

Monomeric and dimeric nitrate lanthanide(III) and yttrium(III) coordination compounds of (2 + 2) imine macrocycle derived from 2,6-diformylpyridine and *trans*-1,2-diaminocyclopentane.

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Streszczenie

Monomeric nitrate coordination compounds [Ln(**L1**)] (NO₃)₃·nH₂O (Ln = Y(III), Tm(III), Yb(III) and Lu(III)); n = 0, 0.75 or 3)¹ of the chiral macrocyclic (2 + 2) imine **L1** (**L1**_{RRRR}, **L1**_{SSSS} and/or **L1**_{rac}), derived from enantiomerically pure or racemic *trans*-1,2-diaminocyclopentane (DACP) and 2,6-diformylpyridine (DFP), have been synthesized in the templated condensation of precursors in the presence of appropriate metal salts. From these monomers their homochiral μ-hydroxodimers [Ln₂(**L1**)₂(μ-OH)₂](NO₃)₄·nH₂O (Ln = Y(III), Tm(III), Yb(III) and Lu(III)); n = 4, 5 or 7) have been obtained and isolated by addition of NaOH to the respective monomeric form of coordination compound solution. All synthesized coordination compounds have been characterized by NMR spectroscopy, mass spectrometry, elemental analyses and/or circular dichroism (CD). ¹H NMR signals of CDCl₃/CD₃OD solutions of the diamagnetic Y(III) and Lu(III) monomers have been assigned on the basis of their COSY and HMQC spectra, and for the remaining paramagnetic lanthanide coordination compounds (Tm(III) and Yb(III)) the signals were tentatively assigned on the basis of linewidths analyses. ¹H NMR signals of D₂O solutions of diamagnetic Y(III) and Lu(III) representatives of dimeric species have been established taking into account their COSY, HMQC, HMBC and NOESY spectra. The NOESY spectra confirm that the structure of the dimers observed in solids is also maintained in a solution.

The axial ligand exchange in all monomeric coordination compounds was investigated by ^1H NMR titration experiments with acetate and chloride anions in organic solvents as well as with hydroxide anion in D_2O . The formation of homochiral heterobimetallic μ -hydroxodimers $[\text{Ln}'\text{Ln}''(\text{L1})_2(\mu\text{-OH})_2](\text{NO}_3)_4$ was investigated in a solution by mixing the solutions of two different $[\text{Ln}'_2(\text{L1})_2(\mu\text{-OH})_2](\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$ and $[\text{Ln}''_2(\text{L1})_2(\mu\text{-OH})_2](\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$ homochiral homobimetallic precursors. This experiment proves the chiral recognition between two macrocyclic units of the same chirality in a solution. The μ -hydroxodimers may convert with time to the corresponding peroxo-dimers of the general formula $[\text{Ln}_2(\text{L1})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)](\text{NO}_3)_4$.

The X-ray crystal structures of the representative monomeric and dimeric coordination compounds $[\text{Yb}(\text{L1}_{RRRR})(\text{NO}_3)_2]\text{NO}_3$, $[\text{Yb}_2(\text{L1}_{SSSS})_2(\text{OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$, $[\text{Yb}_2(\text{L1}_{RRRR})_2(\text{OH})_2(\text{H}_2\text{O})_2][\text{Yb}_2(\text{L1}_{SSSS})_2(\text{OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_8 \cdot 1.5\text{MeOH} \cdot 5\text{H}_2\text{O}$ and $[\text{Y}_2(\text{L1}_{SSSS})_2(\text{O}_2)(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{MeOH}$ with enantiomerically pure or racemic ligand **L1** have been determined. The structure of $[\text{Yb}_2(\text{L1}_{RRRR})_2(\text{OH})_2(\text{H}_2\text{O})_2][\text{Yb}_2(\text{L1}_{SSSS})_2(\text{OH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_8 \cdot 1.5\text{MeOH} \cdot 5\text{H}_2\text{O}$ crystal confirms chiral recognition of macrocyclic units of the same chirality in solids.

Słowa kluczowe

Macrocycle, Lanthanide, Coordination compounds, Chiral recognition, trans-1,2-Diaminocyclopentane

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