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Enantiomeric Self-Recognition in Homo- and Heterodinuclear Macrocyclic Lanthanide(III) Complexes

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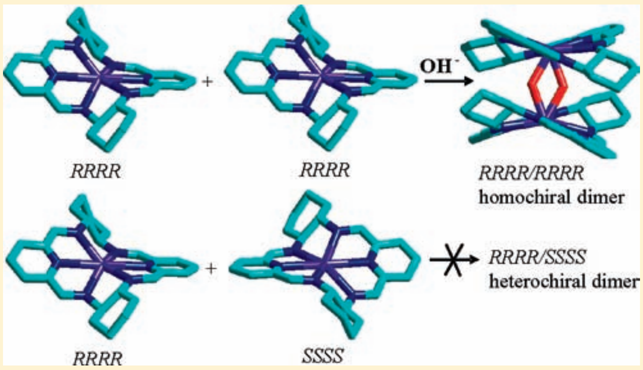
S Supporting Information



ABSTRACT: The controlled formation of lanthanide(III) dinuclear μ-hydroxo-bridged $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$ complexes (where X = H_2O, NO_3^-, or Cl^-) of the enantiopure chiral macrocycle L is reported. The ^{1}H and ^{13}C NMR resonances of these complexes have been assigned on the basis of COSY, NOESY, TOCSY, and HMQC spectra. The observed NOE connectivities confirm that the dimeric solid-state structure is retained in solution. The enantiomeric nature of the obtained chiral complexes and binding of hydroxide anions are reflected in their CD spectra. The formation of the dimeric complexes is accompanied by a complete enantiomeric self-recognition of the chiral macrocyclic units. The reaction of NaOH with a mixture of two different mononuclear lanthanide(III) complexes, $[Ln^1L]^{3+}$ and $[Ln^2L]^{3+}$, results in formation of the heterodinuclear $[Ln^1Ln^2L_2(\mu\text{-}OH)_2X_2]^{n+}$ complexes as well as the corresponding homodinuclear complexes. The formation of the heterodinuclear complex is directly confirmed by the NOESY spectra of $[EuLuL_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, which reveal close contacts between the macrocyclic unit containing the Eu(III) ion and the macrocyclic unit containing the Lu(III) ion. While the relative amounts of homo- and heterodinuclear complexes are statistical for the two lanthanide(III) ions of similar radii, a clear preference for the formation of heterodinuclear species is observed when the two mononuclear complexes contain lanthanide(III) ions of markedly different sizes, e.g., La(III) and Yb(III). The formation of heterodinuclear complexes is accompanied by the self-sorting of the chiral macrocyclic units based on their chirality. The reactions of NaOH with a pair of homochiral or racemic mononuclear complexes, $[Ln^1L^{RRRR}]^{3+}/[Ln^2L^{RRRR}]^{3+}$, $[Ln^1L^{SSSS}]^{3+}/[Ln^2L^{SSSS}]^{3+}$, or $[Ln^1L^{rac}]^{3+}/[Ln^2L^{rac}]^{3+}$, results in mixtures of homochiral, homodinuclear and homochiral, heterodinuclear complexes. On the contrary, no heterochiral, heterodinuclear complexes $[Ln^1L^{RRRR}Ln^2L^{SSSS}(\mu\text{-}OH)_2X_2]^{n+}$ are formed in the reactions of two different mononuclear complexes of opposite chirality.

■ INTRODUCTION

Chirality is an important issue in the chemistry of metal complexes. The stereoselective synthesis of enantiopure metal complexes, particularly multinuclear metal complexes, is still a challenging task. The chirality of metal complexes, in addition to the presence of stereogenic centers on the ligand, may be related to the spatial disposition of chelating ligands around the metal ion, formation of double or triple helices, helical twist of a macrocyclic ligand, or rotation of the side arms of the macrocycle.[1] The combination of these stereogenic elements results in the possible formation of various diastereomeric forms. The most fruitful method of enantio- and diastereoselective synthesis of chiral metal complexes is based on the use of enantiopure chiral ligands.[2] For instance, the enantiopure 2 + 2 or 3 + 3 macrocycles derived form the chiral 1,2-diaminocyclohexane fragment and dicarbonyl compounds are well suited for the formation of chiral, enantiopure complexes with lanthanide(III) ions.[3,4] These complexes adopt a helical structure, and the direction of the helical twist of the macrocycle is dictated by the chirality of the cyclohexane fragment. An example of such a ligand forming helical Ln(III) complexes is the macrocycle L (Scheme 1).[3d−g]

Chiral recognition of molecules in solution plays a pivotal role in many chemical and biological processes. A special case of chiral recognition is the enantiomeric self-recognition (also termed homochiral association, homochiral recognition, self-resolution, or enantioselective self-assembly). This process takes place when a chiral molecule interacts preferably with another molecule of the same chirality, forming a homochiral assembly, rather than with a molecule of opposite chirality, forming a heterochiral assembly (a handshake is an example of a macroscopic chiral self-recognition process). This preferred interaction between components of the same chirality leads to spontaneous selection of enantiomers from the racemic mixture. The enantiomeric self-recognition belongs also to the important category of self-sorting processes.

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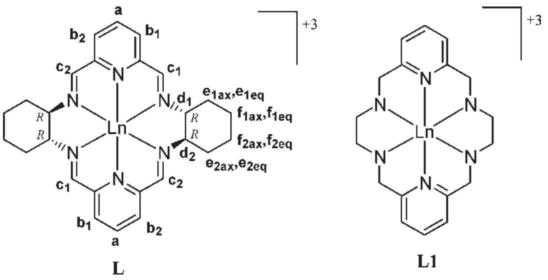
Scheme 1. Ln(III) Complexes of the Macrocycles L and L1 (L^{RRRR} Enantiomer, Axial Ligands Omitted for Simplicity) and the Labeling Scheme of the Macrocycle L in Its C_2-Symmetric Complexes



