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Carbonate-bridged dinuclear lanthanide(III) complexes of chiral macrocycle

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Abstract

Mononuclear Eu(III) and Dy(III) complexes of the chiral hexaaza macrocycle L, 2(R),7(R),18(R),23(R)-1,8,15,17,24,31-hexaazatricyclo[25.3.1.1.0.0]-dotriaconta-10,12,14,26,28,30-hexaene have been obtained as chloride derivatives (1 and 2, respectively) and characterized by using spectroscopic methods. The X-ray crystal structure of 2 has been determined. The reaction of two equivalents of mononuclear 1 or 2 complexes with one equivalent of sodium carbonate results in the formation of dinuclear complexes $[Eu_2L_2(\mu_2-CO_3)(H_2O)_3]Cl_4$ **3** and $[Dy_2L_2(\mu_2-CO_3)(H_2O)_3]Cl_4$ **4**, respectively. The X-ray crystal structure of complex **3** reveals two macrocyclic [EuL]³⁺ units bridged by the carbonate anion. The carbonate anion is bound to the Eu(III) ions using the η^1 : η^2 - μ_2 bridging mode. The binding of carbonate anions to the [EuL]³⁺ or [DyL]³⁺ macrocyclic units has also been studied in solution using spectroscopic methods. The titration of the starting paramagnetic mononuclear chloride derivatives 1 and 2 monitored by ¹H NMR spectroscopy revealed initial formation of dinuclear species, followed by the formation of complexes possessing additional carbonate ligands. The dinuclear carbonate complexes 3 and 4 are also formed in the reactions of the respective mononuclear chloride complexes with gaseous CO₂. Lanthanide(III) complexes of the chiral hexaaza macrocycle L are effective for catalytic hydrolysis of bis(4-nitrophenyl) phosphate BNPP. Within the series of the studied mononuclear complexes: nitrate derivatives $[LnL(NO_3)(H_2O)](NO_3)_2$ (Ln = Ho, Er), $[LnL(H_2O)_2](NO_3)_3$ (Ln = Tm, Yb, Lu) and chloride derivatives $[LnL(H_2O)_2]Cl_3$ (Ln = Tm, Yb, Lu, Y) the catalytic activity of the complexes is increased with increasing ionic size. Kinetic studies revealed that most active is the dinuclear europium(III) complex 3 which catalyzes the

hydrolysis of BNPP with a rate $k_{obs} = 6.5 \times 10^{-5} \text{ s}^{-1}$ (at 0.3 mM concentration of the catalyst) at pH 8.5 and 37°C.

Graphical abstract

Two mononuclear macrocyclic units containing Dy(III) or Eu(III) can be converted to carbonate-bridged dinuclear species both in the reactions with sodium carbonate or gaseous carbon dioxide. The catalytic activity of dinuclear Eu(III) carbonate complex is much higher in comparison with the analogous mononuclear complexes.



Keywords

Macrocycles; lanthanides; carbonate complexes; dinuclear complexes; catalytic hydrolysis; BNPP.

1. Introduction

Multinuclear lanthanide(III) complexes are attracting increasing attention in light of their potential applications as efficient catalysts for the hydrolysis of phosphate esters of different types [1] and single molecule magnets [2, 3]. However, the labile nature of lanthanide(III) ions combined with their poorly expressed stereochemical preferences render the control over the formation of such compounds difficult. The formation of multinuclear lanthanide(III) systems is typically accomplished by the application of bridging ligands. One of the simple bridging ligands that can be applied for the construction of polynuclear lanthanide(III) systems is the carbonate anion [2-4]. For instance, carbonate-bridged dysprosium(III) complexes have been recently intensively studied as molecular magnets [2]. The multitude of coordination modes of carbonate anions in combination with high coordination numbers of lanthanide(III) makes it relatively difficult to predict and control the molecular architectures based on lanthanide carbonate derivatives. Thus, the carbonate anion may bind to a single Ln(III) ion in a simple end-on η^2 coordination fashion [4,3b] or

bridge two, three or six Ln(III) ions using $\eta^1:\eta^1-\mu_2$, $\eta^2:\eta^2-\mu_2$, $\eta^2:\eta^2-\mu_3$, $\eta^1:\eta^1:\eta^2-\mu_3$, $\eta^1:\eta^2:\eta^2-\mu_3$, $\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^2-\mu_6$ coordination modes [2,3]. Moreover, the carbonate-bridged multinuclear lanthanide(III) complexes are most often obtained serendipitously in reactions involving atmospheric CO₂ [2,3].





