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Supramolecular Assemblies Constructed from Inverted Cucurbit[7]uril and Lanthanide Cations: Synthesis, structure and sorption properties.

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Abstract: The interaction of a series of lanthanide cations (Ln^{3+}) with inverted cucurbit[7]uril (iQ[7]) in the presence of $[ZnCl_4]^{2-}$ anions as a structure-directing agent have been investigated. Single-crystal X-ray diffraction analysis has revealed that the $[ZnCl_4]^{2-}$ anions surround the iQ[7] molecules via outer surface interactions of iQ[7]. This results in the formation of honeycomb-like frameworks, and ultimately linear supramolecular chains of iQ[7] in which Ln^{3+} cations occupy voids within the framework. Moreover, these iQ[7]/Ln^{3+}-based supramolecular assemblies exhibit excellent thermal stability as well as permanent porosity, and in one case screening

revealed high CH_3OH uptake capacity compared with other porous organic materials

assembled solely through hydrogen bonding under ambient conditions.

Keywords: inverted cucurbit[7]uril; lanthanide cations; $[ZnCl_4]^{2-}$ anion; coordination;

supramolecular assemblies

Introduction

Inverted cucurbit[n]urils (iQ[n]s, n = 6,7) are characterized by the displacement of two methine hydrogen atoms of a glycoluril unit within their cavities, and were first reported by Isaacs and Kim in 2005.[1] Subsequently, it was demonstrated that iQ[n]s can convert into Q[n]s following heating in concentrated HCl.[2] Given that iQ[7] has a slightly smaller cavity than that of Q[7], it can display some different host-guest properties. For example, iQ[7] binds aromatic guests tighter than linear aliphatic guests.[1] Also, the Ka value of iQ[7] for aromatic guests is somewhat higher than that for voluminous guests such as adamantine, which is in sharp contrast to the behaviour of Q[7], which displays much higher affinity for adamantine 3 than for aromatic guests.[1] However, difficulties associated with the separation of iQ[n]s had hindered the investigation of their chemistry. Indeed, only four studies and one patent involving iQ[n]s have been reported to date.[2-6] However, recently we found that iQ[6] or iQ[7] can be easily isolated from Q[6] or a water-soluble mixture of Q[n]s by column chromatography on Dowex resin.[7-9] The subtle difference in the outer surface interactions of Q[n] and iQ[n] results in a significant difference in their chromatographic behaviour, and their resultant separation has further facilitated the development of iQ[n] chemistry.[7]

Interestingly, polychloride transition metallated anions ($[M_{d-block}Cl_x]^{n-}$), in particular, $[CdCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ have proven effective structure directing agents in the construction of Q[n]/Metal coordination complexes and supramolecular

coordination polymers.[9-12] The interaction of electronegative $[M_{\text{d-block}}Cl_x]^{n-}$ anions and the electropositive outer surface of Q[n]s generally leads to the formation of $[M_{\text{d-block}}Cl_x]^{n-}$-based honeycomb-like frameworks (the so-called honeycomb effect of $[M_{\text{d-block}}Cl_x]^{n-}$), resulting in Q[n]–metal-based coordination polymers, which occupy the cells of the frameworks.[7,20] Our recent studies have shown that both iQ[6] and iQ[7] can coordinate with alkaline-earth metal ions[9] in the presence of the $[ZnCl_4]^{2-}$ anion as a structure-directing agent[10-12] resulting in the formation of different supramolecular assemblies. More recently, investigation of the interactions of iQ[6] with lanthanide cations (Ln^{3+}) in the presence of the $[ZnCl_4]^{2-}$ anion revealed that they give rise to different products and isomorphous groups based on increasing atomic number. The interaction of iQ[6] with La^{3+} and Ce^{3+} immediately yielded precipitates, and likewise crystalline solids were obtained with Pr^{3+} and Nd^{3+}. No solids resulted from the coordination of iQ[6] with Sm^{3+} and Eu^{3+}, whereas crystalline solids were obtained from its coordination with the remaining heavy Ln^{3+}, Ln = Gd–Lu; such observations demonstrated the recognition of lanthanide cations by iQ[6].[8] Moreover, different Q[n]s exhibit different selectivity for Ln^{3+} and the interaction or coordination of Q[n]s with Ln^{3+} is strongly affected by the synthetic conditions employed.[21] Previous studies have proven that Q[n]-based supramolecular assemblies could be used as hydrogelators,[13] for the capture of gases such as acetylene[14] or carbon dioxide,[15] and that both Q[6]- and Q[8]-based porous materials show anisotropic proton conductivity.[16] The combination of Q[n]-based coordination complexes and Q[n]-based supramolecular assemblies could open up

