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One-Dimensional Coordination Polymers of Lanthanide Cations to Cucurbit[7]uril Built Using a Range of Tetrachloride Transition-Metal Dianion Structure Inducers

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Abstract: A number of linear coordination polymers have been assembled from lanthanide cations (Ln^{3+}) and cucurbit[7]uril (Q[7]) in the presence of $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions acting as inorganic structure inducers in HCl solution. X-ray diffraction analysis has revealed that they form three groups of isomorphous structures. Generally, the complexes of Q[7] with light lanthanide cations (those with atomic number below that of neodymium (Nd^{3+})) are in one group. The other two groups, in which the lanthanide cation has atomic number greater than that of europium (Eu^{3+}), seem to follow no obvious rule. For example, the complexes of Q[7] with Eu^{3+} and Gd^{3+} cations are in the second group in the presence of $[\text{CuCl}_4]^{2-}$ anions, while they are in the third group in the presence of $[\text{CoCl}_4]^{2-}$ anions. However, whatever group a given complex belongs to, they all show a common honeycomb-patterned supramolecular assembly, in which $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions

form a honeycomb structure. The Ln^{3+} cations then coordinate to neighboring Q[7] molecules to form 1D coordination polymers that are inserted into the channels of the honeycomb framework, such that each individual coordination polymer is surrounded by $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions.

Keywords: cucurbit[7]uril; lanthanide cation; inorganic inducers; 1D coordination polymers

1. Introduction

Coordination polymers are described as polymers whose repeat units are coordination complexes. Similar supramolecular architectures are also called metal-organic frameworks (MOFs), as well as coordination networks, with some inconsistency in the distinctions between the terms [1–6]. Coordination polymers span scientific fields such as organic and inorganic chemistry, biology, materials science, electrochemistry and pharmacology and have many potential applications [7]. This interdisciplinary nature has led to extensive study over the past few decades [8].

Cucurbit[n]urils(Q[n]s) [9–14] consist of a rigid hydrophobic cavity of low polarity, accessible through two open polar portals rimmed with carbonyl groups, which can interact with various metal ions [15–26], or their complexes [27–40] or clusters [41–50]. Consequently, cucurbit[n]uril(Q[n]s)-based coordination chemistry is becoming an important area of study in cucurbit[n]uril chemistry. In particular, Q[n]s interact with metal ions and form various poly-dimensional coordination polymers [51–60]. For example, Kim *et al.* first demonstrated one-dimensional coordination polymers alternating between alkali-metal ions (K^+ or Rb^+ cation) and Q[6] molecules [51,52]. Chen *et al.* also demonstrated one-dimensional supramolecular chains constructed from the direct coordination of Q[6]s with Na^+ cations [53]. In recent years, there has been a trend towards introducing an organic or inorganic species into the metal-Q[n] systems as a “structure inducer” or trigger, since the properties, structural novelties, and functionalities of the resulting coordination polymers have often exceeded those observed in the absence of such agents. Following on from Fedin’s work [30,32], Thuéry focused on the Q[n] complexation of lanthanides and actinides and demonstrated the formation of a series of lanthanide-Q[n] and uranyl-Q[n] supramolecular assemblies in the presence of added organic ligands [34–37]. Since a novel potassium-Q[5] supramolecular network was first prepared in the presence of *p*-hydroxybenzoic acid [60], coordination of metal ions to Q[n]s in the presence of various organic molecules has been extensively studied in our laboratory, and a strategy for inorganic or organic molecule-induced coordination polymers of metal ions to Q[n]s has gradually been established. A series of Q[n]-based poly-dimensional polymers [54,58–63] have been obtained by using this strategy.

In the present work, in order to better understand how inorganic inducers influence the coordination of metal ions to Q[n], leading to the construction of such coordination polymers, we further investigate the coordination of lanthanides to Q[7] in the presence of $[\text{CuCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$ anions. X-ray diffraction analysis has revealed that coordination of lanthanide ions to Q[7] leads to the formation of linear one-dimensional coordination polymers, while the presence of $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions gives rise to the so called “honeycomb effect”, forming honeycomb-like hollows in which these linear one-dimensional Ln^{3+} -Q[7] polymers can reside.

