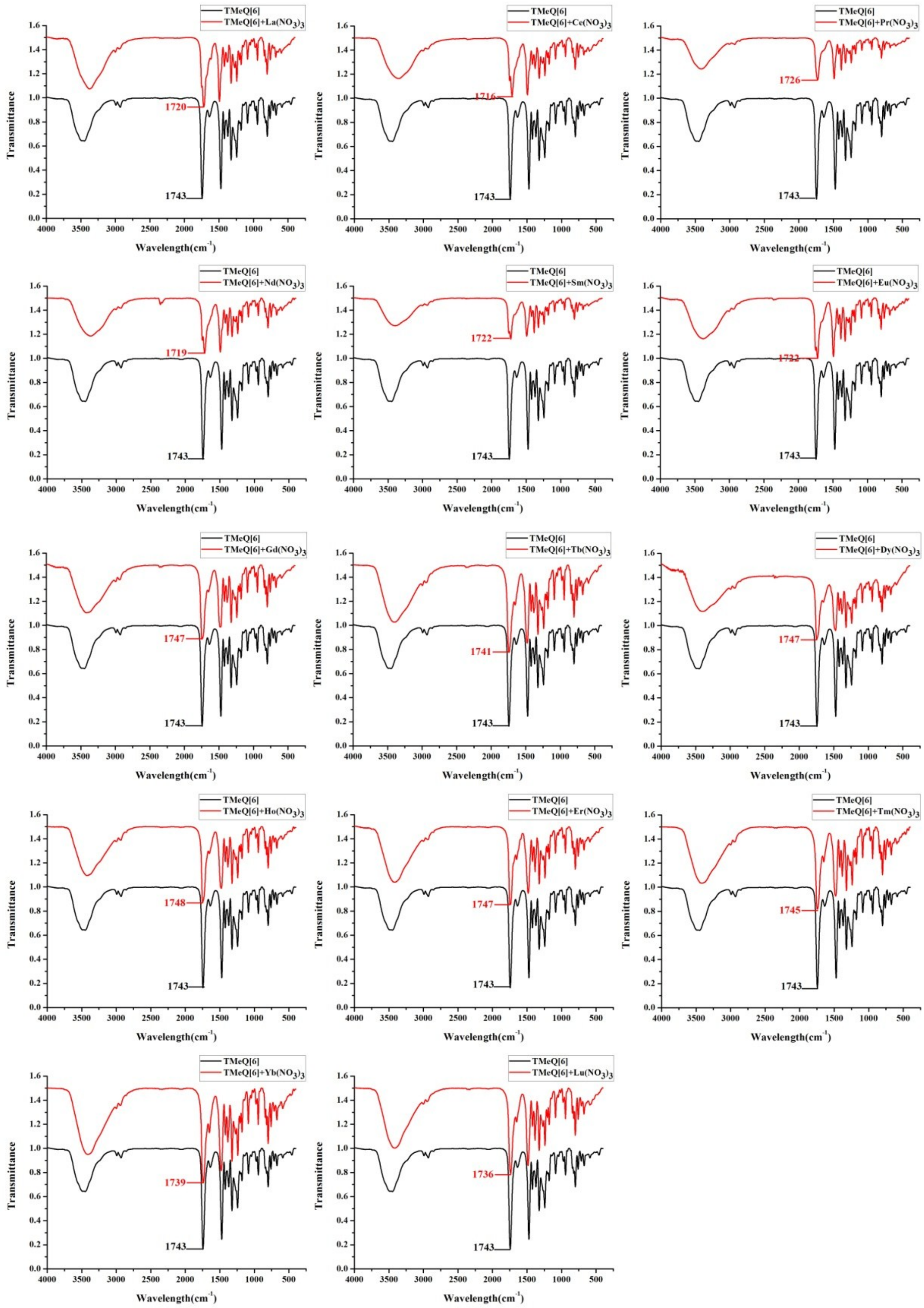

Figure S14 FT-IR spectra of representative crystals with a comparison of TMeQ[6] powders respectively (the molar ratio of TMeQ[6] with lanthanide cations is 1:4 in 6M HCl).