limitless possibilities.

In the present work, the coordination chemistry of iQ[7] (Figure 1) towards lanthanide cations (Ln^{3+}), in the presence of the $[ZnCl_4]^{2-}$ anion as a structure-directing agent, in aqueous HCl has been investigated. Single-crystal X-ray diffraction analysis revealed that $[ZnCl_4]^{2-}$ anions surround iQ[7] molecules via outer surface interactions and form honeycomb-like frameworks, and ultimately result in the formation of linear supramolecular chains of iQ[7] with Ln^{3+} cations, the latter occupying the voids of the framework. Moreover, the linear iQ[7]/Ln^{3+}-based supramolecular chains arrange into novel supramolecular assemblies, which in one case was shown to exhibit high CH_3OH uptake capacity when compared with other porous organic materials assembled solely through hydrogen bonding under ambient conditions[17-19].
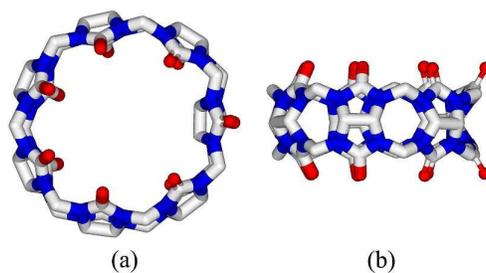

(a)   (b)

Fig. 1. Structure of the inverted cucurbit[7]uril as viewed from the top (left) and from the side (right).

Results and Discussion

Description of the crystal structures.

Figure 2 shows the crystal structure of compound **1** obtained from the

iQ[7]−Eu^{3+}−ZnCl$_2$−HCl system. A supramolecular assembly is evident (Figure 2a) in which the [ZnCl$_4$]$^{2−}$ anions are arranged into a honeycomb-like framework (Figure 2b), and each 'hollow' within the honeycomb has one iQ[7]−Eu^{3+}-based "bee pupa" (Figure 2a, 2c). Each iQ[7] molecule in the "pupa" is surrounded by seven [ZnCl$_4$]$^{2−}$ anions via the outer surface interactions of iQ[7], including dipole-dipole interactions between Cl from [ZnCl$_4$]$^{2−}$ anions and methine or methylene (black dashed lines) of the iQ[7] molecule (Figure 2d). Distances between chloride and methine or methylene carbons fall within the range 3.406–3.445 Å. Additional hydrogen bonding interactions between the inverted carbonyl oxygens and the methylene groups on the outer surface of the iQ[7] molecules (red dashed lines) from two neighbouring linear polymers (Figure 2e) are also evident. The distances between the inverted carbonyl oxygens (O11) and the hydrogens (H23B and H24A) are in the range 2.543−2.645 Å. Unlike the unsubstituted Q[7]/Ln^{3+}-based supramolecular coordination polymers where neighbouring Q[7] molecules are linked by direct coordination with Ln^{3+} cations,[8,13] here each iQ[7]−Eu^{3+}-based supramolecular "pupa" is constructed of 1:1 iQ[7]/Eu^{3+} complexes. Furthermore, a Eu^{3+} cation (Eu1) of a iQ[7]/Eu^{3+} complex coordinates at one portal of the iQ[7] molecule, and interacts with the portal of a neighbouring iQ[7]/Eu^{3+} complex via hydrogen bonding (Figure 2f). Each Eu^{3+} cation (Eu1) coordinates with eight oxygen atoms, two carbonyl oxygens (O1, O2) from a iQ[7] molecule, and six water molecules (O1W, O2W, O3W, O4W, O5W, O6W), which interact with the portal carbonyl oxygens of a neighbouring iQ[7] molecule. Some additional interactions exist between the two neighbouring iQ[7] molecules,