2. Experimental Section

Synthesis: Chemicals, such as lanthanide nitrates and hydrochloric acid, were of reagent grade and were used without further purification. Q[7] was prepared as reported elsewhere [10,11]. Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. Aqueous HCl (6.0 mol L⁻¹) was used to prepare crystals of Q[7]-Ln(III) in the presence of CuCl₂·2H₂O or CoCl₂·6H₂O. A similar process was used to prepare crystals of related compounds: Ln(NO₃)₃·xH₂O (0.136 mmol) and CuCl₂·2H₂O (15.24 mg, 0.089 mmol) were dissolved in 2.0 mL 6.0 mol L⁻¹ HCl (solution A), Q[7] (20 mg, 0.017 mmol) was dissolved in 2.0 mL 6.0 mol L⁻¹ HCl (solution B), and was then added in the solution A with stirring for the Ln³⁺-Q[7]-[CuCl₄]²⁻ systems. Ln(NO₃)₃·xH₂O (0.119 mmol) and CoCl₂·6H₂O (21.28 mg, 0.089 mmol) were dissolved in 2.0 mL 6.0 mol L⁻¹ HCl (solution C), to solution C (2.0 mL) was added in solution B (2.0 mL) with stirring for the Ln³⁺-Q[6]-[CoCl₄]²⁻ systems. X-ray quality crystals were obtained from the solution over a period of 1–7 days. The color of crystals was dependent on the lanthanide ions. Summarizing the preparations, {La₂(H₂O)₁₂Q[7]}·2[CuCl₄]·2Cl·28H₂O (**1**) was obtained from La(NO₃)₃·6H₂O (51.62 mg); {Nd₂(H₂O)₁₂Q[7]}·2[CuCl₄]·2Cl·28H₂O (**2**) was obtained from Nd(NO₃)₃·H₂O (39.37 mg); {La₂(H₂O)₁₂Q[7]}[CoCl₄]·4Cl·57H₂O (**3**) was obtained from La(NO₃)₃·6H₂O (51.62 mg); {Ce₂(H₂O)₁₂Q[7]}[CoCl₄]·4Cl·26H₂O (**4**) was obtained from Ce(NO₃)₃·6H₂O (51.76 mg); {Eu₂(H₂O)₁₀Q[7]}[CuCl₄]·4Cl·39H₂O (**5**) was obtained from Eu(NO₃)₃·6H₂O (53.17 mg); {Gd₂(H₂O)₁₀Q[7]}[CuCl₄]·4Cl·43H₂O (**6**) was obtained from Gd(NO₃)₃·6H₂O (53.81 mg); {Dy₂(H₂O)₁₀Q[7]}[CoCl₄]·4Cl·39H₂O (**7**) was obtained from Dy(NO₃)₃·6H₂O (57.66 mg); {Er₂(H₂O)₁₀Q[7]}[CoCl₄]·4Cl·47H₂O (**8**) was obtained from Er(NO₃)₃·5H₂O (52.86 mg); {Eu₂(H₂O)₁₀Q[7]}[CoCl₄]·4Cl·34H₂O (**9**) was obtained from Eu(NO₃)₃·6H₂O (53.17 mg); {Gd₂(H₂O)₁₀Q[7]}[CoCl₄]·4Cl·34H₂O (**10**) was obtained from Gd(NO₃)₃·6H₂O (53.81 mg); {Dy₂(H₂O)₁₀Q[7]}[CuCl₄]·4Cl·46H₂O (**11**) was obtained from Dy(NO₃)₃·6H₂O (57.66 mg); {Ho₂(H₂O)₁₀Q[7]}[CoCl₄]·4Cl·55H₂O (**12**) was obtained from Ho(NO₃)₃·5H₂O (52.58 mg); Elemental analysis results for the eight compounds are given in Table S1.