Here we present a more controlled approach to lanthanide(III) carbonate complexes based on surrounding the Ln(III) ions by a hexadendate macrocyclic ligand and thus limiting the number of binding sites available for the coordination of carbonate anions. We report the formation of dinuclear carbonate-bridged Ln(III) complexes based on chiral hexaazamacrocycle L [5,6], which can exist in different diastereomeric forms (Chart 1). A similar type of dinuclear complex with a different non-chiral macrocycle has been obtained in the past accidentally in the reaction with atmospheric carbon dioxide [7]. We demonstrate that formation of carbonate bridged macrocyclic Ln(III) complexes is a more general process, and that various carbonate derivatives can be formed in a controlled manner by the gradual addition of simple carbonate salts to the solutions of mononuclear lanthanide(III) complexes. We also report higher catalytic activity of the carbonate dinuclear $[Ln_2L_2(\mu_2-CO_3)(H_2O)_3]Cl_4$ complexes toward the hydrolysis of the BNPP in comparison with that of the mononuclear complexes.

It should be noted that properly designed dinuclear metal-ion complexes are often more effective than the mononuclear ones on catalyzing the phosphodiester hydrolysis reactions because of the cooperative effect of the dinuclear systems that mimic those found in nature [8]. In general, lanthanide(III) complexes are highly active catalyst for hydrolysis of phosphodiester bonds [9]. However, the major drawback of lanthanide complex systems is their very low stability in the alkali solution due to hydrolysis of lanthanide cations. This problem can be circumvented by the application of Ln-binding ligands in order to form artificial hydrolase [10]. For instance, nitrogen or oxygen based ligands lead to active Ln(III) catalysts for hydrolysis [11].

2. Experimental

2.1. Synthesis

Macrocycle L was obtained as described previously described [5, 6].

[EuL(H₂O)₂]Cl₃ (1) 68.7 mg (0.187 mmol) of EuCl₃·6H₂O and 81.5 mg (0.187 mmol) of macrocycle L were dissolved in 3 mL of distilled water. The mixture was refluxed for 2 h, cooled down and the volume was reduced to 0.5 mL by evaporation in a stream of N₂. The formed precipitate was filtered off, washed with a small amount of water and dried in vacuum. The product was purified by recrystallization from methanol. Yield 89.21 mg (66%) final product 1 after recrystallization. Calcd (anal.) for EuC₂₆H₆₀N₆O₁₁Cl₃: C 35.04 (34.85); H 6.79 (6.21); N 9.43 (9.22). ¹H NMR (300 MHz, D₂O, 300K): -9.05, -8.70, -2.40, -1.82, -1.60, -0.79, 1.95, 4.02, 6.16, 19.63.

[DyL(H₂O)₂]Cl₃ (2) 73.9 mg (0.194 mmol) of DyCl₃·6H₂O and 84.4 mg (0.194 mmol) of macrocycle L were dissolved in 3 mL of distilled water. The mixture was refluxed for 2 h, cooled down and the volume was reduced to 0.5 mL by evaporation in a stream of N₂. The formed precipitate was filtered off, washed with small amount of water and dried in vacuum. The product was purified by recrystallization from methanol. Yield 122 mg (90%). Calcd (anal.) for $DyC_{26}H_{54}N_6O_8Cl_3$: C 36.84 (36.78); H 6.42 (5.91); N 9.92 (9.95).). ¹H NMR (300 MHz, D₂O, 300K): -179.90, -108.04, -38.62, 10.45, 20.18, 43.66, 67.95, 87.50, 136.39, 203.36. **1H NMR** (500 MHz, CD₃CN, 300K): δ -114.19, -84.54, -63.72, -35.33, -29.02, -26.18, -13.88, 20.81, 23.34, 31.08, 32.49, 49.27, 51.42, 54.26, 62.46, 116.71, 132.80, 135.96, 158.35.