including: 1) hydrogen bonding between the five coordinated water molecules (O2W, O3W, O4W, O5W, O6W) and the portal carbonyl oxygens (O14, O8, O9, O10, O12) (2.836–2.887 Å in blue dashed lines, Figure 2f); the hydrogen bonding distances are in the range 2.657−2.809 Å. 2) hydrogen bonding interactions between a portal carbonyl oxygen of the iQ[7] molecule and a methylene group from the neighboring iQ[7] molecule with hydrogen bonding distances in the range 2.867−3.010 Å (red dashed lines, Figure 2f). Thus, a combination of all these interactions resulted in the formation of the iQ[7]−Eu^{3+}−$[ZnCl_4]^{2-}$ supramolecular coordination assembly.
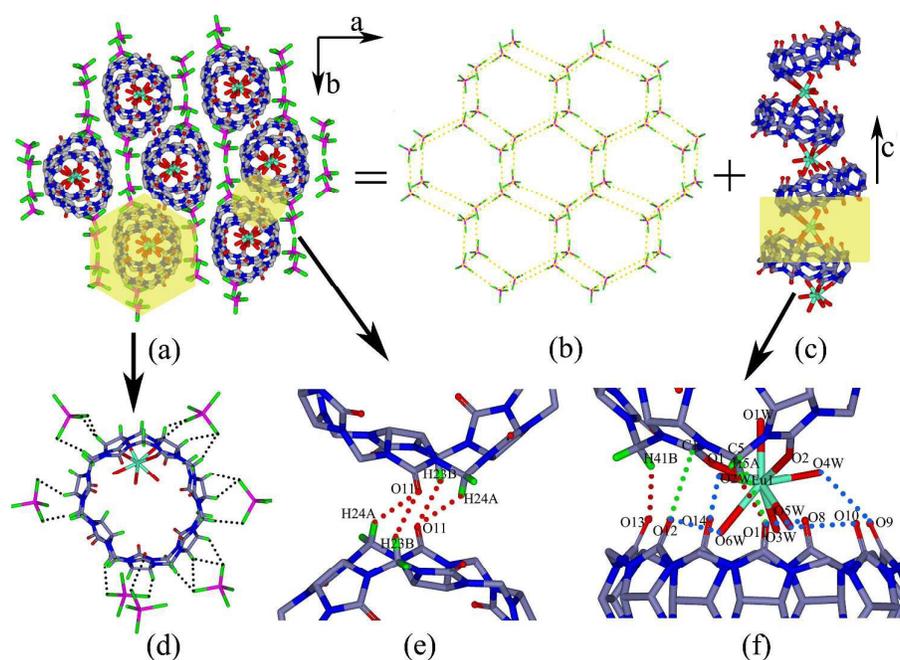

Fig. 2. X-ray crystal structure of compound **1**: (a) overall view of the supramolecular assembly constructed of iQ[7]−Eu^{3+} complexes and $[ZnCl_4]^{2-}$ anions along the c axis; (b) a $[ZnCl_4]^{2-}$−based honeycomb-like framework; (c) a linear iQ[7]−Eu^{3+}−based coordination polymer surrounded by $[ZnCl_4]^{2-}$ anions; (d) interactions between iQ[7] molecules and $[ZnCl_4]^{2-}$ anions; (e) interactions between iQ[7] molecules and neighbouring linear polymers; (f) interactions between the Eu^{3+}−linked iQ[7] molecules.