While there are many examples of enantiomeric self-recognition documented for the solid state, the same process is rarely observed in solutions. The spontaneous resolution of enantiomers during crystallization or diastereoselective formation of homochiral molecules in the solid state usually arises from the subtle energetic effects related to the crystal packing and in most cases does not correspond to enantiomeric self-recognition of components in solution. The process of enantiomeric self-recognition in the liquid or gas phase has been observed previously for organic molecules forming dimers or higher aggregates via hydrogen-bonding or stacking interactions.[5] Apart from spontaneous resolution accompanying crystallization, the most common case of enantiomeric self-recognition in the field of inorganic chemistry is related to interligand interactions. Occasionally the enantiomeric self-sorting of racemic chiral ligands accompanies the formation of a racemic metal complex composed of several ligands. The preferred formation of the homochiral species (e.g., $[ML^{R}_{2}]^{n+}$/$[ML^{S}_{2}]^{n+}$) corresponds to ligand chiral self-recognition,[6−8] while the preferred formation of a heterochiral complex (e.g., $[ML^{R}L^{S}]^{n+}$) corresponds to ligand chiral self-discrimination.[9] The enantiomeric self-recognition of ligands is usually observed for the solid state and in a few cases was also documented for solutions. It should be noted that sometimes the selectivity observed for the solid state is partially or completely lost in solution.[6f,7a,7b,9a,9c] Chiral self-recognition and self-discrimination of ligands in solution is also a key process responsible for nonlinear effects in asymmetric catalysis.[6b,e]

A less common case of the enantiomeric self-recognition encountered in inorganic chemistry is the self-sorting of enantiomers of the complexes. This process does not correspond to the aggregation of ligands during formation of a complex, but to the aggregation of preformed monomeric complex units leading to dinuclear (or polynuclear) systems. Examples of such recognition have been reported for the complexes isolated in the solid state. For instance, X-ray crystal structures illustrating the transformation of racemic monomeric copper(II) complex into the racemic homochiral copper(II) dimers have been reported.[10] The formation of heterochiral dimers and trimers corresponding to enantiomeric self-discrimination of chiral macrocyclic complexes has also been observed for the solid state.[11] Reports on homochiral or heterochiral self-interaction of metal complex units in solution are even more scarce; the chiral conformers of *meso*−*meso*-linked zinc(II) porphyrin dimers form homochiral boxes,[12] while the $\pi-\pi$ stacking interactions in propeller-shaped osmium(II) complexes of eilatin lead to partial enantiomeric self-discrimination (heterochiral recognition).[13]

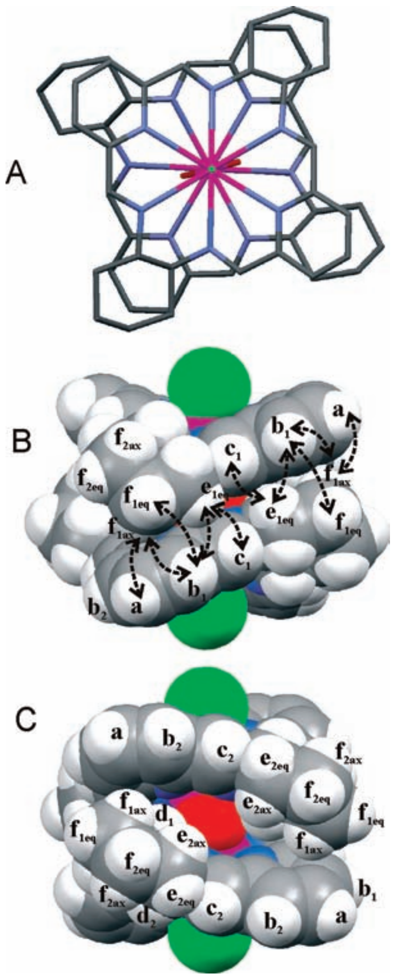


Figure 1. Structure of the complex cation[14] $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ (*all-S* isomer): (A) top view along the Yb−Yb axis, (B) side view in a direction perpendicular to the $Yb_2(\mu\text{-}OH)_2$ plane, (C) side view along the O−O axis. The arrows indicate close contacts (shorter than 4 Å) between the protons of two macrocyclic subunits. Key: white, hydrogen; gray, carbon; green, chlorine; red, oxygen; magenta, ytterbium.

Herein a new type of enantioselective self-recognition of chiral macrocyclic complex units is reported. In the previous reports the X-ray crystal structures of the di-μ-hydroxo-bridged dimers $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and $[Y_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ have been presented[14,15] (see Scheme 1 for the chemical structure of the macrocycle L and Figure 1 for the structure of the $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ complex cation). In this paper it is shown that the solution structures of the homodinuclear $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$ and heterodinuclear $[Ln^1Ln^2L_2(\mu\text{-}OH)_2X_2]^{n+}$ complexes correspond to those observed for the solid state and that these dimers are formed exclusively from the helical monomeric complex units of the same chirality.

Macrocyclic,[16] dinuclear,[17] and polynuclear[18] lanthanide complexes have been shown to be very effective catalysts for the cleavage of the phosphate ester bond and can potentially function as artificial nucleases. It has been shown that lanthanide hydroxo derivatives play a pivotal role in this hydrolytic reaction. The hydroxo-bridged dinuclear lanthanide complexes proved to be

