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Dalton Transactions

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New Lanthanide-CB[6] Coordination Compounds: Relationships Between the Crystal Structure and Luminescent Properties

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The reaction between cucurbit[6]uril (CB[6]) and lanthanide chlorides (Eu, Sm, Tb and Tm) in acidic aqueous media led to four new structures. The compounds obtained are isostructural with general formula $[Ln_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$ (Ln = Eu^{3+} **(1)**, Sm^{3+} **(2)**, Tb^{3+} **(3)** and Tm^{3+} **(4)**) and crystallize in the $P2_1/c$ space group. For the complexes with Eu^{3+}, Sm^{3+} and Tb^{3+}, the luminescent properties in solid state and aqueous media were explored and all spectroscopic observations are in excellent agreement with the single crystal structure data. The excitation and emission spectra show the typical *f-f* transitions characteristic of the trivalent lanthanide ions. The transitions $^7F_J \leftarrow ^5D_1$ (J = 0,1,2) in the europium compound and $^7F_J \leftarrow ^5D_4$ (J = 0,1,2) in the terbium compound, not yet reported in lanthanide-CB[n] compounds, were also observed.

Introduction

Ligand selection is an important point in coordination chemistry. Their characteristics define many physicochemical properties and applications of the resulting coordination compounds. Macrocyclic ligands seem a good option, since they have great affinity for several cations, forming coordination compounds with interesting supramolecular properties such as inclusion complexes and host-guest chemistry[1].

Considering this class of molecules (macrocyclic ligands), the cucurbit[n]urils – CB[n] – (Figure 1) seem interesting systems able to produce new inorganic structures[2]. They have many carbonyl groups capable of linking to metal cations and of forming coordination complexes and networks[3]. Another attractive property is their molecular structure, featuring by hydrophobic and hydrophilic environments and an intrinsic cavity, enabling applications in several fields such as ion separations, molecular switching, etc[4]. In addition, cucurbit[n]urils and their compounds have biological[5a] and catalytic activity[5b].

Many coordination complexes and networks have been synthesized using these ligands, with CB[6] being the most common of them. The single crystal structure of the coordination compounds with these ligands shows interesting supramolecular interactions between the CB[n], water molecules (coordinated and non-coordinated) and, when present, the auxiliary ligand[6]. Polycarboxylate molecules are often employed as auxiliary linkers to increase the structure dimensionality through intermolecular or coordination bonds[7]. Dimeric and trimeric lanthanide coordination compounds have been found in the literature[7c], as well as polymeric structures[7c].
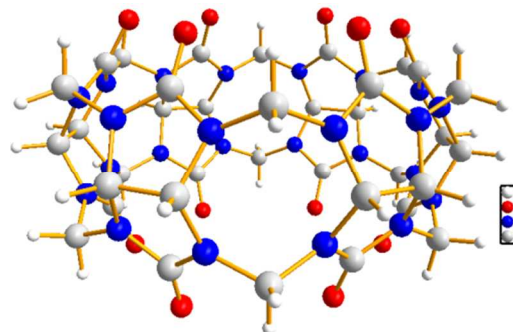

Figure 1. Structure of the cucurbit[6]uril ligand.

The special place in the field of coordination chemistry occupied by lanthanides and their compounds stems from their interesting magnetic and especially luminescent properties[8a]. Systems with Eu^{3+} and Tb^{3+} are the ones most often reported, although other ions have been studied as well. Our group has been very active in this research field, having reported works about the influence of the synthesis parameters[8b], combinatorial chemistry[8c], and applications in forensic science[8d] and OLED's[8e].

Considering the versatility and applications of cucurbit[n]uril and their coordination compounds, we focused on the synthesis and characterization of new structures obtained by the reaction between cucurbit[6]uril and Ln^{3+} ions (Ln = Sm^{3+}, Eu^{3+}, Tb^{3+} and Tm^{3+}). It is noteworthy that there are few reports on coordination compounds with lanthanides and only CB[6][6a,9]. The compounds synthesized are isostructural, crystallizing in the monoclinic system, in space group $P2_1/c$ with molecular formula $[Ln_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$ (Ln = Eu^{3+} **(1)**, Sm^{3+} **(2)**, Tb^{3+} **(3)** and Tm^{3+} **(4)**). The void

volume within the CB[6] cavity is about 110 Å^3 and as such, it can encapsulate small molecules. The integration of residual density indicate that the site is occupied by disordered H$_2$O molecules (about one) adsorbed in the CB[6] cavity. The products were further characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and luminescence spectroscopy.

Results and discussion

Several coordination compounds and coordination polymers with cucurbit[n]uril ligands have been reported, particularly with CB[6]. In many cases, organic molecules such as polycarboxylates are used in the synthesis, and can act as auxiliary ligands and/or counter-ions. Few compounds, however, have been reported with lanthanide ions and CB[6] alone. In this work, the products **(1)-(4)** were obtained in an acidic aqueous medium, which was used to improve ligand solubility. The synthesis procedure was similar to the one reported by Fedin and co-workers[6a], but we started from lanthanide chloride instead of the nitrate salt. This change seemed essential because the Ln-CB[6] compounds obtained by Fedin[6a,9] had the counter-ion (nitrate) in the first coordination sphere with chelating coordination mode, generating a different structure. This was also due to the higher lanthanide coordination number and intermolecular hydrogen bound present in the structure.