X-ray crystallography: A suitable single crystal (~0.2 × 0.2 × 0.1 mm³) 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 F² with the SHELXS-97 and SHELXL-97 program packages, respectively [64,65]. 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 twelve compounds are summarized in Table S2. In addition, the crystallographic

data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-919403 (1), 919404 (2), 919405 (3), 919406 (4), 919407 (5), 919408 (6), 919411 (7), 919412 (8), 919409 (9), 919410 (10), 919413 (11), 919414 (12). These data can be obtained free of charge via CCDC CIF Depository Request [66], 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.

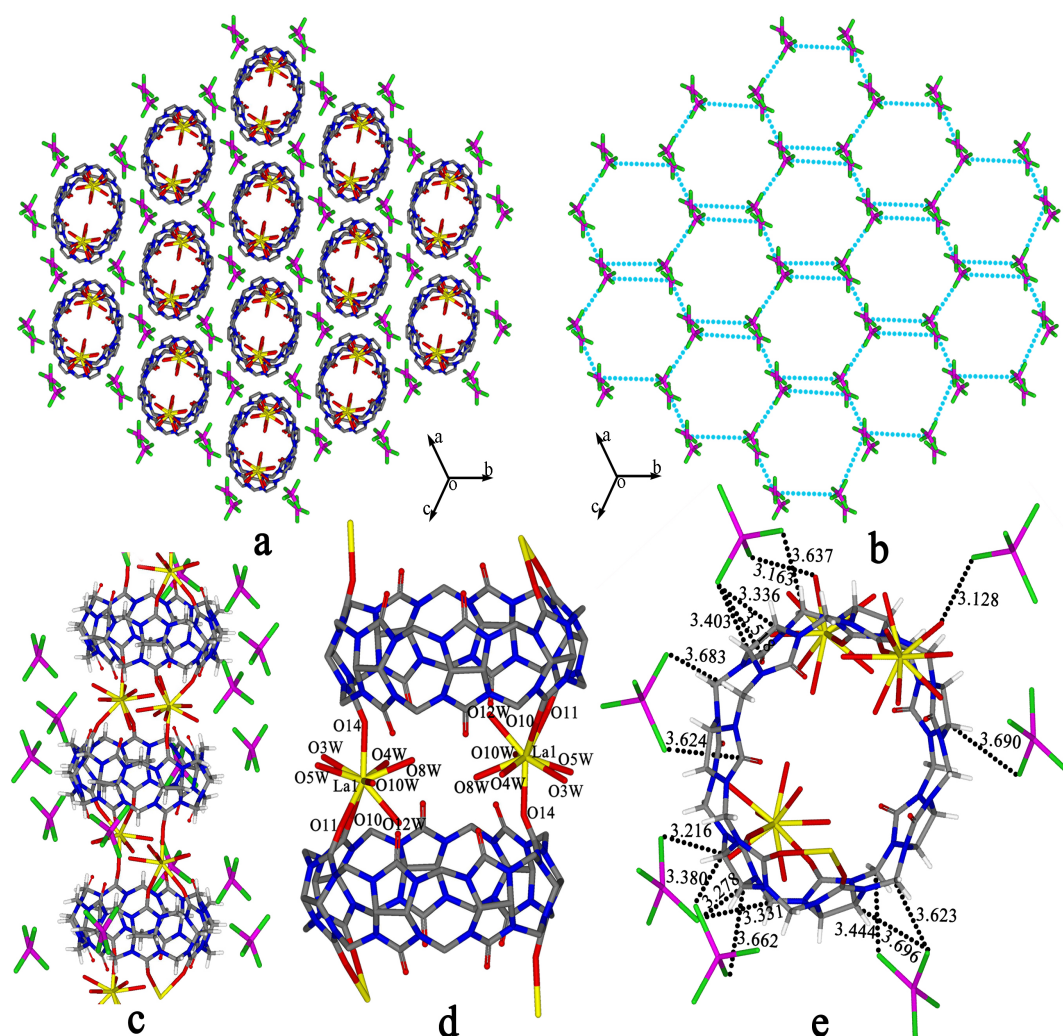
3. Results and Discussion

In previous studies, there have been numerous attempts to grow single crystals of complexes in which lanthanide cations are coordinated to Q[7] in various acidic media, but all have proved unsuccessful. However, it was discovered that when lanthanide cations are introduced into a $[\text{CdCl}_4]^{2-}$ -Q[7] solution, Ln^{3+} -Q[7] linear coordination polymers are readily produced, and the cadmium cation in the form of the tetrachloride, *i.e.*, $[\text{CdCl}_4]^{2-}$, can be arranged into honeycomb-like hollows. These hollows can then accommodate the one-dimensional Ln^{3+} -Q[7] coordination polymers through ion-dipole and C–H \cdots Cl interactions coupled with metal coordination [61]. Subsequent research has revealed that several transition metal ions, such as Zn^{2+} , Cu^{2+} , and Co^{2+} *etc.*, in the form of the tetrachloride anions, $[\text{MCl}_4]^{2-}$, can play a similar role in triggering the formation of the one-dimensional Ln^{3+} -Q[*n*] coordination polymers [62,63]. In the present work, we demonstrate the synthesis of a series of supramolecular assemblies of lanthanide cations and Q[7] molecules in the presence of $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions. Considering the similar chemical properties of the lanthanides, it is likely that the interaction of the various lanthanide cations with Q[7] molecules will give rise to similar coordination features and supramolecular assemblies. Indeed, the solid-state structures, as determined by X-ray crystallography, of the obtained complexes formed three isomorphous groups. Complexes of Q[7] with light lanthanide cations (those with atomic