Although compound **2** obtained from the iQ[7]−Yb^{3+}−ZnCl$_2$ −HCl system does not belong to the same isomorphous group as that of compound **1**, the two compounds form similar supramolecular assemblies. Indeed, one can see such a supramolecular assembly constructed of iQ[7], Yb^{3+}, and [ZnCl$_4$]$^{2-}$ anions (Figure 3a). [ZnCl$_4$]$^{2-}$ anions are attracted by the positively charged outer surface of the iQ[7] molecules and thus surround them, resulting in the formation of a [ZnCl$_4$]$^{2-}$-based honeycomb-like framework (the honeycomb effect of the [ZnCl$_4$]$^{2-}$ anion; Figure 3b). Meanwhile, the negatively charged environment around the iQ[7] molecules leads to a strong affinity for metal ions, such as Yb^{3+} cations. Thus, linear iQ[7]/Yb^{3+}-based supramolecular chains are formed, which reside in the channels of the [ZnCl$_4$]$^{2-}$-based honeycomb (Figures 3a, 4c). Typical outer surface interactions of iQ[7]s with [ZnCl$_4$]$^{2-}$ anions comprise mainly dipole–dipole interactions between Cl from [ZnCl$_4$]$^{2-}$ anions and methine or methylene units (black dashed lines) of the iQ[7] molecule (Figure 3d). The distances between the chloride and the methine or methylene carbons are in the range 3.288−3.423 Å. The hydrogen bonding interactions can also be observed between the inverted portal carbonyl oxygen atoms of one iQ[7] molecule and the methylene groups on the outer surface of another between neighbouring iQ[7]/Yb^{3+}-based supramolecular chains (red dashed lines), with the hydrogen bonding distances in the range 2.932−3.129 Å (Figure 3e). Close inspection reveals that every two neighbouring iQ[7] molecules in a supramolecular chain are linked by one Yb^{3+} cation (Yb1), which directly coordinates to two carbonyl oxygen atoms (O1, O2) from an iQ[7] molecule. Moreover, a coordinated water molecule (O1W) resides

at the portal of the iQ[7] molecule. The Yb^{3+} cation (Yb1) also interacts with the neighbouring iQ[7] molecule via hydrogen bonding of coordinated water molecules (O2W, O3W, O4W, O5W, O6W; Figure 3f). Thus, the Yb1 cation coordinates with eight oxygen atoms. The distances between Yb^{3+} and the portal carbonyl oxygen atoms are in the range 2.289−2.303 Å, and the distances between carbonyl oxygen atoms and O_{water} are in the range 2.710−2.955 Å.
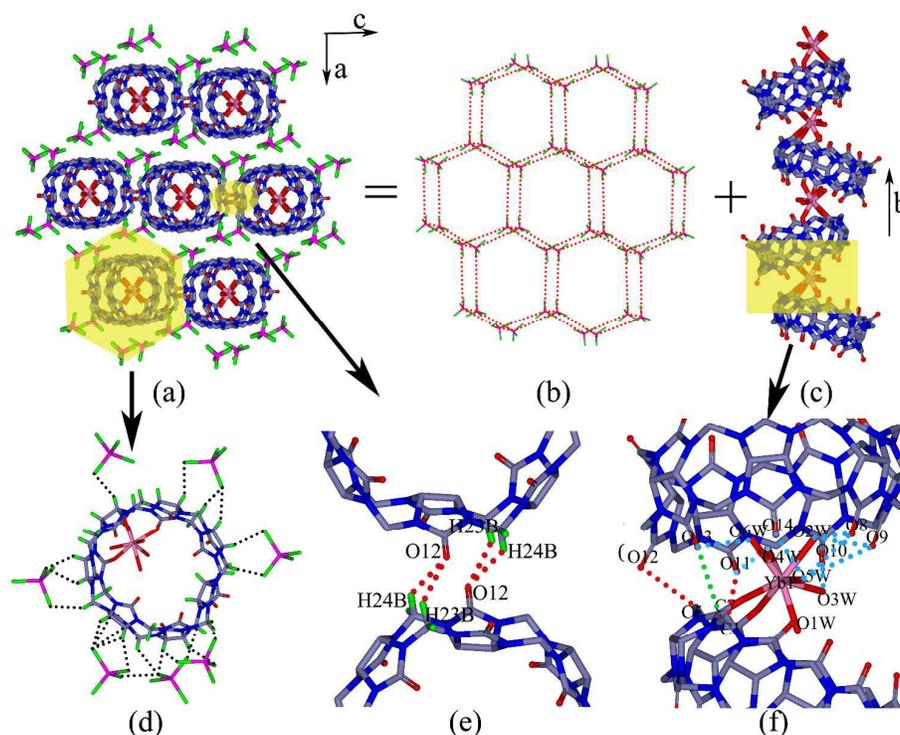