The X-ray single crystal analysis revealed that compounds **(1)**, **(2)**, **(3)** and **(4)** are isostructural. They crystallize in the space group $P2_1/c$, with general molecular formula [Ln$_2$(H$_2$O)$_{12}$(H$_2$O@CB[6])]Cl$_6$(H$_2$O)$_4$ (Ln = Eu^{3+} **(1)**, Sm^{3+} **(2)**, Tb^{3+} **(3)** and Tm^{3+} **(4)**). A decrease on the Ln-O bond lengths due to lanthanide ionic radii also took place (Table 1) causing a decrease on the unit cell volume.

The structures, feature two symmetry equivalent lanthanide ions located at each side of the cucurbit[6]uril moiety, distanced by 10.75-10.62 Å. Within the crystal, the distance between the lanthanide ions from different molecules, can be shorter i.e. 7.900, 7.937, 7.842, 7.813 Å, respectively in **(1)-(4)**. Each one of these ions is octacoordinated and bonded by two oxygen atoms from the cucurbituril ligand and six oxygen atoms from water molecules, forming a distorted square antiprism geometry (Figure 2). The square base is formed by four oxygen atoms from water molecules. They are quasi-coplanar causing a slight distortion on the coordination environment, as we can see in Figure 2. This distortion is attenuated with the decrease of the lanthanide ionic radius, once the torsion angles (O9-O10-O11-O12 or equivalent) torsion angles decrease: 3.25º in **(1)**, 2.94º in **(2)**, 2.32º in **(3)**, 0.08º in **(4)**.
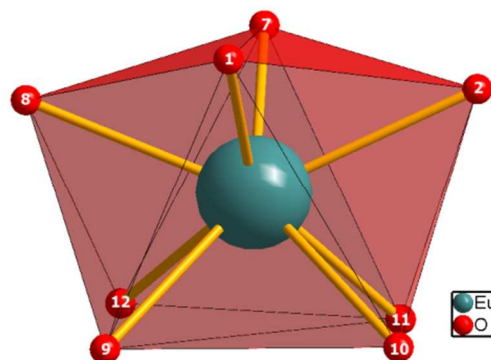

Figure 2. Coordination environment of Eu^{3+} in compound **(1)**.

Since all compounds are isostructural, the detailed discussion below is based on the example of the europium complex **(1)**. In the second coordination sphere of the lanthanide ions are located three chloride ions distanced by 4.664 Å (Cl(1)) and 4.696 Å (Cl(2'), symmcode: 1-x, ½+y, ½-z), and 4.848 Å (Cl(3)), respectively from Eu^{3+} cation, and also two hydration water molecules (O13 and O14). The next symmetry equivalent Cl(1) anion (symmcode: x, ½-y, ½+z) is bridges two cations and is also closer to the Eu^{3+}: 4.833 Å. Although water molecules and chloride ions can interact with Ln^{3+} ions, the water molecules provide probably more stability in the first coordination sphere due to the intermolecular hydrogen bonds with the other water molecules and the carbonyl groups of cucurbit[6]uril ligand. Figure 3 presents the coordination unit of compound **(1)**.
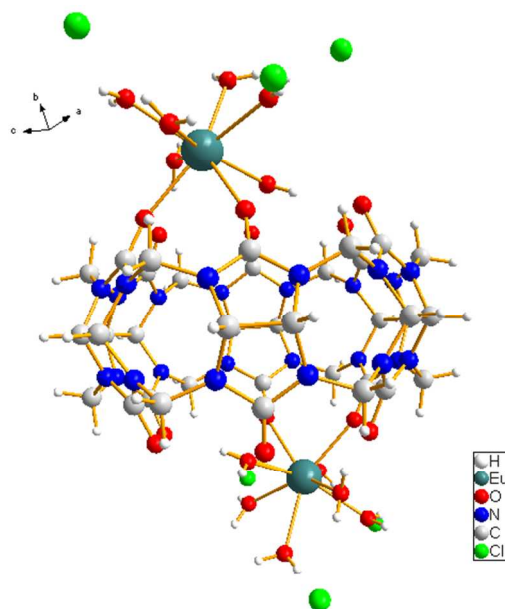

Figure 3. Coordination unit for **(1)**.