number less than that of neodymium (Nd^{3+})) are in the same group. There are two other groups for lanthanide cations with atomic numbers greater than europium (Eu^{3+}), but these seem to follow no obvious rule. For example, the complexes of Q[7] with Eu^{3+} and Gd^{3+} cations are in the second group in the presence of $[\text{CuCl}_4]^{2-}$ anions, while they are in the third group in the presence of $[\text{CoCl}_4]^{2-}$ anions. However, whichever complex belongs to which group, they all show a common supramolecular assembly, in which $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions form a honeycomb structure, and the Ln^{3+} cations coordinate to neighboring Q[7] molecules to form a 1D coordination polymer that is inserted into the channels of the honeycomb framework, so that each individual coordination polymer is surrounded by $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions.

An overall view of the coordination features and the supramolecular assembly of compound 1, as a representative example, is given in (Figure 1a). The $[\text{CuCl}_4]^{2-}$ anions form a honeycomb structure (Figure 1b). The La^{3+} cations coordinate to neighboring Q[7] molecules and form the 1D coordination polymers inserted into the channels in the honeycomb. As a result, each individual tubular coordination polymer is surrounded by $[\text{CuCl}_4]^{2-}$ anions (Figure 1c). Close inspection reveals that the neighboring Q[7] molecules in the coordination polymer are linked by two La^{3+} cations (2La1). Each La1 cation coordinates to nine oxygen atoms, namely three carbonyl oxygen atoms from two neighboring Q[7] molecules (O10, O11, and O14), and six water molecules (O3W, O4W, O5W, O8W,

O10W and O12W). The bond lengths of La–O_{carbonyl} are in the range 2.514–2.557 Å, and the bond lengths of La–O_{water} are in the range 2.514–2.600 Å (see Figure 1d).

Figure 1. X-ray crystal structure of compound **1**: (a) an overall view of the coordination features and supramolecular assembly; (b) the honeycomb-like framework composed of $[\text{CuCl}_4]^{2-}$ anions; (c) a 1D coordination polymer of La^{3+} cations and Q[7] molecules surrounded by the $[\text{CuCl}_4]^{2-}$ anions; (d) coordination of the La^{3+} cations by the portal carbonyl oxygens of the Q[7] molecules; (e) interaction of the $[\text{CuCl}_4]^{2-}$ anions with the Q[7] molecules.