Fig. 3. X-ray crystal structure of compound **2**: (a) overall view of the supramolecular assembly constructed of iQ[7]−Yb^{3+} complexes and $[ZnCl_4]^{2-}$ anions along the b axis; (b) a $[ZnCl_4]^{2-}$-based honeycomb-like framework; (c) a linear iQ[7]−Yb^{3+}-based coordination polymer surrounded by $[ZnCl_4]^{2-}$ anions; (d) interactions between iQ[7] molecules and $[ZnCl_4]^{2-}$ anions; (e) interactions between iQ[7] molecules and neighbouring linear polymers; (f) interactions between the Yb^{3+}−linked iQ[7] molecules.

Our previous work [20] revealed that normal Q[7] can form crystalline solids with a

series of Ln^{3+} cations under similar experimental conditions, that is, with the aid of $[ZnCl_4]^{2-}$ anions as a structure-directing agent. There was apparently no special selectivity of the normal Q[7] for the lanthanide cations, with almost all of the $Q[7]–Ln^{3+}–[ZnCl_4]^{2-}$ systems yielding crystalline solids, although they could be classified into different isomorphous groups with increasing atomic number of the lanthanide. However, the inverted iQ[7] seems to display specific recognition properties for the lanthanide cations. Experiments showed that the iQ[7]$–Ln^{3+}–[ZnCl_4]^{2-}$ systems with lighter Ln, that is, La, Ce, Pr, Nd, and Sm, gave no precipitate, whereas the remaining heavier Ln gave crystalline solids, which could be divided into two isomorphous groups (Table S1 in the SI), for which Eu, Gd, and Lu constitute one group, and Tb, Dy, Ho, Er, Tm, and Yb the other. X-ray powder diffraction patterns of two representative crystals of each of these compounds, and comparison with simulated patterns, revealed that the samples essentially consisted of pure crystalline phases (Figure 4).
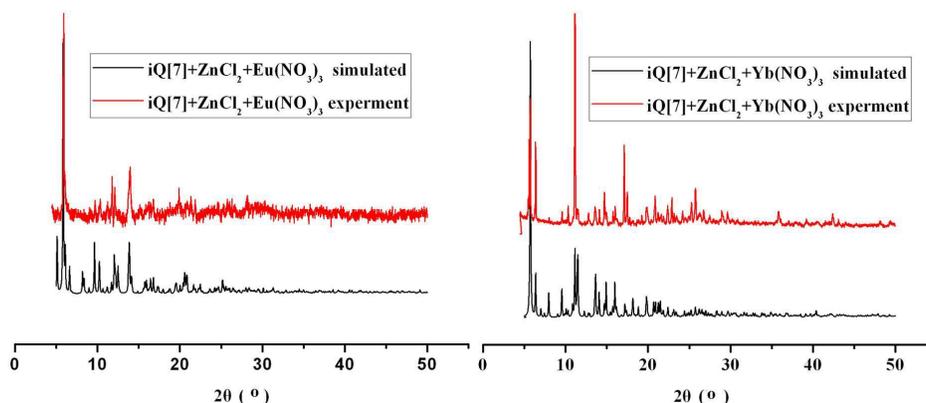

Fig. 4. X-ray powder diffraction patterns of compounds **1** and **2**: as simulated (black) from single crystal XRD data, and as experimental (red).