All structures can be described as discrete 0D coordination compounds (no-polymeric frameworks). In this case, the crystal growth is directed by intermolecular hydrogen bonds present in the structure. Atoms O(1) and O(2), from the ligand, do not participate in hydrogen bonding due to their coordination to the metal cations (Figure S1 in the supplementary information[6] and water molecules in the first sphere were observed: O(3)…O(7) (2.805 Å), O(4)…O(9) (2.918 Å) and O(6)…O(8)

Table 1. Coordination bond lengths (Å)

	Sm	Eu	Tb	Tm
Ln-O1	2.408(4)	2.394(4)	2.354(2)	2.309(3)
Ln-O2	2.418(4)	2.412(4)	2.377(2)	2.339(3)
Ln-O7w	2.367(5)	2.354(5)	2.324(3)	2.268(4)
Ln-O8w	2.408(4)	2.403(5)	2.359(3)	2.314(4)
Ln-O9w	2.445(5)	2.429(5)	2.387(3)	2.337(6)
Ln-O10w	2.470(5)	2.453(5)	2.414(3)	2.362(4)
Ln-O11w	2.426(5)	2.408(6)	2.364(3)	2.319(4)
Ln-O12w	2.508(5)	2.482(5)	2.438(3)	2.392(4)

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(2.662 Å). The hydrogen bond between O(5) (CB[6]) and O(14) (hydration water) at 2.815 Å, was also observed.

The hydration water molecules play an important role in intermolecular interactions, since they interconnect the 0D units and also the chloride counter-ions (Table S1-S4 in the supplementary information). There are two symmetry independent hydration water molecules and regarding them as acceptor of hydrogen bonds, the interactions O(14)…O(7) (2.710 Å) and weaker O(14)…H(A)-O(9) (2.730 Å) were observed with coordinated water molecules. This water molecule also interacts as a donor with a chloride ion through the intermolecular bond Cl(3)…O(14) with hydrogen bond distance 3.190 Å. Another hydration water molecule makes hydrogen bonds only with chloride ions: Cl(2)…O(13) (3.149 Å) and Cl(3)…O(13) (3.257 Å). Each one of the chloride ions still makes other interactions with the coordinated water molecules. So that, each anion makes three intermolecular hydrogen bonds, although the Cl(1) connects only coordination molecules, and the other chloride ions interact with two coordinated water molecules and one hydration water molecule. The 0D coordination units are interconnected by all those interactions (Figure 4) generating the final crystal packing as shown in Figure 5. Once the other compounds are isostructural to (1), the description for the hydrogen bonds is relevant also for them.
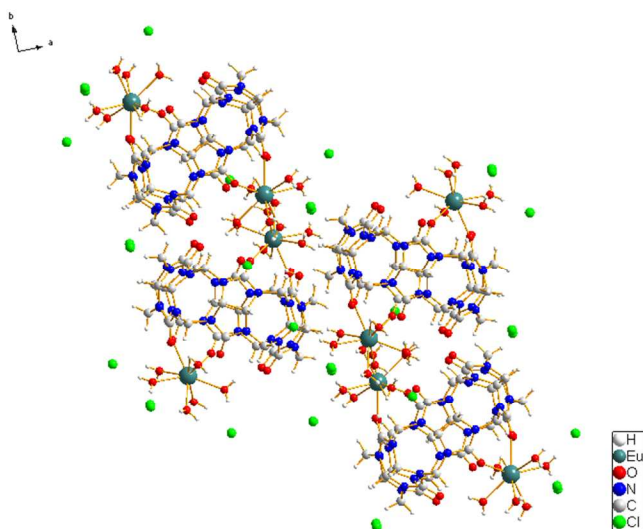

Figure 4. Mutual orientation of the coordination units in (1) viewed along the **c**-axis.
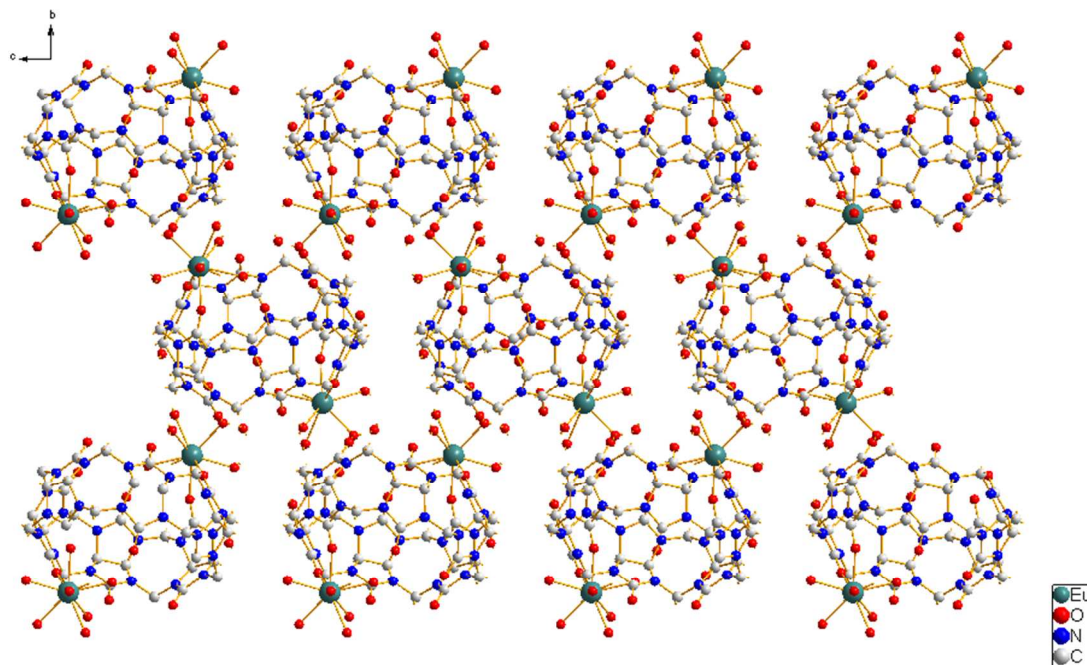
Thermal Decomposition