 $[Eu_2L_2(\mu_2-CO_3)(H_2O)_3]Cl_4$ (3) The solution of 1.5 mg (0.011 mmol) of sodium carbonate in 69.3 µl of water was added to a solution of 16.3 mg (0.022 mmol) of $[EuL(H_2O)_2]Cl_3$ in 2 mL of water. The clear solution was left to evaporate for 7 days till the volume was reduced to ca. 0.5 mL. The crystalline product (4) was collected and dried in vacuum. Yield 33 mg (95%). Calcd (anal.) for $Eu_2C_{53}H_{100}N_{12}O_{15}Cl_4$: C 40.00 (40.22); H 6.33 (6.21); N 10.56 (10.57). ¹H NMR (500 MHz, D₂O, 300K): -19.12, -17.81, -14.11, -11.27, -6.89, -5.04, -3.31, -2.42, -1.70, -0.86, 1.82, 3.84, 6.54, 21.73, 27.52.

 $[Dy_2L_2(\mu_2-CO_3)(H_2O)_3]Cl_4$ (4) was obtained in a similar manner as the above complex **3**. Yield 33 mg (92%). Calcd (anal.) for $Dy_2C_{53}H_{94}N_{12}O_{12}Cl_4$: C 40.85 (40.72); H 6.08 (6.20); N 10.79 (10.56). ¹H NMR (300 MHz, CD₃CN, 300K): -115.27, -112.13, -84.69, -80.76, -70.18, -62.73, -49.40, -36.07, -29.80, -23.52, -13.72, 21.17, 23.13, 29.40, 31.36, 31.11, 49.01, 51.36, 54.10, 62.34, 67.04, 75.67, 80.37, 82.33, 116.05, 123.50, 132.52, 136.83, 158.39.

2.2 Methods

The NMR spectra were taken on Bruker Avance 500 and AMX 300 spectrometers. The CD spectra were measured on Jasco J-715 Spectropolarimeter. The electrospray mass spectra were obtained using Bruker microOTOF-Q instrument. The elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer.

The diffraction data for the crystals $[DyLCl(H_2O)[Cl_2 \cdot 0.5MeOH \cdot 2.5H_2O$ (2) and $[Eu_2L_2(CO_3)(H_2O)_3]Cl_4 \cdot 10H_2O$ (3) were collected at 100(2) K on κ -geometry automated fourcircle diffractometers with graphite-monochromatized MoK α radiation: Kuma KM4-CCD or Agilent Technologies Xcalibur *R* (ω scans) (see details in Table S1). Data collection, cell

refinement, data reduction and analysis were carried out with *CrysAlisPRO* [13]. The structures were solved by direct methods using the *Shelxt-2014* [14] program and refined on F^2 by a full-matrix least-squares procedure using *Shelxl-2014* [15]. Figures presenting the molecular structures were made using the *Diamond* program [16] and Mercury program [17]. Details of structure solution and refinement are presented as Supplementary Material.

Kinetic experiments for the hydrolysis of the model substrate bis(4-nitrophenyl) phosphate (BNPP) [18] were performed by following the absorbance of 4-nitrophenol (NP) using AquaMate UV-vis spectrophotometer (see Supplementary Material for details). The instrumental pH values measured in D₂O calibrated with standard buffers in H₂O were corrected to pH values according to Krężel and Bal formula: pH=pH*×0.929+0.42 [12].

3. Results and Discussion

3.1. Crystal structures

As it has been observed previously, the macrocycle L can exist in two diastereomeric forms (form I and form II) in its lanthanide complexes [5]. In the mononuclear $[DyL^{R/}Cl(H_2O)]Cl_2 \cdot MeOH \cdot 2H_2O$ complex **2**, isomorphic to the Yb(III) complex [5], the eight-coordinate Dy(III) ion is bound to six nitrogen atoms of the macrocycle L and to an axial water molecule and chloride anion (Figure 1, Supporting Figure S12). The two axial ligands are positioned on the same side of the macrocycle. This arrangement is accompanied by the presence of the diastereomeric form I of the ligand L. In this form the nitrogen atoms adopt the RRRR configuration (Chart 1) and the macrocycle is highly twisted in such a way that only one face of the macrocycle is available for axial ligands.



Fig. 1. Molecular structure of the complex cation $[DyL^{RI}Cl(H_2O)]^{2+}$ of complex **2**.