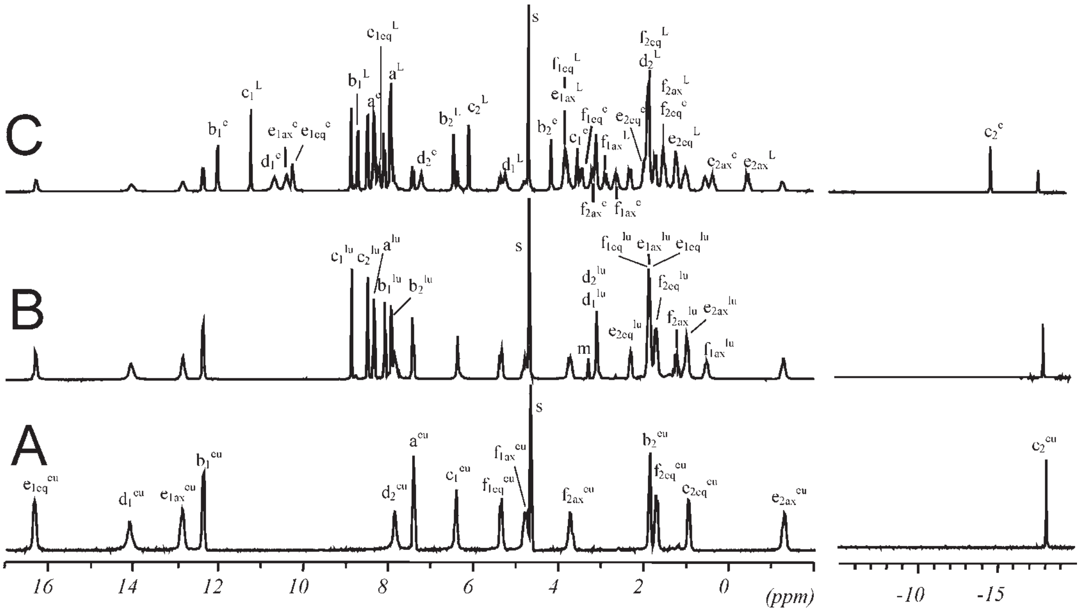


Figure 2. ^{1}H NMR spectra (D_2O, 300 K) measured after the addition of 1 equiv of NaOH to a solution containing (A) 1 equiv of [EuL^{RRRR}(NO$_3$)$_2$](NO$_3$), (B) a mixture of 0.55 equiv of [EuL^{SSSS}(NO$_3$)$_2$](NO$_3$) and 0.45 equiv of [LuL^{RRRR}(NO$_3$)$_2$](NO$_3$), and (C) a mixture of 0.4 equiv of [EuL^{RRRR}(NO$_3$)$_2$](NO$_3$) and 0.6 equiv of [LuL^{RRRR}(NO$_3$)$_2$](NO$_3$). The signals of the [Eu$_2$L$^{RRRR}{}_2$(μ-OH)$_2$(H$_2$O)$_2$]$^{4+}$ complex are labeled with the superscript "eu", and the signals of the [Lu$_2$L$^{RRRR}{}_2$(μ-OH)$_2$(H$_2$O)$_2$]$^{4+}$ complex are labeled with the superscript "lu". The signals of the two macrocyclic subunits containing Eu(III) and Lu(III) in the heterodinuclear [EuLuL$^{RRRR}{}_2$(μ-OH)$_2$(H$_2$O)$_2$]$^{4+}$ complex are labeled with the superscripts "e" and "L", respectively, and the remaining unlabeled signals correspond to signals labeled in (A) and (B).

very active catalysts, which are more effective than the corresponding mononuclear species. In particular, the dimeric Y(III) and Nd(III) complexes of the macrocycle L, [Ln$_2$L$_2$(μ-OH)$_2$(H$_2$O)$_2$](NO$_3$)$_4$, were demonstrated to be effective catalysts for the hydrolytic cleavage of DNA.[15] While many polynuclear hydroxo-bridged solid-state clusters[18] and coordination polymers[19] containing f elements have been characterized in the past decade, the number of hydroxo-bridged polynuclear f−f complexes well-defined and well-characterized in solution is limited.[2e,4a,7c,7d,16b,20]

EXPERIMENTAL SECTION

The monomeric complexes [LnL^{RRRR}(NO$_3$)$_2$](NO$_3$)·nH$_2$O, [LnL^{SSSS}(NO$_3$)$_2$](NO$_3$)·nH$_2$O [LnL^{RRRR}Cl$_3$]·nH$_2$O, and [LnL^{rac}Cl$_3$]·nH$_2$O have been synthesized as previously described.[3c−8] The macrocycle L1 has been synthesized as protonated derivative[21] L1·4HBr·H$_2$O, and its hydroxo−Yb(III) complex has been generated in solution in the reaction of 1 equiv of protonated ligand, 1 equiv of YbCl$_3$·6H$_2$O, and 6 equiv of NaOH. The [Ln$_2$(μ-OH)$_2$X$_2$]$^{n+}$ complexes (where X = H$_2$O, NO$_3^-$, or Cl$^-$) have been generated in solution directly before the measurements by a stepwise addition of the NaOH solution in the appropriate deuterated solvent to the D$_2$O, CD$_3$OD, or CD$_3$OD/CDCl$_3$ solutions of the monomeric complexes [LnL^{RRRR}(NO$_3$)$_2$](NO$_3$)·nH$_2$O, [LnL^{SSSS}(NO$_3$)$_2$](NO$_3$)·nH$_2$O [LnL^{RRRR}Cl$_3$]·nH$_2$O, and [LnL^{rac}Cl$_3$]·nH$_2$O. The resulting hydroxo complexes were moderately stable in water solutions (up to 10% hydrolytic decomposition was observed after one day in some cases). The NMR spectra were taken on Bruker Avance 500 and AMX 300 spectrometers. The TOCSY, COSY, NOESY, and HMQC spectra were acquired using 512 × 1K data points and zero filled to a 1K × 1K matrix. Mixing times varying from 25 to 400 ms were used in NOESY experiments. The CD spectra were measured on a Jasco J-715 spectropolarimeter. Molecular structures were drawn using the MERCURY and HyperChem programs.[22]

RESULTS AND DISCUSSION

Formation of the Homodinuclear Complexes [Ln$_2$L$^{RRRR}{}_2$(μ-OH)$_2$X$_2$]$^{n+}$ and [Ln$_2$L$^{SSSS}{}_2$(μ-OH)$_2$X$_2$]$^{n+}$. It has been shown previously that the exchange of axial ligand has a dramatic effect on the NMR spectra of the macrocyclic lanthanide complexes.[3d,23] This effect is used here to monitor the reactions of NaOH with macrocyclic lanthanide complexes [LnL(NO$_3$)$_2$](NO$_3$)·nH$_2$O or [LnLCl$_3$]·nH$_2$O and check whether the solid-state structure[14,15] of the dimers [Ln$_2$L(μ-OH)$_2$X$_2$]$^{n+}$ (where X = H$_2$O or Cl$^-$) is preserved in solution. Because of the very fluxional character of the lanthanide(III) ions, the molecular solid-state structures of their complexes do not have to correspond to the structures in solution. Often the solid-state Ln(III) complexes fall apart in solution, or different types of complexes are formed.