The thermal analyses for the compounds were performed under N_2 atmosphere (Figure S2) and all complexes gave mass losses associated to the water molecules (hydrated and coordinated) and the decomposition of the CB[6]. For compound (1), the thermal decomposition starts with two mass loss steps (25ºC-286ºC) related to four hydrated water molecule and twelve coordinated water molecules (totalling 16.82% calc.; 17.1% exp.). Then, a mass loss of 63.7% corresponding to the organic ligand and the chloride ions (63.9% calc.) was observed. The complete decomposition of (1) results in the formation of europium oxide, Eu_2O_3 (19.3 calc.; 19.2 exp.). For (2)-(4), the thermal analysis shows similar results.

Vibrational and ^{13}C NMR Spectroscopy

The infrared spectra of compounds (1) to (4) (Figure S3, supplementary information) as expected, are very similar and show the main absorption bands related to the organic ligand. In (1), for example, an intense broad band centred in 3360 cm^{-1} corresponding to the asymmetric O-H stretching of the water molecules was observed, indicating the high hydration degree of the compound. Another evidence for these molecules is the intense peak associated to the hydrogen bonds (HO…H) located at 961 cm^{-1}. The asymmetric carbonyl stretching of the amide groups is located at 1713 cm^{-1}, displaced by 23 cm^{-1} in comparison to the free CB[6] due to the complexation with the lanthanide cation. The C-N stretching signal at 1496 cm^{-1} was also noticed.

Compound (2) was dissolved in D_2O and the ^{13}C NMR spectrum was acquired (Figure S4, supplementary information). Three signals at 52.8, 71.0 and 157.7 ppm were observed and are related to the CH_2, CH and C=O of the CB[6] ligand, respectively. The CH_2 and CO signals are shifted by 0.6 and 0.5 ppm in comparison to the free ligand, due to coordination with the metallic center. Those signals are in agreement with the literature[10]. For (1), the ^{13}C-NMR showed the same peaks related to the CH_2 and CH groups, however, the spectrum does not showed the signal corresponding to the C=O group, due to the higher paramagnetic properties of the europium ions. It was not possible to obtain the NMR data for the compounds (3) and (4), once those cations are too paramagnetic.

Figure 5. Crystal packing viewed along the **a**-axis for **(1)** (the hydrogen atoms, cavity water and chloride ions are omitted).

Luminescent Properties

Since luminescence is the most important and explored property of the trivalent lanthanide ions, room temperature solid state photoluminescence measurements of compounds **(1)**, **(2)** and **(3)** were carried out. Even though the excitation and emission spectra can provide a wealth of information, especially about the Ln^{3+} ions coordination environment; there are few reports on those properties for CB[n]-lanthanide compounds[7d,10]. The literature regarding these compounds has focused mainly on the structural aspect[5b,6,7a,7b,9c].

For all compounds, the excitation and emission processes were relative to the metal ions. In the excitation spectra of **(1)**, **(2)** and **(3)** (Figures S6-S8), the typical intra-4f transitions characteristic of the Eu^{3+}, Sm^{3+} and Tb^{3+} ions, respectively from the fundamental states $^7F_{0,1}$, $^6H_{5/2}$ and $^5F_6$ to the ion excited levels, were observed. The bands relative to the ligand are not observed and this indicates a non-effective intramolecular energy transfer from the ligand to the metal ions. The emission spectrum of CB[6] (Figure S9) shows an emission band in the blue region (centred in 464 nm). This band is not detected in any emission spectra due to the higher emission intensity of the lanthanide ions. These observations are in good agreement with the literature, as it has been reported that luminescence of those ligands decrease with the metal complexation[11].

The complex **(1)** was excited in 394 nm, corresponding to the $^5L_6 \leftarrow {^7F_{0,1}}$ transition, and the emission spectrum is shown in Figure 6. Transitions from the $^5D_0$ and $^5D_1$ excited levels to the levels ^7F_J (J = 0-4) were observed, suggesting a slow non-radiative decay $^5D_0 \leftarrow {^5D_1}$. Those low order transitions (from the $^5D_1$) have not reported in lanthanide-cucurbit[n]uril compounds before. Only one peak for the $^7F_0 \leftarrow {^5D_0}$ transition was observed, indicating one Eu^{3+} emission center, in agreement with the crystallographic results. The relative intensities of the transitions $^7F_1 \leftarrow {^5D_0}$, $^7F_2 \leftarrow {^5D_0}$ and $^7F_4 \leftarrow {^5D_0}$ suggests that the coordination environment of the Eu^{3+} is near to a high symmetry point group[12a]. This also agrees well with the crystallographic data, as other works show that this behaviour is consistent with a square antiprism geometry on Eu^{3+} ion which

the coordination polyhedron slightly distorts from D_{4d} point group[12b].