Complex **3** is composed of two macrocyclic Eu(III) units bridged by carbonate anion (Figure 2, Figures S13, S14). This anion is disordered in such a way that with 50% occupancy one of its oxygen atom is bound to one of the two Eu(III) while two of its oxygen atoms are bound to the other Eu(III) ion and with 50% occupancy the mode of binding to the two Eu(III) ions is reversed. Thus the carbonate anion is bound in a $\eta^1:\eta^1-\mu_2$ fashion and the two Eu(III) ions in

a given molecule are not equivalent. Both ions are eight-coordinate, but their sets of axial ligands are different. For one of the Eu(III) ions the set of axial ligands correspond to a monodendate carbonate and water molecule at one side of the macrocycle as well as additional axial water molecule at the opposite side; for the other Eu(III) ion in a dimer the set of axial ligands corresponds to a bidendate carbonate anion and a water molecule at the opposite side of the macrocycle. The bridging carbonate anion resides in a kind of cleft formed by the pyridine fragments of the macrocyclic ligands. Unlike in the case of **2**, the axial ligands are coordinated at both faces of the macrocycle and the diastereomeric form II of the macrocycle L is observed in the dimeric Eu(III) complex **3**. This form of the ligand is related to the RSRS configuration at amine nitrogen atoms and a saddle conformation of the macrocycle.

The mutual orientation of pyridine rings in the diastereomeric form II observed in 3 can be characterized by the value of the pseudo-torsion angle C2-C4-C15-C17 equal to 82°; in comparison this value is equal to -5° for the diastereomeric form I observed in the mononuclear Dy(III) complex **2**.

Although the quality of the crystals of the dinuclear Dy(III) carbonate derivative **4** were not sufficient to satisfactory solve the crystal structure [20], crude structural model indicated complex similar to that of the above complex **3**. Here too, the disordered carbonate anion bridges two lanthanide(III) ions in a $\eta^1:\eta^{1}-\mu_2$ fashion.



Fig. 2. Molecular structure of the complex cation $[Eu_2L_2(CO_3)(H_2O)_3]^{4+}$ of complex **3**.

3.2. Synthesis and spectra



The mononuclear chloride derivatives **1** and **2** form easily from the free macrocycle L and appropriate lanthanide chloride in water solution (Scheme **1**). The solid samples of these complexes can be obtained by slow evaporation of water solutions in an inert atmosphere. On the other hand, slow evaporation of water solutions of the **1** and **2** complexes results in the formation of carbonate derivatives. In particular, an attempt to obtain single crystal of **1** by slow evaporation of water solution resulted in the formation of single crystals of **3**. In the latter complex the carbonate anion must have originated from the fixation of atmospheric carbon dioxide. In order to verify the formation of carbonate complexes, the starting mononuclear chloride complex **1** and **2** were dissolved in D₂O. CO₂ was passed through these solutions and changes over time were monitored by ¹H NMR spectroscopy (Figure 3). The starting ¹H NMR spectrum of the D₂O solution of the mononuclear Eu(III) chloride derivative **1** changes in time under CO₂ exposition. The reaction with the gaseous carbon dioxide for 1h results in a final spectrum practically identical to that of the synthesized dinuclear complex **3** (Supporting Fig. S3). This experiment clearly indicates fixation of carbon dioxide and formation of dinuclear complex **3** from mononuclear complex **1**.



Fig. 3. ¹H NMR spectras of the D_2O solution of the **1** complex with CO_2 passed through these solution.

The accidental formation of lanthanide(III) carbonate complexes from atmospheric carbon dioxide has been observed previously, in fact the majority of the reported polynuclear Ln(III) complexes with bridging carbonate anions have been obtained in this way [2,3]. The formation of carbonate derivative is often facilitated by the presence of a base during exposition to air, in the present case, however, the fixation of CO₂ must correspond to the evolution of HCI as required by the reaction balance. This effect must arise from the stronger binding of the carbonate anion to the Eu(III) ion in comparison with the binding of the chloride anion. The conversion of the chloride derivative to the carbonate derivative upon exposition to atmospheric carbon dioxide was also observed for the Dy(III) complex **2**, although it was much slower. This qualitative difference may result from the various preferences of the diastereomeric forms I and II of the macrocycle L; as it was previously observed [5,6] the larger Ln(III) ions tend to prefer form II, while the smaller Ln(III) ions prefer the form I. Since the conversion of Ln(III) chloride derivative to the Ln(III) carbonate derivative requires conversion of the ligand form I to the ligand form II, this process is more difficult for the Dy(III) complexes of L in comparison with the Eu(III) complexes.