Most lanthanide cations can coordinate to the portal carbonyl oxygens of Q[$n = 6, 7, 8$] molecules to form zigzag or tubular one-dimensional coordination polymers in the presence of $[\text{MCl}_4]^{2-}$ anions ($\text{M} = \text{Cd}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}$ and so on) [61–63], suggesting that these anions play the role of a structural inducer. The question then arises as to how the $[\text{MCl}_4]^{2-}$ anions induce this coordination process. Kögerler *et al.* demonstrated a novel crystal structure, consisting of a hybrid complex based on Q[6], in which the driving forces for the interaction between Q[6 or 8] and the polyoxometallate were the electron-deficient carbon sites of the carbonyl dipole of Q[6 or 8] and the V=O bonds of the polyoxometallate, as well as hydrogen bonding between the methine groups on an adjacent glycoluril unit and the oxygen of the polyoxometallate [67]. Based on this suggestion, it is reasonable to assume

that the formation of the $[\text{MCl}_4]^{2-}$ honeycomb is a consequence of ion-dipole interactions between the portal carbonyl carbon atoms and the chlorine atoms of the anions, as well as hydrogen bonding between the chlorine atoms of the anions and the methine groups on the surface of the $\text{Q}[n]$ molecules. Moreover, the formation of the $[\text{MCl}_4]^{2-}$ honeycomb is conducive to the coordination of lanthanide cations to $\text{Q}[n]$ molecules. In the case of $\text{La-Q}[7]\text{-}[\text{CuCl}_4]^{2-}$, each coordinated $\text{Q}[7]$ molecule in the coordination polymer is surrounded by seven $[\text{CuCl}_4]^{2-}$ anions (see Figure 1e). These interactions can include the ion-dipole interaction $\text{O}=\text{C}^{\delta+}\cdots\text{Cl}^- - \text{CuCl}_3^-$ where the interaction distances (black dashed lines) are in the range 3.469–3.624 Å, the hydrogen bonding of $\text{C}_{\text{methylene}}\cdots\text{Cl}^- - \text{CuCl}_3^-$ in the range 3.332–3.690 Å and the hydrogen bonding of $\text{O}_{\text{water}}\cdots\text{Cl}^- - \text{CuCl}_3^-$ in the range 3.128–3.216 Å (dashed lines).

Compounds **2**, **3**, **4** have similar coordination and supramolecular assemblies and form the first isomorphous group with in which compound **2** was prepared in the presence of $[\text{CuCl}_4]^{2-}$ anions, while compounds **3** and **4** were prepared in the presence of $[\text{CoCl}_4]^{2-}$ anions (see Figures S1–S4). Generally, the tetrachloride transition-metal dianions form a tetrahedral pattern, such as $[\text{CdCl}_4]^{2-}$ and $[\text{ZnCl}_4]^{2-}$, where the bond angles of $\angle\text{Cl-M}_{\text{transition-metal}}\text{-Cl}$ are close to $109^\circ 28'$, generally in the range $105^\circ\text{--}112^\circ$ [61,62]. In the present case, however, the bond angles $\angle\text{Cl-Cu-Cl}$ are in the range $101^\circ\text{--}122^\circ$, so the $[\text{CuCl}_4]^{2-}$ anions form a distorted tetrahedron. Similar results can be observed in the crystal structures of compounds with $[\text{CuCl}_4]^{2-}$ anions, such as compounds **2**, **5**, **6** and **11**, where the bond angles $\angle\text{Cl-Cu-Cl}$ are in the range $101^\circ\text{--}121^\circ$. The bond angles $\angle\text{Cl-Co-Cl}$ in the $[\text{CoCl}_4]^{2-}$ anions are similar to those of $[\text{CdCl}_4]^{2-}$ and $[\text{ZnCl}_4]^{2-}$ and are in the range $106^\circ\text{--}112^\circ$ for compounds with the $[\text{CoCl}_4]^{2-}$ anions, such as compounds **3**, **4**, **7**, **8**, **9**, **10** and **12**.