Figure 7 shows the room temperature emission spectrum of **(2)** excited in 401 nm, corresponding to the $^6P_{3/2} \leftarrow {^6H_{5/2}}$ transition of the Sm^{3+} ion. All observed transitions were from the excited $^4G_{5/2}$ level to the ^6H_J levels (J = 5/2; 7/2; 9/2 and 11/2). The most intense peak at 594 nm , is due to $^6H_{7/2} \leftarrow {^4G_{5/2}}$ transition, and is responsible for the light orange emission. The transitions $^6H_{5/2} \leftarrow {^4G_{5/2}}$ and $^6H_{7/2} \leftarrow {^4G_{5/2}}$ are allowed by magnetic dipole, but the transitions $^6H_{9/2} \leftarrow {^4G_{5/2}}$ and $^6H_{11/2} \leftarrow {^4G_{5/2}}$ are purely allowed by electric dipole. The higher intensity of the electric dipole transitions in comparison to the magnetic dipole transitions indicates the asymmetry around the lanthanide ion.[13b,13c]. Again, those results are in good agreement with the crystal structure.

The compound **(3)** was excited in 368 nm, corresponding to the $(^5G_4, {^5L_{10}}) \leftarrow {^7F_6}$ transition and the emission spectrum is shown in Figure 8. Transitions from the emission level $^5D_4$ to the states ^7F_J (J = 0-6) were observed. The less intense emissions $^7F_{0,1,2} \leftarrow {^5D_4}$ were not reported before in compounds with this ligands. Emissions from the $^5D_3$ level were not observed, indicating a fast non-radiative decay $^5D_4 \leftarrow {^5D_3}$. The strongest peak located at 543 nm due to the transition $^7F_5 \leftarrow {^5D_4}$, is responsible for the green light emission of the compound.

The compound **(1)** was dissolved in water and the room temperature luminescence properties were analysed. In the excitation spectrum (Figure S13, supporting information), the same signals corresponding to the metal cation were observed, similar to the solid state spectrum. However, in the emission spectrum (Figure S14, supporting information) a strong decrease in the intensity of the $^7F_2 \leftarrow {^5D_0}$ transition in comparison to the $^7F_1 \leftarrow {^5D_0}$ and $^7F_4 \leftarrow {^5D_0}$ transitions was observed, indicating an increase in the symmetry around the Eu^{3+} ion[8]. Due to the decrease of the lanthanide luminescence in aqueous media, a broad band centred at 456 nm was also observed, related to the emission of the cucurbit[6]uril ligand and overlapped by the water Raman band. In the dissolution process, occurs changes in the first coordination sphere of the Eu^{3+} ion, possibly, the replacement of the CB[6] for water molecules, increasing the local symmetry of the lanthanide ion and the luminescence of the ligand in solution.
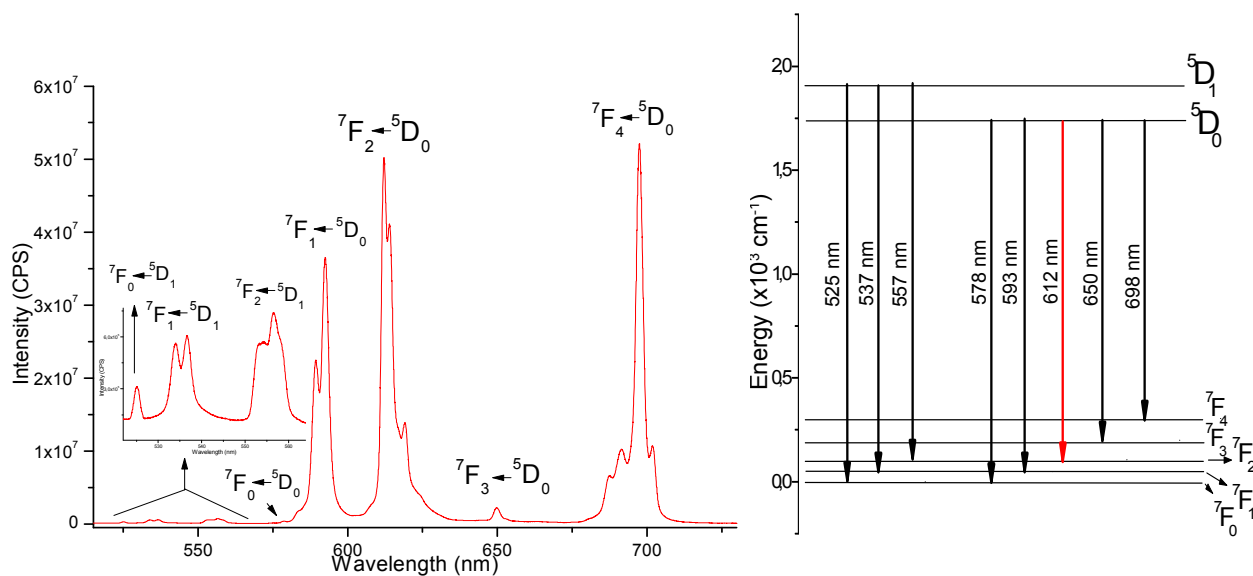
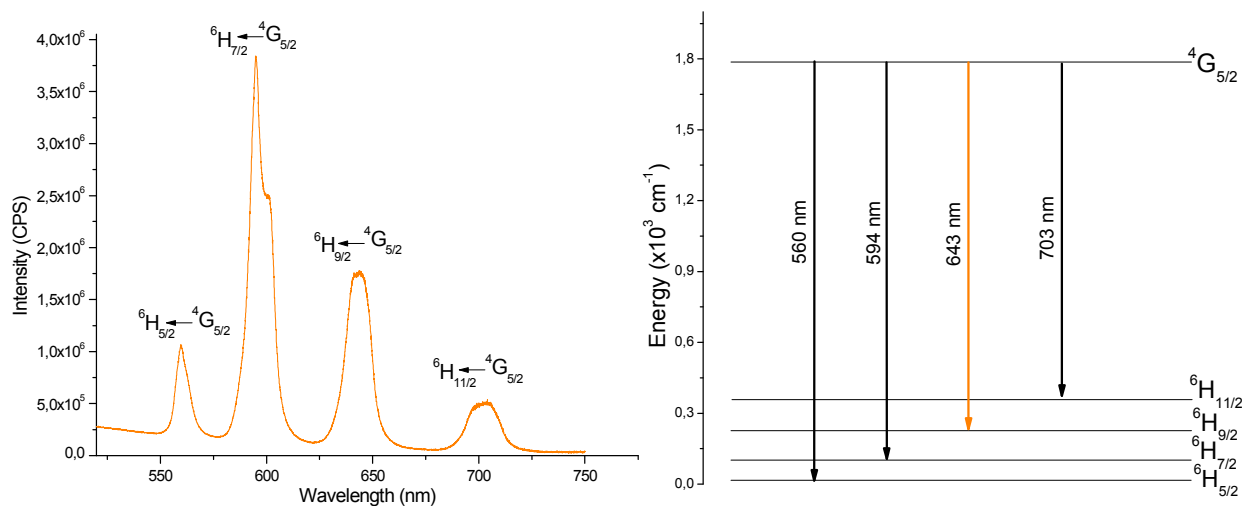Figure 6. Solid state emission spectrum (λexc. = 394 nm) and the experimental emission energy levels of **(1)**.