In order to verify the formation of carbonate complexes, the starting mononuclear chloride derivatives were reacted with 1/2 equivalent of sodium carbonate. The isolated product **3** was identical to that originating from atmospheric carbon dioxide. The binding of carbonate anions in solution was also studied with the use of NMR titration experiments (Figure 4).



Fig. 4. NMR titration of the 1 complex with potassium carbonate solution (D_2O , 300 MHz, 300 K).

The starting ¹H NMR spectrum of the D₂O solution of the mononuclear Eu(III) chloride derivative 1 does not show all the 17 non-exchangeable signals expected for the C₂ symmetry; moreover the signals are much broader than those observed in the NMR spectrum of CDCl₃/CD₃OD solution of Eu(III) mononuclear nitrate derivative [5]. In contrast, 19 signals were observed in the case of NMR spectrum of [EuL(H₂O)₂]Cl₃ in deuterated organic solvents. This fact indicates additional broadening of the signals due to a dynamic chemical exchange process, most likely an exchange of axial ligands. The addition of 1/2 equivalent of sodium carbonate to the D_2O solution of the mononuclear Eu(III) complex 1 results in a spectrum practically identical to that of the synthesized dinuclear complex 3 (Supporting Fig. S3). This indicates clean formation of a complex where one carbonate anion bridges two macrocyclic Eu(III) units in agreement with the X-ray and elemental analyses data. Further addition up to 2 equivalents of carbonate anions results in a gradual shift of the broad ¹H NMR signals (e.g. down-field shift of the signals with the most negative chemical shifts). These spectral changes point to a chemical exchange between 3 and another macrocyclic Eu(III) carbonate derivative. The process that corresponds to a chemical exchange is fast on the NMR time-scale for most of the signals while for signals with the largest differences in δ values the intermediate exchange regime is reached. The addition of 3 equivalents of sodium carbonate results in turn in an up-field shift of the signals with the most negative chemical shifts. This spectral change indicates the formation of yet another carbonate derivative. The addition of further portions of carbonate results in the sharpening of signals with little effect on chemical shifts.

A similar situation was observed in the case of NMR titration of Dy(III) derivative **2** (Figure 5). In this case the signals of the D₂O solution of the starting mononuclear complex **2** were even more severely broadened with most of the signal broadened beyond detection due to chemical exchange and paramagnetic broadening – only three signals are clearly observed at 300 K and four signals at 350 K. The addition of 1/2 equivalent of sodium carbonate to the D₂O solution of the complex **2** results in a spectrum practically identical to that of the synthesized dinuclear $[Dy_2L_2(\mu_2-CO_3)(H_2O)_3]Cl_4$ complex **4** (Supporting Fig. S4). The addition of 1.25 equivalents leads to a new spectrum corresponding to a mixture of two new carbonate complexes. A further addition of sodium carbonate up to 3 equivalents results in an increase of the signals of one of these species at the expense of the other. For instance the two up-field signals at ca -80 and -130 ppm practically vanish, while the signals at ca -78 and -118 ppm grow in intensity. The final spectrum is dominated by the set of 15 signals corresponding to a macrocyclic complex of C₂ symmetry.

The above NMR titration experiments reveal that apart from the dinuclear complex with one carbonate anion bridging two macrocyclic units, at least two other carbonate derivatives can be formed when more sodium carbonate is added. These new species may correspond to dinuclear carbonate-bridged forms with additional carbonate anions bound on the outside of the macrocyclic system, such as $[(LnL)_2(\mu_2-CO_3)(CO_3)_2]$ or mononuclear derivatives with two carbonate anions bound at the two faces of the macrocycle L, such as $[LnL(CO_3)_2]^-$.

The two diastereomeric forms **2** and **4** give rise to different CD spectra (Fig. 5). The difference is, however, much less pronounced in comparison with the difference in CD spectra of diasteromers I and II in their nitrate derivatives [5, 6].