The $\text{Ln}^{3+}\text{-Q}[7]\text{-}[\text{CuCl}_4]^{2-}$ or $\text{Ln}^{3+}\text{-Q}[7]\text{-}[\text{CoCl}_4]^{2-}$ systems, with light lanthanides, generally give compounds isomorphous with those in the first group, while complexes containing heavier lanthanides can give complexes in the second or third groups. Although they belong to different isomorphous groups, the coordination of the lanthanide cation to the $\text{Q}[7]$ molecules and the corresponding supramolecular assemblies are similar to those of the compounds in the first group. Firstly, the $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions form a “honeycomb effect” and are arranged into honeycomb structures (see Figure 2a,b and Figures S5–S12). Secondly, two Ln^{3+} cations are coordinated to neighboring $\text{Q}[7]$ molecules to form tubular coordination polymers (see Figure 2c,d and Figures S5–S12). Finally, the tubular coordination polymers are inserted into the channels in the $[\text{CuCl}_4]^{2-}$ - or $[\text{CoCl}_4]^{2-}$ -honeycomb framework, so that each individual tubular coordination polymer is surrounded by $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions. Eu^{3+} cations connect two neighboring $\text{Q}[7]$ molecules resulting in the formation of tubular $\text{Eu}^{3+}\text{-Q}[7]$ polymers. Each Eu^{3+} cation is coordinated to eight oxygen atoms, three carbonyl oxygens belonging to two neighboring $\text{Q}[7]$ molecules and five water molecules. Each $\text{Q}[7]$ molecule is surrounded by four $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions through a combination of electrostatic interaction between Eu^{3+} cations and $[\text{CuCl}_4]^{2-}$ or $[\text{CoCl}_4]^{2-}$ anions, hydrogen bonding and ion-dipole interactions (see Figure 2c,f and Figures S5–S12). There exist two very similar tubular coordination polymers constructed from Eu^{3+} cations and $\text{Q}[7]$ molecules. For example, a pair Eu^{3+} cations connects two neighboring $\text{Q}[7]$ molecules, resulting in the formation of tubular $\text{Eu}^{3+}\text{-Q}[7]$ polymers. Close inspection reveals that the two Eu^{3+} cations in the pair are different in the two systems; they are the same in the $\text{Eu}^{3+}\text{-Q}[7]\text{-}[\text{CuCl}_4]^{2-}$ system (the second isomorphous group) but different in the $\text{Eu}^{3+}\text{-Q}[7]\text{-}[\text{CoCl}_4]^{2-}$ system (the second isomorphous group). However, the neighboring pair are

different in the $\text{Eu}^{3+}\text{-Q[7]-[CuCl}_4\text{]}^{2-}$ and the same in the $\text{Eu}^{3+}\text{-Q[7]-[CoCl}_4\text{]}^{2-}$ system. Thus, the distances between the two Eu^{3+} cations in the pair are different, as shown in Figure 2c,d.

Figure 2. X-ray crystal structure of compounds with light lanthanides: (a) and (b) an overall view of the coordination features and supramolecular assembly; (c) and (d) 1D coordination polymer of Eu^{3+} cations and Q[7] molecules surrounded by the $[\text{CuCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$ anions; (e) and (f) interaction of the $[\text{CuCl}_4]^{2-}$ anions with the Q[7] molecules for compounds **5** and **9**, respectively.