Upon gradual addition of NaOH to the solutions of [LnL^{RRRR}(NO$_3$)$_2$](NO$_3$)·nH$_2$O in D$_2$O, the initial eight ^{1}H NMR resonances of the D_2-symmetric monomeric complexes gradually disappear and at the same time a new set of fifteen signals of equal intensity appear. This process is complete when 1 equiv of OH$^-$ anion per macrocyclic unit is added (Figure 2A, Figures S1 and S2, Supporting Information). The 15 observed resonances indicate the C_2 symmetry of the hydroxo complex and different axial ligation at the two sides of the macrocycle. The C_2 symmetry of the formed hydroxo derivatives is also indicated by the observation of 13 ^{13}C NMR resonances (Figure S3, Supporting Information). The symmetry of the complexes and the amount of the added OH$^-$ are in accord with the solid-state structures[14,15] of the hydroxo-bridged dimeric [Ln$_2$L$_2$(μ-OH)$_2$X$_2$]$^{n+}$ complexes (Figure 1).

For water solutions identical spectra are obtained in the reactions of the [LnLCl$_3$] complexes and in the reactions of the [LnL(NO$_3$)$_2$](NO$_3$) complexes. This fact indicates that nitrate and chloride anions are dissociated in water solutions of

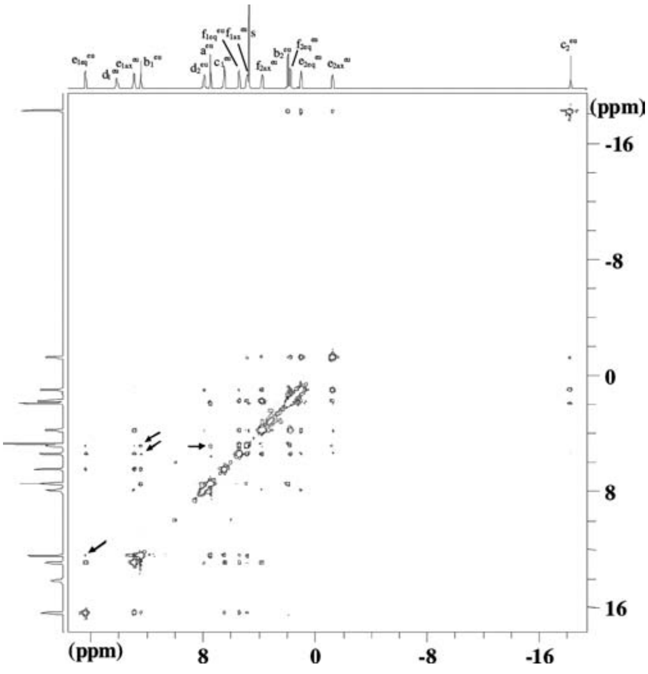


Figure 3. NOESY spectrum (D_2O, 298 K) of the complex $[Eu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ generated in solution by the addition of 1 equiv of NaOH to the solution of $[EuL^{RRRR}(NO_3)_2](NO_3)$. Arrows indicate NOE cross-peaks between protons of two different macrocyclic units (see the text for details).

these complexes, and the $[Ln_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes are formed. On the contrary, the NMR spectra observed for the reactions of mononuclear complexes with NaOH in organic solvents, e.g., $CDCl_3/CD_3OD$, differ for the nitrate and chloride derivatives, although the general spectral patterns are similar to those of the dinuclear species generated in water solutions (Figure 2A; Figure S1, Supporting Information). Presumably, in the organic solvents the outer faces of the macrocyclic dimeric complexes are occupied by the coordinated anions, and the $[Ln_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ or $[Ln_2L_2(\mu\text{-}OH)_2(NO_3)_2]^{2+}$ complexes are formed. After the $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$ dimers are formed, additional hydroxo anions can be bound, as indicated by further spectral changes in the ^1H NMR titrations with NaOH. The additional hydroxo ligands likely replace the outer ligands X to form complexes such as $[Ln_2L_2(\mu\text{-}OH)_2(OH)_2]^{2+}$ or $[Ln_2L_2(\mu\text{-}OH)_2(OH)_4]$.

The ^1H and ^{13}C NMR spectra of the paramagnetic $[Eu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and $[Eu_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and the diamagnetic $[Lu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes were assigned on the basis of 2D NMR spectra (Figures 2 and 3; Figures S4−S11, Supporting Information). While some of the ^1H NMR aliphatic signals of $[Lu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ are overlapped (Figure 2B; Figure S2, Supporting Information), all the 15 ^1H NMR signals of the paramagnetic $[Eu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are well resolved. The signal assignment was based on the combined analysis of the NOESY, COSY, and HMQC data. The coupling patterns for the pyridine and cyclohexane rings were assigned on the basis of COSY spectra, and the pairs of geminal protons of the cyclohexane fragment were identified on the basis of the HMQC spectra. The signals were assigned sequentially using the NOESY and COSY correlations, starting from the unique signal a (see Scheme 1 for the labeling; see the Supporting Information for a detailed discussion of the signal assignments).

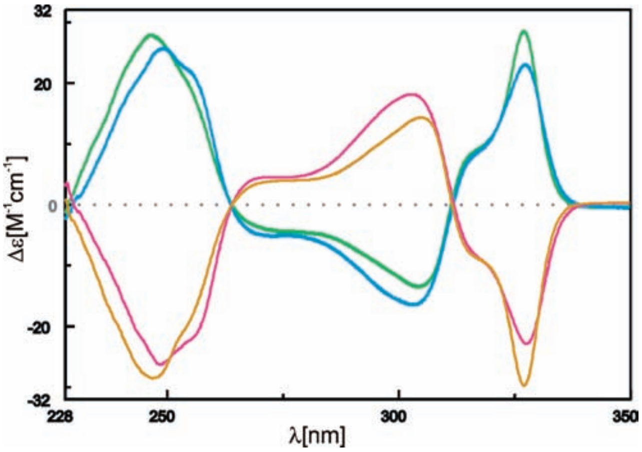


Figure 4. CD spectra (H_2O) of the enantiomers of the starting mononuclear complexes $[SmL^{RRRR}(NO_3)_2](NO_3)$ (red) and $[SmL^{SSSS}(NO_3)_2](NO_3)$ (blue) and the enantiomers of the dinuclear complexes $[Sm_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (yellow) and $[Sm_2L^{SSSS}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (green) generated by the addition of 1 equiv of NaOH.