Fig. 5. The comparison of the CD spectra of water solutions of 2 and 4.

3.3. Catalytic activity towards hydrolysis of phosphodiester bonds of BNPP

The Ln(III) complexes of chiral macrocycle **L'**, which is the Schiff base analogue of amine macrocycle L, were shown to act as enantioselective catalysts towards hydrolytic cleavage of plasmid DNA [21]. Since the analogous complexes of L should be more resistant to hydrolytic ligand decomposition, we have tested them as catalyst for this reaction. While initial results regarding cleavage of plasmid DNA indicated substantial DNA aggregation, we turned our attention to a model substrate – bis(p-nitrophenyl)phosphate (BNPP). The hydrolysis of BNPP generates 4-nitrophenol (NP) and 4-nitrophenyl phosphate (NPP); the latter in turn is hydrolysed into the mixture of inorganic phosphate and 4-nitrophenol (Scheme 2). In most cases the rate of the second step is much faster than that of the first one. Therefore, for these particular cases production of 2 equiv. of 4-nitrophenol at a rate constant k₁ can be assumed.



Scheme 2. Sequential hydrolysis of bis(4-nitrophenyl)phosphate.

We have tested the catalytic activity of carbonate, nitrate and chloride derivatives of Ln(III) complexes with macrocycle L. For the nitrate derivative $[YbL(H_2O)_2](NO_3)_3]$ the rates were measured at pHs varying from 7.0 to 9.0 (Figure 6).

Table 1. pH dependence of the rate constants (k_{obs}) for the hydrolysis of BNPP at 37 °C. ([[YbL(H₂O)₂](NO₃)₃] = 3 x 10⁻⁴ M, [BNPP] = 2 x 10⁻³ M, [TRIS-HCI] = 5 x 10⁻² M).



Fig. 6. Plot of the initial rate vs. pH for the hydrolysis of BNPP at 37 °C. For each case, the concentration of $[YbL(H_2O)_2](NO_3)_3$ complex was 3 x 10⁻⁴ M and the concentration of BNPP was 2 x 10⁻³ M.

The rate constants were found to increase with increasing pH until pH 8.5 at which value the highest activity toward BNPP hydrolysis is observed. The pH dependence of the rate constants can be best rationalized by considering the Brønsted acidity of water molecules bound to the metal centres (*vide infra*). In other word, increasing the pH of the solution will produce deprotonated species (LnM-OH), and activate OH- nucleophile, in addition to possible formation of dimeric hydroxo-bridged species. The cationic lanthanide complexes

can form hydrate-, hydroxo-, or oxo-bridged species at high pH due to the presence of innersphere coordinated water molecules/hydroxide ions, thereby altering their reactivity [22]. Indeed, the ¹H NMR spectra (Figure S6) measured for the [YbL(H₂O)₂](NO₃)₃ complex in D₂O buffers with different pH values corresponding to catalytic studies indicate formation of new complex species at higher pH.

For comparison, ¹H NMR titration of $[YbL(H_2O)_2](NO_3)_3$ complex with NaOH solution in D₂O was performed (Figure S7). The spectral changes are more complicated in comparison with analogous titrations of Ln(III) complexes of macrocycle L' [21,23] and more difficult to interpret because of combination of fast and slow exchange regimes on the NMR time-scale as well as accompanying line broadening effects. Nevertheless, these spectra indicate formation of at least four different hydroxo-type complexes (see Supporting Scheme S1 for the possible forms of hydroxo complexes).

The above ¹H NMR spectra of the derivatives $[YbL(H_2O)_2](NO_3)_3$ complex indicate that the catalytically active form pH = 8.5, which produces the most prominent catalyst in the hydrolysis of BNPP, is a hydroxo derivative, e.g. mononuclear complex cation $[YbL(H_2O)(OH)]^{2+}$. At higher pH values likely the dimeric di-µ₂-hydroxo-bridged species of complex are formed (Supporting Scheme S1).