Figure 7. Solid state emission spectrum (λexc. = 401 nm) and the experimental emission energy levels of **(2)**.
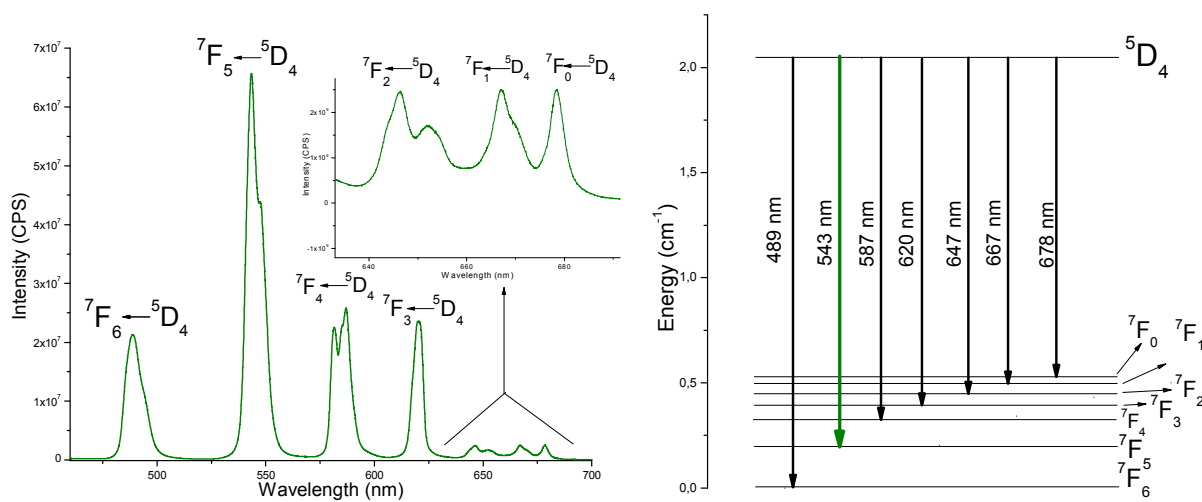

Figure 8. Solid state emission spectrum (λexc. = 368 nm) and the experimental emission energy levels of **(3)**.

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A decrement in the lifetime luminescence from 149 μs (in the solid state) to 108 μs (in aqueous medium) was also noticed in agreement with the reduction in the europium luminescence.

In the aqueous medium luminescence spectrum of **(2)**, the typical excitation signals (Figure S17, supporting information) of the Sm^{3+} ion were observed, similar to the solid state spectra. The emission spectrum (Figure S18, supporting information) also showed the emission band of the ligand superimposed by the Raman band of the water molecule in 469 nm and the Sm^{3+} $^6H_J \leftarrow {}^4G_{5/2}$ (J = 5/2; 7/2; 9/2 and 11/2) transitions. A decrease in the lifetime luminescence from 8 μs to 4.8 μs was also observed (Figure S21, supporting information).