The NOESY spectra of the $[Eu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and $[Lu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes exhibit additional weak correlations between signals of protons that are far apart within the single macrocycle, i.e., pairs of protons b_1-e_{1eq}, b_1-f_{1ax}, b_1-f_{1eq}, and $a-f_{1ax}$ (Figure 3, Scheme 1). These correlations are not observed for the mononuclear $[LnL]^{3+}$ complexes because the distances between the relevant protons are too long to expect NOE connectivities, particularly for a paramagnetic complex. For instance, the proton−proton distances in the above pairs of protons are equal to 4.45, 6.75, 6.36, and 8.99 Å, respectively, for the mononuclear $[TmL(NO_3)_2]^+$ complex cation.[3f] As a consequence, the above NOE connectivities have to arise from the proximity of two macrocyclic units. In fact, the observed NOESY cross-peaks correspond exactly to the close contacts between two macrocyclic subunits in the dimeric $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$ complexes. The characteristic feature of the crystal structures of $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and $[Y_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex cations is the positioning of the pyridine rings of one macrocyclic unit roughly atop the cyclohexane rings of the other macrocyclic unit.[14,15] This arrangement results in close intermacrocyclic contacts between the protons b_1 and e_{1eq}, b_1 and f_{1ax}, b_1 and f_{1eq}, and a and f_{1ax}, which are equal to 3.12, 3.28, 3.65, and 3.42 Å, respectively, for the cation $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ (Figure 1B). On the other hand, the analogous pairs of protons b_2-e_{2eq}, b_2-f_{2ax}, b_2-f_{2eq}, and $a-f_{2ax}$ correspond to longer distances equal to 6.28, 5.24, 6.39, and 5.97 Å, respectively, for the cation $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ (Figure 1C). While the edges of the two macrocycles, which are further from the μ-OH bridges, are arranged in a close parallel fashion (Figure 1B), the edges that are perpendicular to the $Yb_2(\mu\text{-}OH)_2$ plane (closer to the μ-OH bridges) form a kind of cleft (Figure 1C), which results from the steric interactions with the μ-OH groups. This subtle structural feature of the $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$ dimers explains why NOESY cross-peaks are not observed within the pairs of signals b_2-e_{2eq}, b_2-f_{2ax}, b_2-f_{2eq}, and $a-f_{2ax}$, while they are observed within the pairs b_1-e_{1eq}, b_1-f_{1ax}, b_1-f_{1eq}, and $a-f_{1ax}$. The close contacts between the specific protons of two macrocyclic units in the $[Eu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and

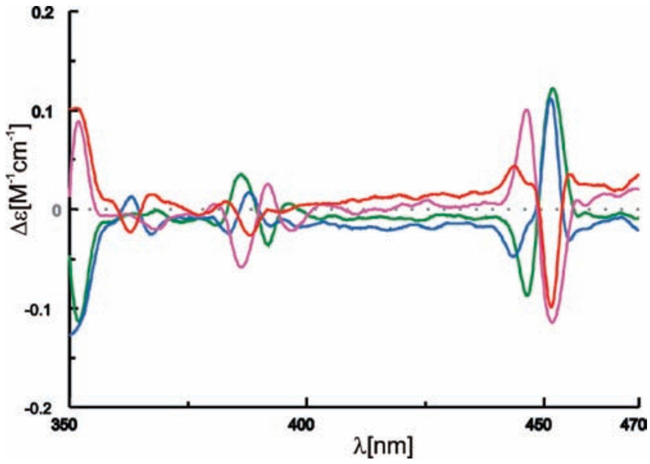


Figure 5. Region of the CD spectra (H_2O) of the enantiomers of the starting mononuclear complexes $[DyL^{RRRR}(NO_3)_2](NO_3)$ (magenta) and $[DyL^{SSSS}(NO_3)_2](NO_3)$ (green) and the enantiomers of the dinuclear complexes $[Dy_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (red) and $[Dy_2L^{SSSS}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (blue) generated by the addition of 1 equiv of NaOH.

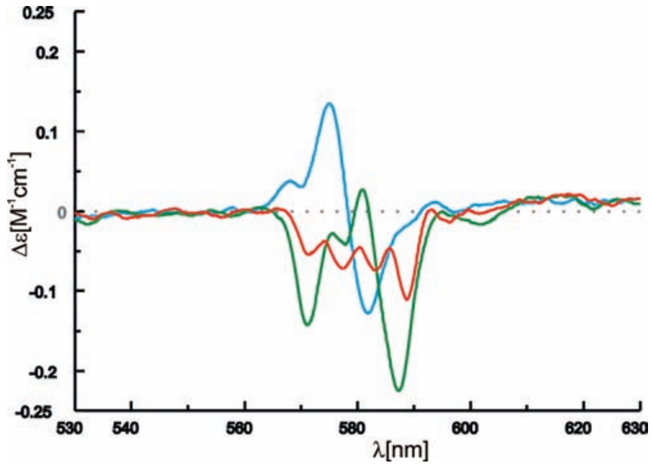


Figure 6. Region of the CD spectra (H_2O) of the starting mononuclear complex $[NdL^{RRRR}(NO_3)_2](NO_3)$ (blue), the dinuclear $[Nd_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex generated by the addition of 1 equiv of NaOH (red), and the dinuclear $[Nd_2L^{RRRR}{}_2(\mu\text{-}OH)_2(OH)_2]^{2+}$ complex generated by the addition of 2 equiv of NaOH (green).

$[Lu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ dimers, revealed by their NOESY spectra, directly confirm the dinuclear structure of the discussed complexes *in solution*. The similarity of the X-ray crystal structures of $[Yb_2L_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and $[Y_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, as well as the agreement with the solution structures of Eu(III) and Lu(III) dimeric complexes, points to a common conformation of the whole series of $[Ln_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes.

The CD spectra of the studied complexes exhibit two types of bands. The intensive bands below 350 nm are related to the organic chromophores of the macrocycle L, and they are very similar for all the studied complexes. For instance, the spectrum of the $[Sm_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex consists of a negative band at 246 nm ($\Delta\varepsilon = -28.5$), a positive band at 304 nm ($\Delta\varepsilon = +14.4$), and a negative band at 327 nm ($\Delta\varepsilon = -29.7$) (Figure 4). The latter two bands can be attributed to exciton coupling of the two $N{=}C{-}C_5H_3N{-}C{=}N$ chromophores comprising the pyridine fragments conjugated with the imine bonds.[3g] The positions of the high-energy CD bands of the discussed dimeric complexes are very similar to those of the starting mononular $[LnL(H_2O)_{2-3}]^{3+}$ complexes (Figure 4). Small changes of band intensities accompanying formation of dimers may be caused by the small changes of intramacrocyclic coupling of chromophores (related to the changes of the dihedral angle between the pyridine rings) and the appearance of intermacrocyclic coupling of the chromophores (related to the formation of dimeric hydroxo derivatives). As expected, the CD spectra of the generated dinuclear complexes $[Ln_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and $[Ln_2L^{SSSS}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ are mirror images of each other (Figures 4 and 5).