Notes on crystal structures

See CCDC numbers 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''**).

T=20 celcius in all

Structures are inherently difficult because of the large regions of space between the cucurbital groups. This is filled with disordered solvent in many of the structures. This has been modelled with the SQUEEZE routine in several cases. The determination of the water in this way is at best an approximation.

The hydrogen atoms on water were not located in this study. The addition of hydrogens to water molecules in structures such as this is a difficult problem. The models employed do not have hydrogen atoms on the water molecules. To add them at arbitrary positions would be an extremely dubious procedure.

1 Composition $2(C_{40}H_{44}N_{24}O_{12})$, $La(NO_3)(H_2O)_5.4(NO_3)$, $13(H_2O)$

1′ squeeze applied.

Around 976 electrons per cell not accounted for in ordered model. A conservative estimate is that this is 54 water molecules. Composition $C_{120}H_{132}La_2N_{72}O_{44}$, $6NO_3$, $58H_2O$

$3(C_{40}H_{44}N_{24}O_{12})\ (La(H_2O)_4)_2.\ 6NO_3.58H_2O$

10″ squeeze applied

284 electrons in the cell not accounted for by the model. (approx. 16 water molecules) This gives a composition of $C_{40}H_{44}N_{24}O_{12}$, Dy $(H_2O)_8$, 3Cl, $8H_2O$

11″ squeeze applied.

300 electrons per cell. This is roughly 16 extra water molecules per cell. This gives a composition $C_{40}H_{44}N_{24}O_{12}$, Ho $(H_2O)_8$, 3Cl, $10H_2O$

12″ squeeze applied

Approximately 400 electrons per cell. This is roughly 22 water molecules. Composition: $C_{40}H_{44}N_{24}O_{12}$, Er $(H_2O)_8$, 3(Cl), $17H_2O$

13″ squeeze applied

Approx 394 electrons in cell. This is roughly 22 water molecules. Composition:

$C_{40}H_{44}N_{24}O_{12}$, $Tm(H_2O)_8$, 3(Cl). $11H_2O$

14″ squeeze applied

Approx 393 electrons in cell. This is roughly 22 water molecules. Composition:

$C_{40}H_{44}N_{24}O_{12}$, $Yb(H_2O)_8$, 3(Cl).$11H_2O$

15″ squeeze applied

Approx 452 electrons in cell. Roughly 24 water molecules. Composition:

$C_{40}H_{44}N_{24}O_{12}$, Lu $(H_2O)_8$, 3(Cl), $14H_2O$

2′ squeeze applied. Nitrate not fully ordered and has not been determined crystallographically.

Approximately 624 electrons located by squeeze. *ie* 312 for asymmetric unit which has been partitioned between 2 further nitrates (less 2 oxygen atoms) [92 electrons], and a further 12 water molecules [216 electrons]. This gives a composition:

$3(C_{40}H_{44}N_{24}O_{12})\ (Ce(H_2O)_4)_2.\ 6NO_3.10(H_2O)$

2 Composition: $C_{40}H_{44}N_{24}O_{12}$, $Ce(H_2O)_5$, $3(NO_3)$, $7H_2O$

3″ SQUEEZE applied.

The structure contains both nitrate and chloride bound at the metal (there is some disorder). Further order anions are not identified. The SQUEEZE analysis revealed about 434 electrons which equates to approximately 2 further nitrate anions and 17 water molecules. Composition is therefore $C_{80}H_{88}N_{48}O_{24}$, O_6 Pr_2, 3(Cl) 3(NO_3^-).17(H_2O).

2($C_{40}H_{44}N_{24}O_{12}$) ($Pr(H_2O)_3)_2$.3Cl.3(NO_3).17(H_2O)

3′ squeeze applied

The structure contains only two order nitrate anions. The further anions were not ordered and this electron density was modelled using SQUEEZE. Approximately 824 electrons due to disordered components. This equates to about 2 nitrates and 39 water molecules in the unit cell. The composition is therefore:

$C_{120}H_{132}N_{72}O_{42}Pr_2$, 6($NO_3$), 18$H_2O$

3($C_{40}H_{44}N_{24}O_{12}$) 2(Pr ($H_2O)_3$). 6(NO_3). 18H_2O

3 no evidence for ordered chloride in the structure. It is not reasonable to derive a model that contains ordered chloride for this structure. Given that the charge must be balanced by anions, either hydroxide or disordered nitrate is possible. It would be expected that nitrate would be partially ordered by hydrogen bonding if present. Therefore the simplest solution is that there is some hydroxide present. It has not been possible to resolve the hydroxide from water present in the structure.

