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

Autorzy

Aleksandra Gerus

Katarzyna Ślepokura

Jerzy Lisowski

Rok wydania

2019

Czasopismo

Polyhedron

Numer woluminu

170

Strony

115-121

DOI

10.1016/j.poly.2019.05.005

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

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 $[Eu_2L_2(\mu_2\text{-}CO_3)(H_2O)_3]Cl_4$ **3** and $[Dy_2L_2(\mu_2\text{-}CO_3)(H_2O)_3]Cl_4$ **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 $\eta^1{:}\eta^2\text{-}\mu_2$ 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 CO_2. 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 $k_{obs}=6.5\times10^{-5}s^{-1}$ (at 0.3mM concentration of the catalyst) at pH 8.5 and 37°C.