In addition to the CD bands related to the chromophores of the macrocycle, some of the studied complexes, such as $[Dy_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and $[Nd_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, give rise to very weak bands ($\Delta\varepsilon$ less than ±0.2) in the visible region corresponding to the f−f transitions of the Ln(III) ion (Figures 5 and 6). The transformation of the starting mononuclear complexes to the μ-hydroxo-bridged dimers is accompanied by profound changes of some of the f−f CD bands. These changes reflect the exchange of axial ligands in the coordination sphere of the Ln^{3+} ions, i.e., formation of di-μ-OH bridges and subsequent binding of additional hydroxide anions at the outer sides of the dimeric complex. The sensitivity of the f−f CD bands to the type of axial coordination was previously observed for the NIR CD spectra of mononulear Yb(III) complexes of L.[3d] The formation of the dinuclear $[Ln_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes does not change profoundly the conformation of the macrocycle and the sense of the helical twist, as indicated by the minor changes of the CD signals of the aromatic chromophores. On the other hand, a profound change of the coordination sphere of the Ln^{3+} ion (resulting in a change of the crystal field parameters) leads to large changes in some f−f CD bands as well as NMR dipolar shifts.

Formation of the Heterodinuclear Complexes $[Ln^1Ln^2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$. Due to the similar ionic radii and chemical nature of the Ln(III) ions, it is very difficult to selectively obtain heterodinuclear complexes containing two different Ln(III) ions.[24,25] More often, statistically substituted solids or mixtures of homo- and heterodinuclear complexes are obtained starting from two different Ln(III) salts or two different Ln(III) complexes.[26] The latter strategy has been used here to generate heterodinuclear $[Ln^1Ln^2L_2(\mu\text{-}OH)_2X_2]^{n+}$ complexes in solution. To further prove the existence of the well-defined dinuclear hydroxo-bridged species in solution, NaOH titrations of mixtures of mononuclear $[LnL^{RRRR}(NO_3)_2](NO_3)\cdot nH_2O$ complexes containing two different lanthanide(III) ions have been performed. If the dimeric complexes are formed in solution, one should observe, apart from the signals of the homodinuclear species mentioned above, an additional set of signals corresponding to the heterodinuclear dihydroxo dimer. The ^1H NMR titrations revealed that this is indeed the case. For instance, the spectrum obtained after the mixture of the $[YbL^{RRRR}(NO_3)_2](NO_3)$ and $[TmL^{RRRR}(NO_3)_2](NO_3)$ complexes had been reacted with NaOH indicated 15 signals of the homodinuclear complex $[Yb_2L^{RRRR}(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, 15 signals of the homodinuclear complex $[Tm_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, and 30 signals of the mixed heterodinuclear complex $[YbTmL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (Figure 7D; Figures S12 and S13, Supporting Information). Similar formation of heterodinuclear species was observed with other pairs of lanthanide ions, such as Yb(III) and Lu(III), Yb(III) and La(III),

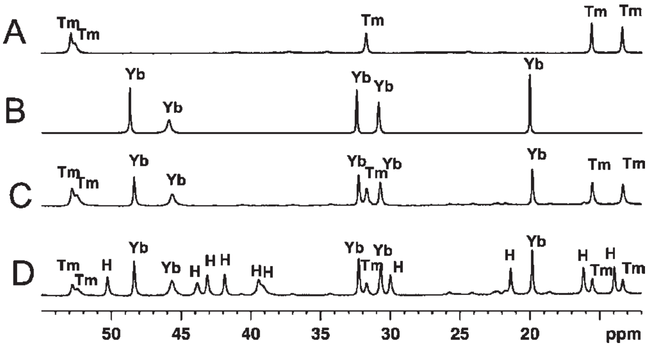


Figure 7. Region of the ^1H NMR spectra (D_2O, 298 K) measured after the addition of 1 equiv of NaOH to a solution containing (A) 1 equiv of $[TmL^{RRRR}(NO_3)_2](NO_3)$, (B) 1 equiv of $[YbL^{RRRR}(NO_3)_2](NO_3)$, (C) a mixture of 0.55 equiv of $[YbL^{SSSS}(NO_3)_2](NO_3)$ and 0.45 equiv of $[TmL^{RRRR}(NO_3)_2](NO_3)$, and (D) a mixture of 0.55 equiv of $[YbL^{RRRR}(NO_3)_2](NO_3)$ and 0.45 equiv of $[TmL^{RRRR}(NO_3)_2](NO_3)$. The signals of the $[Tm_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "Tm", and the signals of the $[Yb_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ or $[Yb_2L^{SSSS}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "Yb". The signals of the heterodinuclear $[YbTmL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "H".

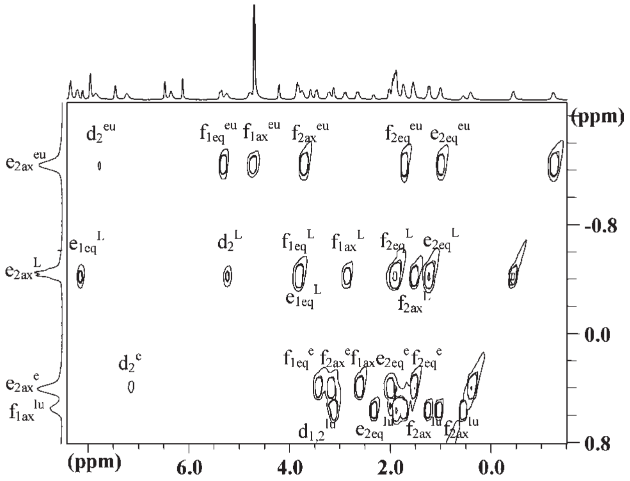


Figure 8. Region of the TOCSY spectrum (D_2O, 300 K) obtained after the addition of 1 equiv of NaOH to a solution containing a mixture of 0.4 equiv of $[EuL^{RRRR}(NO_3)_2](NO_3)$ and 0.6 equiv of $[LuL^{RRRR}(NO_3)_2](NO_3)$. The signals of the $[Eu_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "eu", and the signals of the $[Lu_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "lu". The signals of the two macrocyclic subunits containing Eu(III) and Lu(III) in the heterodinuclear $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscripts "e" and "L", respectively.