For **(3)**, the same peaks in comparison to the solid state excitation spectrum (Figure S19, supporting information) were observed. The emission spectrum (Figure S20, supporting information) showed the transition characteristic of the terbium ion with the most intense peak at 542 nm also related to the $^7F_5 \leftarrow {}^5D_4$ transition and a weak broad band at 421 nm corresponding water Raman band. The ligand emission was not observed. The increase in the relative intensity of the $^7F_6 \leftarrow {}^5D_4$ transition was also observed, indicating the change in the symmetry around the Tb^{3+} ion. The lifetime luminescence in solid state (546 μs) is higher than in solution (435 μs), similar to **(1)** and **(2)**.

Conclusions

In the present work, four new coordination compounds were reported, obtained from the reaction between lanthanide chlorides (Eu, Sm, Tb and Tm) and the CB[6] ligand in acidic aqueous media with satisfactory yields. The compounds synthesized are isostructural and the lanthanide ions are octacoordinated with square antiprism geometry. For the compounds with Eu, Sm and Tb, the luminescent properties in solid state and aqueous solutions were investigated and all results are in excellent agreement with the single crystal structure. The emission spectra show the typical *f-f* transitions for the Eu^{3+}, Sm^{3+} and Tb^{3+} ions. In the case of Eu-CB[6] and Tb-CB[6] systems, low order transitions were observed, not yet reported before in compounds with cucurbit[n]uril ligands and this cations.

Experimental

General: Cucurbit[6]uril and lanthanide oxides (99.99%) were purchased from Aldrich and used without further purification. $LnCl_3 \cdot 6H_2O$ (Ln = Sm^{3+}, Eu^{3+}, Tb^{3+} e Tm^{3+}) were obtained by reaction of hydrochloric acid with the corresponding lanthanide oxide.

Syntheses of $[Eu_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$ (1)

The synthesis was carried out in aqueous medium containing $EuCl_3.6H_2O$ and cucurbit[6]uril. The CB[6] (0.05 mmol, 0.049 g) was added to 5 mL of distilled water and heated to 80 ºC under stirring. Concentrated hydrochloric acid was dropwise until complete dissolution of CB[6]. $EuCl_3.6H_2O$ (0.3 mmol, 0.110 g) were then dissolved and the solution was left to cool down to room temperature. After one week, colourless block crystals were filtered, rinsed with ethanol and water, and air-dried. Yield: 75% (68 mg) (based on CB[6]). Elemental analysis: Calc. for $[Eu_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$: C 24.40%; H 3.85%; N 18.47%. Found: C 23.70%; H 4.59%; N 17.97%.

Syntheses of $[Sm_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$ (2)

The synthesis of **(2)** were carried out similarly to that of **(1)**, just replaced $EuCl_3.6H_2O$ by $SmCl_3.6H_2O$ (0.3 mmol, 0.109 g). After one week, colorless block crystals were filtered, rinsed with ethanol and water, and air-dried. Yield: 63% (57 mg) (based on CB[6]). Elemental analysis: Calc. for $[Sm_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$: C 24.44%; H 3.85%; N 18.5%. Found: C 23.37%; H 4.20%; N 17.85%.

Syntheses of $[Tb_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$ (3)

The synthesis of (3) were carried out similarly to that of **(1)**, just replaced $EuCl_3.6H_2O$ by $TbCl_3.6H_2O$ (0.3 mmol, 0.112 g). After three weeks, colourless block crystals were filtered, rinsed with ethanol and water, and air-dried. Yield: 67% (61 mg) (based on CB[6]). Elemental analysis: Calc. for $[Tb_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$: C 23.56%; H 3.82%; N 18.32%. Found: C 24.11%; H 4.7%; N 17.94%.

Syntheses of $[Tm_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$ (4)

The synthesis of (4) were carried out similarly to that of **(1)**, just replaced EuCl3.6H2O by $TmCl_3.6H_2O$ (0.3 mmol, 0.115 g). After three weeks, colourless block crystals were filtered, rinsed with ethanol and water, and air-dried. Yield: 40% (37 mg) (based on CB[6]). Elemental analysis: Calc. for $[Tm_2(H_2O)_{12}(H_2O@CB[6])]Cl_6(H_2O)_4$: C 23.40%; H 3.69%; N 17.71%. Found: C 23.65%; H 4.39%; N 17.48%.

Physical Measurements:

Elemental CHN analyses were performed on a CE Instruments model EA1110 elemental analyzer. The IR spectroscopy was carried out with a Bruker FT-IR model IFS66 spectrometer, in range of 4000–400 cm^{-1}. The TGA curves were obtained in a Shimadzu TGA 60-H thermogravimetric analyzer under an N_2 atmosphere, from room temperature to 1000 °C, at a heating rate of 10 °C/min. For ^{13}C and ^1H NMR spectra, the compounds were dissolved in deuterated water and the spectra were recorded in a Varian Unitty Plus operating with a 1H proton frequency of 400 MHz The photoluminescence spectra were obtained in a modular spectrofluorometer Horiba Jobin-Yvon Fluorolog-3 with double monochromator, using a 450 W xenon lamp.