Sorption properties towards volatile materials: Moreover, both types of crystalline materials generally showed porous structural features, which could be utilized for selective sorption properties and can therefore be utilized for separation/purification applications.[22] Figure 5 displays the sorption profiles for several volatile materials when using the *i*Q[7]-based porous supramolecular assembly **1**. A remarkable sorption capacity for methanol was observed at over 16 mmol per gram, which is at least 20 times more than those of the other volatile materials screened at room temperature under atmospheric pressure. In contrast, powdered *i*Q[7] exhibited far less sorption capacities for methanol, in fact only one third of that of the *i*Q[7]-based porous materials, although it displayed better sorption capacity for the remaining volatile materials. In particular, for acetonitrile, the sorption capacity was about 30 times more than that of the *i*Q[7]-based porous materials (Figure S1 in the SI).

Comparison of the sorption capacities of *i*Q[7]-based porous material with those of *i*Q[7], under the same conditions, reveals that 1) the former show more obvious selectivity for polar volatile materials, especially methanol, due to the polar channels of the porous materials; 2) the channel sizes of the porous materials can influence the sorption capacities for polar volatile materials, for example, the significant difference between methanol and ethanol; 3) the latter shows no obvious selectivity for these volatile materials. These observations suggest that the *i*Q[7]-based honeycomb-like framework play a pivotal role in the sorption processes.
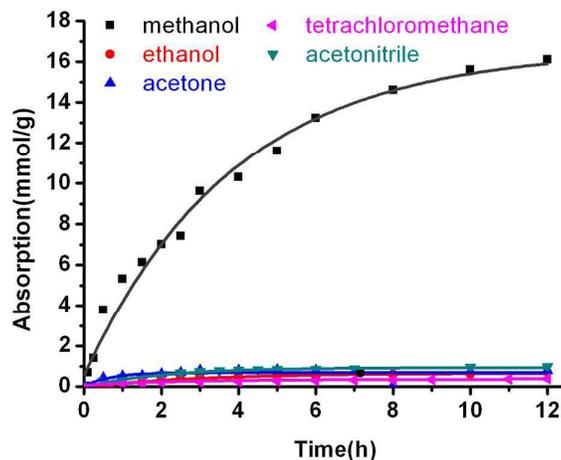
Fig. 5. Sorption profiles of volatile materials on the *i*Q[7]-based porous supramolecular assembly **1**: (■) methanol, (●) ethanol, (▲) acetone, (◄) tetrachloromethane, (▼) acetonitrile

Conclusion

In continuation of our previous work,[11] we further selected *i*Q[7] as a ligand, and investigated its coordination behaviour and resulting supramolecular assemblies with Ln^{3+} cations in the presence of $[ZnCl_4]^{2-}$ anions as structure-directing agents. Single-crystal X-ray diffraction analyses revealed that the honeycomb effect of $[ZnCl_4]^{2-}$ anions results in the formation of linear coordination polymers of Ln^{3+} with *i*Q[7] molecules. The supramolecular assemblies constructed from the 1D *i*Q[7]/Ln^{3+}-based coordination polymers display porous structural features, the remarkable selective sorption properties of which have the potential to be used for separation/purification technologies. Moreover, unlike Q[7], which shows no special selectivity for the lanthanides, *i*Q[7] displays selectivity for lanthanides in the presence of $[ZnCl_4]^{2-}$ anions. In particular, *i*Q[7] coordinates to heavy lanthanides, from Gd to Lu, forming crystalline solids, whereas no solid products are formed with

the light lanthanides, from La to Sm. Further investigations into these separation

properties are ongoing in our laboratory.