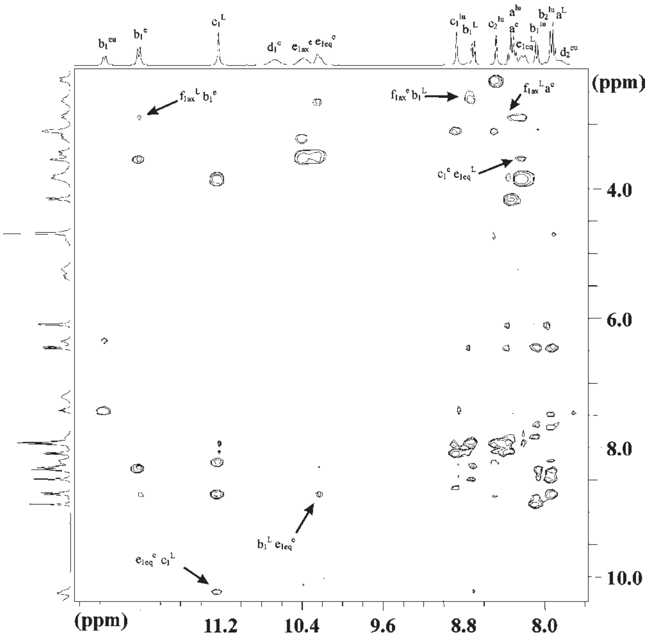


Figure 9. Region of the NOESY spectrum measured after the addition of 1 equiv of NaOH to a solution containing a mixture of 0.4 equiv of $[EuL^{RRRR}(NO_3)_2](NO_3)$ and 0.6 equiv of $[LuL^{RRRR}(NO_3)_2](NO_3)$. The signals of the $[Eu_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "eu", and the signals of the $[Lu_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "lu". The signals of the two macrocyclic subunits containing Eu(III) and Lu(III) in the heterodinuclear $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscripts "e" and "L", respectively.

Eu(III) and Lu(III), and Eu(III) and Tb(III) (Figure 2C; Figures S14−S19, Supporting Information). Remarkably, 59 out of a total of 60 signals of the homo- and heterodinuclear Yb(III)/Tm(III) complexes were resolved due to a substantial paramagnetic contribution to the chemical shifts of both Tm(III) and Yb(III) complexes that leads to a favorable spreading of the resonances (Figure S12). Despite the similar geometry of a given macrocyclic subunit $[LnL^{RRRR}]^{3+}$ in the homodinuclear complex $[Ln^1{}_2L^{RRRR}{}_2(\mu\text{-}OH)_2X_2]^{n+}$ and in the heterodinuclear complex $[Ln^1Ln^2L^{RRRR}{}_2(\mu\text{-}OH)_2X_2]^{n+}$, the sensitivity of ^1H NMR signals of the paramagnetic, macrocyclic lanthanide(III) complexes to minor structural changes[3d,4c,4d,23] allows easy distinction of the $[Ln^1L^{RRRR}]^{3+}$ subunits in different dimeric complexes. Moreover, the chemical shifts of the diamagnetic macrocyclic subunits $[LuL^{RRRR}]^{3+}$ and $[LaL^{RRRR}]^{3+}$ in the homodinuclear complexes are different from the relevant chemical shifts of the same subunits in the heterodinuclear complex $[YbLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, $[YbLaL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, or $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (Figure 2; Figures S14 and S15). In these cases clear paramagnetic shifts are observed for some of the protons of the diamagnetic macrocyclic subunit. These shifts arise from the through-space dipolar (pseudocontact) contribution to the paramagnetic shift and indicate a close proximity between the diamagnetic $[Ln^1L^{RRRR}]^{3+}$ unit and the paramagnetic $[Ln^2L^{RRRR}]^{3+}$ unit.

The full spectral assignment and structure elucidation was possible for the heterodinuclear $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex formed in solution. The assignment of all 60 ^1H NMR signals of the mixture of the $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, $[Eu_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, and $[Lu_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes was based on the combined analysis of 2D NMR spectra (Figures 8 and 9; Figures S20−S23, Supporting Information; see the Supporting Information for a detailed discussion of signal assignments).

In particular, the TOCSY (Figure 8) and HMQC data were used to edit the overlapped signals of the cyclohexane rings. Importantly, the NOESY spectrum (Figure 9; Figure S22, Supporting Information) of the $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex reflects the close contacts between the macrocyclic unit

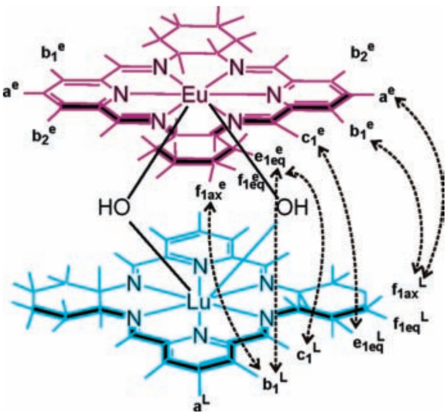


Figure 10. Observed NOE connectivities between the two macrocyclic units of the $[EuLuL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex.

containing the Eu(III) ion and the macrocyclic unit containing the Lu(III) ion, in addition to close contacts within each macrocycle. The observation of NOESY cross-peaks (Figure 9) between the signals $b_1{}^e$ and $f_{1ax}{}^L$, a^e and $f_{1ax}{}^L$, $c_1{}^e$ and $e_{1eq}{}^L$, $b_1{}^L$ and $e_{1eq}{}^e$, $b_1{}^L$ and $f_{1ax}{}^e$, and $c_1{}^L$ and $e_{1eq}{}^e$ (the subscript "e" refers to the macrocyclic subunit containing Eu(III), and the superscript "L" refers to the macrocyclic subunit containing Lu(III), Figure 10) directly confirms the heterodinuclear nature of this complex. In addition, these cross-peaks identify the initially arbitrarily assigned set of signals with subscript "1" as belonging to the edges of the macrocycles that are more remote from the hydroxo groups (Figure 1B). On the other hand, for the set of signals with subscript "2" there is no observable NOESY cross-peak between protons belonging to the Eu(III) subunit and protons belonging to the Lu(III) subunit, so this set of protons belongs to the edges of the macrocycle that form a cleft due to the proximity of hydroxo bridges (Figure 1C). Similarly, there are no observable NOESY cross-peaks between the set of protons with subscript "1" belonging to the Eu(III) subunit and the set of protons with subscript "2" belonging to the Lu(III) subunit (and vice versa), so the macrocyclic units in the dimers $[Ln_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ do not rotate freely in solution around the Ln(III)−Ln(III) axis.