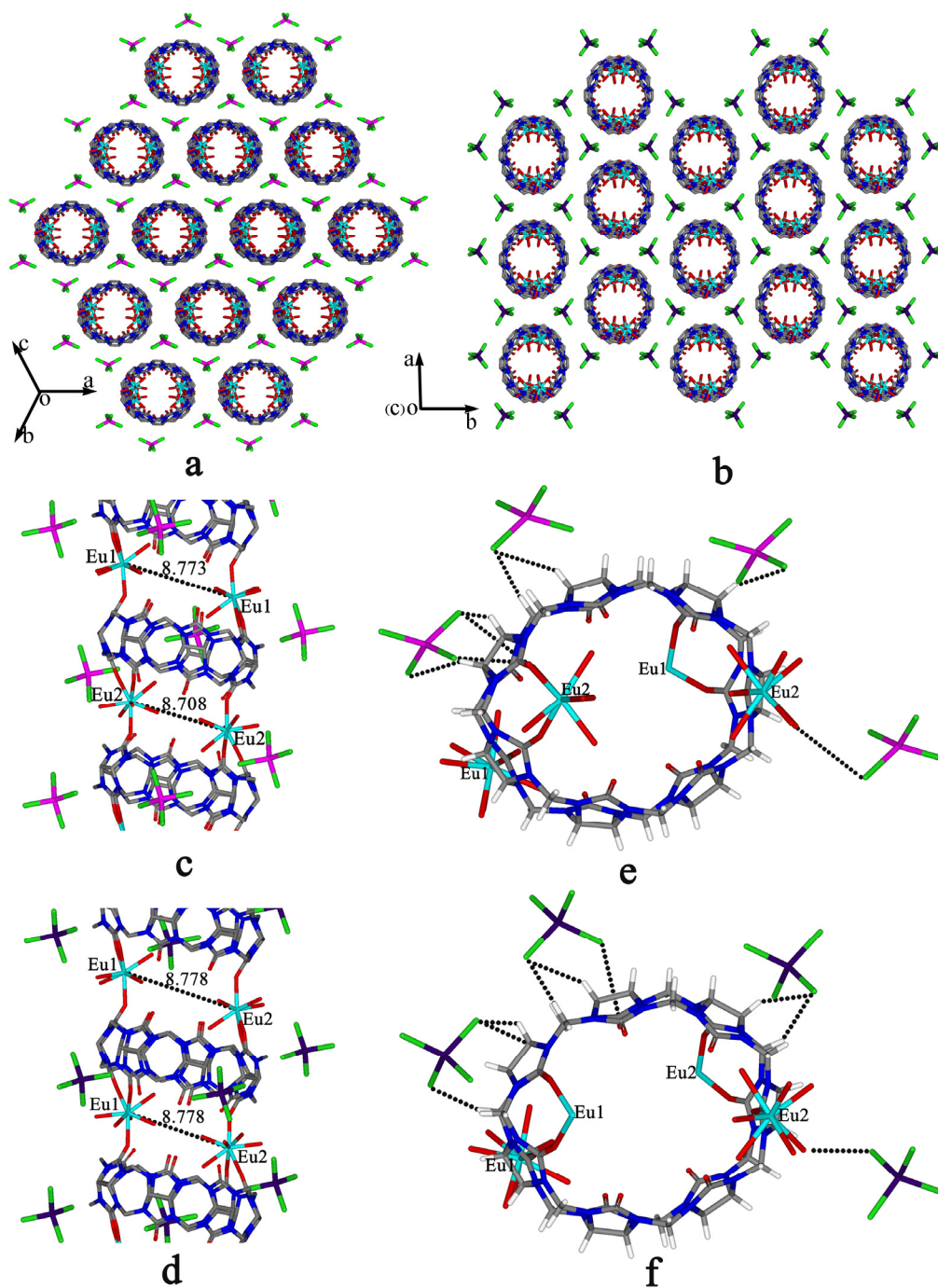
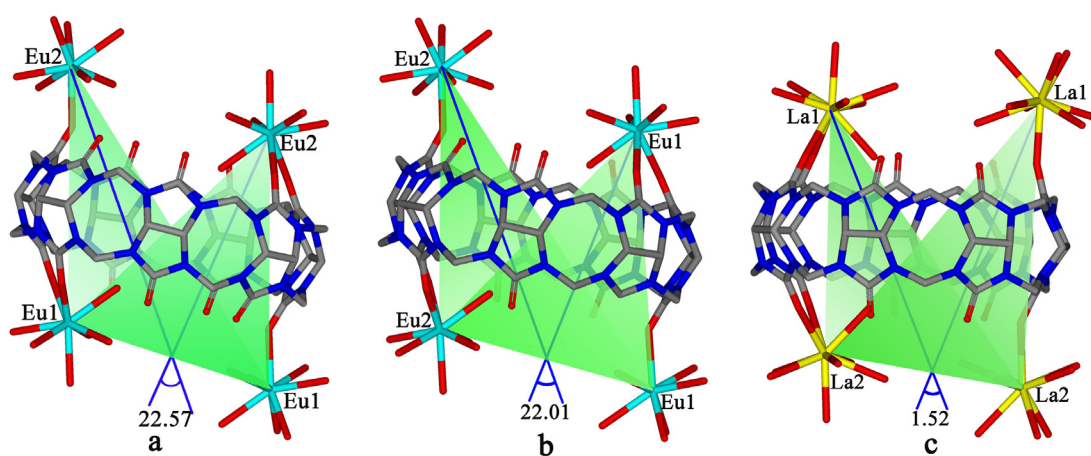