X-ray Structure Determination:

Experimental data were collected on a KUMA KM4CCD 4-axis diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were processed using the CrysAlisPro (Oxford Diffraction) program package[15a]. Measurement of diffraction data was performed at 298 K. Empirical absorption correction was applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm of the CrysAlisPro package. An initial structure model was obtained by charge flipping (SUPERFLIP, Palatinus)[15b]. Calculations were carried out using the SHELX system[15c] run under WINGX environment[15d]. All C-H type hydrogen atoms were located in calculated positions and refined as riding with the standard restraints. Hydrogen atoms of the O-H type were refined as restrained to O-H bond length of 0.82Å and 1-3 hydrogen atoms distance of 1.27Å on O14 and O14. In the centre of cucurbituril cavity two strong electron

Table 2. Crystallographic data for compounds **(1)-(4)**.

	(1)	**(2)**	**(3)**	**(4)**
Empirical Formula[†]	$C_{36}H_{70}Cl_6Eu_2N_{24}O_{29}$	$C_{36}H_{70}Cl_6Sm_2N_{24}O_{29}$	$C_{36}H_{70}Cl_6Tb_2N_{24}O_{29}$	$C_{36}H_{70}Cl_6Tm_2N_{24}O_{29}$
Fw[†]	1819.74	1816.53	1833.66	1853.68
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	12.2845(11)	12.2767(9)	12.1719(2)	12.1396(3)
b, Å	19.8525(14)	19.8927(11)	19.6814(2)	19.5834(4)
c, Å	14.8338(13)	14.8807(10)	14.7268(2)	14.6748(4)
α, °	90	90	90	90
β, °	112.880(11)	112.937(8)	112.728(2)	112.690(3)
γ, °	90	90	90	90
V, Å³	3333.0(6)	3346.8(4)	3254.01(9)	3218.70
Z	2	2	2	2
λ, Å	0.71073	0.71073	0.71073	0.71073
D_{calcd}, gcm⁻³	1.811	1.801	1.869	1.911
T, K	293	293	293	293
μ, mm⁻¹	2.20	2.08	2.50	3.09
$F000$	1824.0	1820.0	1832.0	1848.0
$h, k, l\ max$	14,23,17	14,23,17	14,23,17	14,23,17
N_{ref}	11842	11459	39814	21167
$\theta_{min}, \theta_{max,}$ °	2.5, 25.1	2.5, 25.0	2.6, 25.0	2.6, 25.1
R_1 (refl. I>2σ(I))	0.048(4561)	0.05(5255)	0.030(5278)	0.036(4943)
wR_2 (refl.)	0.135(5899)	0.119(5912)	0.078(5762)	0.093(5697)

density maxima were found, at ca 1.53 Å from one another, placed on both sides of local inversion centre. They were interpreted as a disordered water molecule with site occupation factor equal to ½. The residual electron density was so smeared out that attachment of hydrogen atoms to those disordered oxygen would be very arbitrary and was omitted. The images were processed using the Diamonds 3.0 software[15e].

Crystallographic data for the structures of **(1)** to **(4)** (Table 2) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 912044-912047. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

Notes and references

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† Calculated with the corrected number of H-atoms at disordered water.

Electronic Supplementary Information (ESI) available: IR spectra, Excitation spectra, emission spectrum of the CB[6], TGA analysis and lifetime decays of the complexes. See DOI: 10.1039/b000000x/

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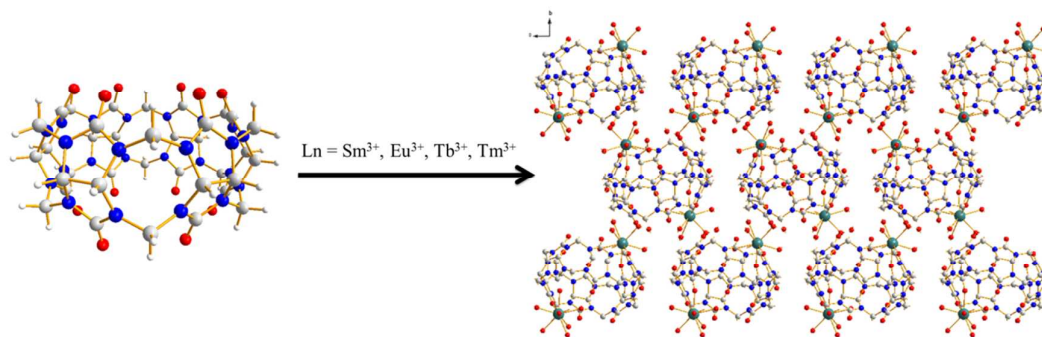
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New Lanthanide-CB[6] Coordination Compounds: Relationships between the Crystal Structure and Luminescent Properties.

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GRAPHICAL ABSTRACT

$Ln = Sm^{3+}, Eu^{3+}, Tb^{3+}, Tm^{3+}$

Four new isostructural complexes were obtained with Ln^{3+} and CB[6]. The compounds crystallize in a P2$_1$/c monoclinic structure. These compounds present interesting spectroscopic properties, not observed before in complex with cucurbit[n]uril.