The influence of the size of central Ln(III) ion on the catalytic activity was investigated for a series of nitrate derivatives $[LnL(NO_3)(H_2O)](NO_3)_2$ (Ln = Ho, Er) and $[LnL(H_2O)_2](NO_3)_3$ (Ln = Tm, Yb, Lu) as well as chloride derivatives $[LnL(H_2O)_2]Cl_3$ (Ln = Tm, Yb, Lu, Y) [5]. These kinetic studies were limited to the complexes soluble in water and were performed at the optimum pH value of 8.5 established for Yb(III) complex. For the series of monomeric nitrate species the catalytic activity was increasing with the radius of metal ion and $[HoL(NO_3)(H_2O)](NO_3)_2$ complex was shown to have the highest reactivity (Supporting Figure S10, S11, Table 2).

The complexes in series of chloride derivatives $[LnL(H_2O)_2]Cl_3$ (Ln = Tm, Yb, Lu, Y) are much less reactive for promoting BNPP hydrolysis in comparison with nitrate derivatives (Figure 5, Table 2) which may suggest inhibitory effect of Cl⁻ anions, what is observed by simple anions indicating high affinity of neutral hydroxo complexes toward anionic species of BNPP [24]. On the other hand, it was found that dimeric carbonate species **3** and **4** were more reactive than all measured monomeric species (Supporting Figures S10, S11, Table 2). Complex **4** is about 4.1 times more active catalyst than HoL(NO₃)(H₂O)](NO₃)₂ complex and complex **3** is about 5.4 times more active than HoL(NO₃)(H₂O)](NO₃)₂ complex. The higher activity of carbonate complexes likely result from cooperative action of the two Ln(III) ions within the dinuclear carbonate-bridges species. The catalytic activity of dinuclear **3** complex in hydrolysis of BNPP is comparable with other active lanthanide(III) complexes with macrocyclic or polychelate ligands [25].

Table 2. The complex dependence of the rate constants (k_{obs}) for the hydrolysis of BNPP at 37°C. ([complex] = 3 x 10⁻⁴ M, [BNPP] = 2 x 10⁻³ M, [TRIS-HCI] = 5 x 10⁻² M).

Complex	V ₀	k _{obs}	
[LuL(H ₂ O) ₂](NO ₃) ₃	5,43E-09	2,72E-06	
[YbL(H ₂ O) ₂](NO ₃) ₃	6,59E-09	3,30E-06	
[TmL(H ₂ O) ₂](NO ₃) ₃	7,94E-09	3,97E-06	
[ErL(NO ₃)(H ₂ O)](NO ₃) ₂	9,99E-09	5,00E-06	
[HoL(NO ₃)(H ₂ O)](NO ₃) ₂	2,42E-08	1,21E-05	
[TmL(H ₂ O) ₂]Cl ₃	4,22E-09	2,11E-06	
[YbL(H ₂ O) ₂]Cl ₃	4,21E-09	2,11E-06	\mathbf{O}
[LuL(H ₂ O) ₂]Cl ₃	4,32E-09	2,16E-06	
[YL(H2O)2]Cl3	3,72E-09	1,86E-06	
$[Eu_2L_2(CO_3)(H_2O)_3]Cl_4$	1,30E-07	6,50E-05	
$[Dy_2L_2(CO_3)(H_2O)_3]Cl_4$	1,00E-07	5,00E-05	

4. Conclusions

The chloride derivatives of mononuclear lanthanide(III) complexes of macrocyclic ligand L can be converted into carbonate derivatives not only by serendipitous sequestering of atmospheric carbon dioxide, but also by controlled addition of CO₂ or reaction with carbonate salts. The crystal structure of the Eu(III) complex indicates the presence of dinuclear complex, where two macrocyclic units are linked by the bridging carbonate anion bound in the $\eta^1:\eta^1-\mu_2$ fashion. This dinuclear macrocyclic complex turned out to be more active catalyst for the hydrolysis of BNPP in comparison with the corresponding mononuclear species.

Appendix A. Supplementary data

CCDC Nos. 1891898–1891899 contains the supplementary crystallographic data for complexes **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Synopsis

Two mononuclear macrocyclic units containing Dy(III) or Eu(III) can be converted to carbonate-bridged dinuclear species both in the reactions with sodium carbonate or gaseous carbon dioxide. The catalytic activity of dinuclear Eu(III) carbonate complex is much higher in Acception comparison with the analogous mononuclear complexes.