The data were treated with the SQUEEZE routine and this revealed 460 electrons in the unit cell corresponding to around 24 further water molecules. Overall composition: ($C_{40}H_{44}N_{24}O_{12}$), $Pr(H_2O)_8$, 3(OH). 23(H_2O)

4″ SQUEEZE applied.

One chloride and one nitrate bound at the metal. The extra anion to balance the charge is not located. This is most probably a nitrate that is disordered between the Q units. 572 electrons in void from SQUEEZE. This gives a composition:

($C_{40}H_{44}N_{24}O_{12}$) 2($Nd(H_2O)_3$)2Cl.2NO_3. 20H_2O. NO_3 (disordered)

4′ SQUEEZE applied.

Unmodelled contents approximately 600 electrons. This is close to two nitrates and 26 water molecules. The nitrate was added as an ordered component and the some additional water was located. The composition is thus: C_{120} $H_{132}N_{72}Nd_2O_{44}$, 6(NO_3), 40H_2O

$3(C_{40}H_{44}N_{24}O_{12})\ (Nd(H_2O)_4)_2.\ 6(NO_3),\ 40H_2O$

4 SQUEEZE applied.

The structure only contains two ordered parts: the hydrated metal ion and the Q-ring. There was no other indication from the electron density map of ordered parts. The anions and solvent water were then added to the structure using the squeeze routine. Number of electrons located in disordered region = 440. This equates to $6(OH^-)$ and 18 H_2O to give composition: $C_{40}H_{44}N_{24}O_{12}$, Nd $(H_2O)_8$. $3(OH^-).10H_2O$

6″ SQUEEZE applied.

There is evidence in the Fourier difference map for another nitrate anion located near to N4 (on the position occupied by O4w). We have not been able to establish a chemically sensible model for this nitrate, but the composition give below reflects this. SQUEEZE found 292 electrons. This equates to about 16 water molecules.

Composition: $C_{40}H_{44}N_{24}O_{18}Sm_2Cl_2$, $16H_2O$. $4NO_3$

$C_{40}H_{44}N_{24}O_{12}\ (Sm(H_2O)_3)_2\ 2Cl.16H_2O.4NO_3$

6 SQUEEZE applied.

No evidence for ordered nitrate or chloride here. Around 450 electrons present as the disordered component. This equates to around $6(OH^-)$ and 18 water. Thus composition:

$(C_{40}H_{44}N_{24}O_{12})\ Sm(H_2O)_8.\ 3(OH^-).\ 9H_2O$

7′ SQUEEZE applied.

No evidence for ordered nitrate or chloride here. Around 500 electrons present as the disordered component. This equates to around $6(OH^-)$ and 22 water. Thus composition:

$C_{40}H_{44}N_{24}O_{12}\ Eu(H_2O)_8.\ 3(OH^-).\ 13H_2O$

8″ SQUEEZE applied.

Partially ordered chloride detected in the difference map and added to the refinement. SQUEEZE used to deal with disordered water. A single void within the unit cell containing 316 electrons was identified. This corresponds to about 18 water molecules.

Composition: $(C_{40}H_{44}N_{24}O_{12})$, $Gd(H_2O)_9$, 3(Cl), $9H_2O$

9″ SQUEEZE applied.

Partially ordered chloride detected in the difference map and added to the refinement. SQUEEZE used to deal with disordered water. A single void within the unit cell containing 162 electrons was identified. This corresponds to 9 water molecules.

$C_{40}H_{48}N_{24}O_{12}$, $Tb(H_2O)_8$, 3(Cl). $4.5H_2O$