Anion and solvent induced chirality inversion in macrocyclic lanthanide complexes.

Autorzy

Aleksandra Gerus

Katarzyna Ślepokura

Jerzy Lisowski

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Streszczenie

A series of the lanthanide(III) or yttrium(III) complexes of the type $[LnL(NO_3)(H_2O)_2](NO_3)_2$, $[LnL(NO_3)(H_2O)](NO_3)_2$, $[LnL(H_2O)_2](NO_3)_3$, and $[LnLCl(H_2O)_2]Cl_2$ where L is an all-*R* or all-*S* enantiomer (L^R or L^S) of the chiral hexaaza macrocycle, 2(*R*),7(*R*),18(*R*),23(*R*)- or 2(*S*),7(*S*),18(*S*),23(*S*)-1,8,15,17,24,31-hexaazatricyclo[25.3.1.1.0.0]-dotriaconta-10,12,14,26,28,30-hexaene, and Ln(III) = Sm(III), Tb(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), or Y(III), have been synthesized and structurally characterized. The crystal structure of the free macrocycle shows a highly twisted molecule, preorganized for the formation of helical complexes. The crystal structures of the lanthanide(III) complexes show two different diastereomeric forms of the macrocycle with different configurations at the stereogenic amine nitrogen atoms: (*RRRR*) or (*RSRS*) (denoted as L^{RI} and L^{RII}, respectively). The L^{RI} diastereomeric form of the 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) convert slowly to the L^{RII} form in methanol or acetonitrile solutions, while this process is not observed for the L^{RI} diastereomers of analogous chloride derivatives $[LnL(H_2O)_2]Cl_3$ (Ln = Tm, Yb, Lu). On the other hand, the $L^{RI} \rightarrow L^{RII}$ conversion for these Tm(III), Yb(III), and Lu(III) chloride derivatives can be triggered by the addition of external nitrate anions. The circular dichroism (CD) and ^1H NMR data indicate initial fast exchange of axial chloride for axial nitrate ligand, followed by slow chirality inversion of the equatorial macrocyclic ligand.

Adres publiczny

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https://www.acs.org/content/acs/en.html