Figure 3a,b shows the coordination complexes for the two $\text{Eu}^{3+}\text{-Q[7]}$ compounds **5** and **9** obtained in the presence of the $[\text{CuCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$ anions, respectively. They belong to the second and

third isomorphous groups, respectively. The angles of two planes of three of the four Eu^{3+} cations at the two portals of the Q[7] molecule are different, but the differences are not significant, both being close to 20° (22.57° and 22.01° , respectively). These structural features can be observed in the other Ln^{3+} -Q[7]-[CuCl_4] $^{2-}$ or Ln^{3+} -Q[7]-[CoCl_4] $^{2-}$ systems, in which the Ln^{3+} are those with an atomic number greater than that of europium (Eu^{3+}) but smaller than erbium (Er^{3+}), which are compounds **5**, **6**, **9**, **10** and **12** (referring to Figures S5–S12). Figure 3c gives the coordination complex in compound **1** belonging to the first isomorphous group. The angle is significantly different to the values in the second and third groups, being only 1.52° . Note that the torsion in complexes of other compounds in the first isomorphous group is similar to this value, close to zero, such as the complexes in compounds **2–4** (see Figures S1–S4). Thus, the differences in the three isomorphous groups basically depend on the coordination environment of the Ln^{3+} cations to Q[7] molecules. The tubular coordination polymers containing Tm, Yb or Lu cations have not been synthesized since the slightly shorter ionic radii of these lanthanides make it difficult to coordinate to the cucurbit[*n*]urils. A similar situation has been observed in the Ln^{3+} -Q[7]-[CdCl_4] $^{2-}$ [61], Ln^{3+} -Q[6]-[CdCl_4] $^{2-}$ and Ln^{3+} -Q[6]-[ZnCl_4] $^{2-}$ systems.

Figure 3. X-ray crystal structure of compounds **5** and **9**: (a) and (b) torsions of the four Eu^{3+} cations at the two portals of a Q[7] molecule in compounds **5** and **9**, respectively; (c) torsion of the four La^{3+} cations at the two portals of a Q[7] molecule in compound **1** for comparison.



4. Conclusions

We have reported a series of coordination polymers prepared from Ln^{3+} cations and Q[7] molecules, in the presence of [CuCl_4] $^{2-}$ or [CoCl_4] $^{2-}$ anions as structure inducers. X-ray diffraction analysis has revealed that the compounds obtained can be divided into three isomorphous groups, namely the Ln^{3+} -Q[7]-[CuCl_4] $^{2-}$ or [CoCl_4] $^{2-}$ systems with light lanthanides in the first group, with systems with heavier lanthanides in the second or third groups. However, the crystal structures of these compounds show no significant differences. The [CuCl_4] $^{2-}$ or [CoCl_4] $^{2-}$ anions are present in a typical “honeycomb effect” and form honeycomb-like arrangements with hexagonal cells. The Ln^{3+} cations coordinate to the portal carbonyl oxygens of the Q[7] molecules to form tubular coordination polymers which occupy these hexagonal cells. Further detailed investigations are ongoing in our laboratories, with the aim of developing a useful practical synthetic technique.

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