Experimental Section

Synthesis. Chemicals such as lanthanide metal chlorides or nitrates were of reagent

grade and were used without further purification. Elemental analyses were carried out

on a EURO EA-3000 elemental analyzer. iQ[7] was synthesized and separated as

described in our previous work.[9]

Preparation of compounds 1 and 2. Similar processes were used to prepare

crystals of related compounds: $Ln(NO_3)_3$ (0.12 mmol) and $ZnCl_2$ (12.18 mg, 0.089

mmol) were dissolved in 1.0 mL of H_2O to prepare solution A, iQ[7] (20 mg,

0.015mmol) was dissolved in 1.0 mL 3M of HCl to prepare solution B, which was

then added with stirring to solution A. X-ray quality crystals were obtained from the

solution on prolonged standing (≤10 days). The data for two representative

compounds, namely {$Eu(H_2O)_6(i$Q[7]}·Cl·2[$ZnCl_4$]·2H_3O 10H_2O (**1**), and

{$Yb(H_2O)_6i$Q[7]}2[$ZnCl_4$]·Cl·2H_3O·10H_2O (**2**) which were obtained from $Eu(NO_3)_3$

(53.17 mg) and $Yb(NO_3)_3$ (53.54 mg) respectively, are presented herein. Anal. calcd.

for compound **1**, $C_{42}H_{100}N_{28}O_{42}EuZn_2Cl_9$ (%): C, 22.21; H, 4.44; N, 17.27, found: C,

22.14; H, 4.48; N, 17.18. Anal. calcd for compound **2**, $C_{42}H_{104}N_{28}O_{44}YbZn_2Cl_9$ (%): C,

21.67; H, 4.50; N, 16.84 , found: C, 21.58; H, 4.53; N, 16.73.

X-ray crystallography. A suitable single crystal (~0.2 × 0.2 × 0.1 mm³) was

embedded in paraffin oil. The resulting specimen was mounted on a Bruker SMART

Apex II CCD diffractometer equipped with a graphite-monochromated Mo-K_α radiation source ($\lambda = 0.71073$ Å, $\mu = 0.828$ mm^{-1}), which was operated in the ω-scan mode at room temperature. Data were corrected for Lorentz and polarization effects by using the SAINT program, and semi-empirical absorption corrections based on equivalent reflections were also applied by using the SADABS program. The structure was elucidated through direct methods and then refined by the full-matrix least-squares method on F^2 using the SHELXS-97 and SHELXL-97 program packages, respectively.[23,24] 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 by using the SQUEEZE option of the PLATON program. There were 22 and 24 squeezed water molecules for compounds **1** and **2**, 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 three compounds are summarized in Table 1. In addition, crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1025388 (**1**) and 1025389 (**2**). These data may be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, 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 1**⟩

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Table 1. Crystal data and structure-refinement details for compounds **1** and **2**

Compound	1	2
Chemical formula	C42 H42 Eu N28 O20, 2(ZnCl$_4$), Cl. 2(H$_3$O).10(H$_2$O)	C42 H42 N28 O20 Yb, 2(ZnCl$_4$), Cl. 2(H$_3$O). 10(H$_2$O)
Formula weight	2078.78	2099.86
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/n$
a, Å	17.837(5)	17.2855(9)
b, Å	26.629(7)	18.4861(9)
c, Å	18.949(5)	27.8919(15)
α, deg	90.00	90.00
β, deg	104.892(9)	96.995(2)
γ, deg	90.00	90.00
V, Å^3	8698(4)	8846.3(8)
Z	4	4
Dcalcd, g cm^{-3}	1.421	1.413
T, K	223(2)	223(2)
μ, mm^{-1}	1.606	1.928
Unique reflns	20388	20261
Obsd reflns	12619	14428
Params	935	937
Rint	0.0676	0.0494
R[I> 2σ(I)]^a	0.0689	0.0564
wR[I> 2σ(I)]^b	0.2047	0.1729
R(all data)	0.1066	0.0811
wR(all data)	0.2331	0.1915
GOF on F2	1.070	1.045

[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 $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.