When the two lanthanide ions forming the $[Ln^1Ln^2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are of similar size, e.g., Tm(III) and Yb(III) or Yb(III) and Lu(III), there is no selectivity in formation of heterodinuclear species; i.e., the concentrations of the generated complexes $[Ln^1Ln^2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, $[Ln^1{}_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, and $[Ln^2{}_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ correspond to a statistical mixture. There is, however, a clear preference for the formation of the heteronuclear species when the two ions differ markedly in the ionic radii. For instance, the concentrations of the $[LaYbL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, $[La_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, and $[Yb_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complexes generated from the equimolar mixtures of mononuclear La(III) and Yb(III) complexes are in a ratio of 4:1:1, respectively (Figure 11; Figure S14, Supporting Information). This ratio corresponds to a 2:1:1 ratio of signal intensities, respectively. On the other hand, the statistical 2:1:1 mixture of hetero- and homodinuclear complexes would correspond to a 1:1:1 ratio of signal intensities. The preference for the heterodinuclear complex in this case may result from the interplay of two effects. First, the hydroxide−Ln(III) bond energy increases as the radius of the Ln(III) ion decreases. Second, a more twisted conformation of the ligand L in the complexes with smaller lanthanide ions leads to greater steric interactions between two macrocyclic units within the dimer. Hence, the formation of a mixed dimer containing relatively large and relatively small Ln(III) ions is a compromise between these two factors.

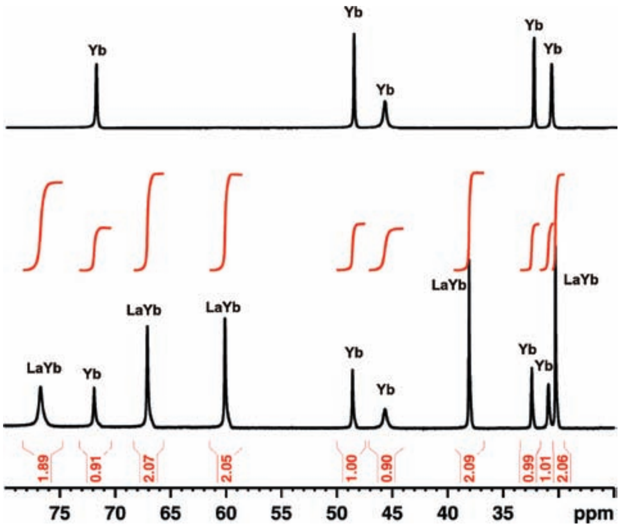


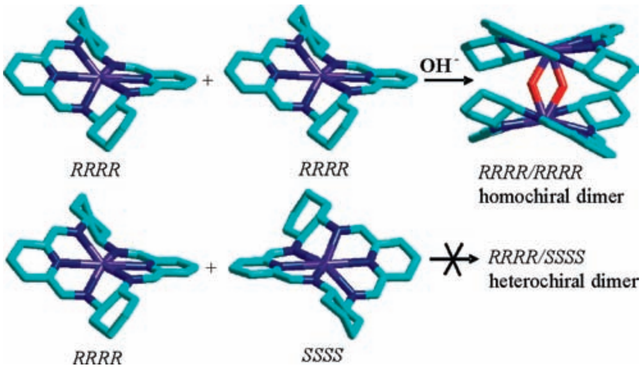
Figure 11. Region of the ^1H NMR spectra (D_2O, 298 K) measured after the addition of 1 equiv of NaOH to a solution containing (A) 1 equiv of $[YbL^{RRRR}(NO_3)_2](NO_3)$ and (B) a mixture of 0.5 equiv of $[YbL^{RRRR}(NO_3)_2](NO_3)$ and 0.5 equiv of $[LaL^{RRRR}(NO_3)_2](NO_3)$. The signals of the $[Yb_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "Yb", and the signals of the heterodinuclear $[LaYbL^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ complex are labeled with the superscript "LaYb".

Enantiomeric Self-Recognition. The analysis of the previously published structure[14] of the dimer $[Yb_2L^{rac}{}_2(\mu\text{-}OH)_2Cl_2]Cl_2 \cdot 4CH_3COH \cdot 2H_2O$ obtained from the racemic form of the ligand, L^{rac}, reveals enantiomeric self-recognition in the solid state. The unit cell of this compound contains two homochiral cationic dimeric complexes $[Yb_2L^{RRRR}{}_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and two homochiral dimers $[Yb_2L^{SSSS}{}_2(\mu\text{-}OH)_2Cl_2]^{2+}$. Similarly, the unit cell of the $[Y_2L^{rac}{}_2(\mu\text{-}OH)_2(H_2O)_2](NO_3)_4 \cdot 6H_2O$ complex[15] contains two homochiral dimers $[Y_2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and two homochiral dimers $[Y_2L^{SSSS}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$. In both cases the heterochiral dimers $[Ln_2L^{RRRR}L^{SSSS}(\mu\text{-}OH)_2X_2]^{n+}$ are not formed in the solid state. The question arises of whether this sorting of macrocyclic units is caused by the crystal packing effects and lower solubility of the racemic homochiral dimers or the chiral self-recognition is an intrinsic feature of these macrocyclic units, which is operating in solution. To answer this question, the formation of dimeric complexes using various enantiomers of the starting mononuclear complexes was studied. As expected, the reactions of $[LnL^{SSSS}]^{3+}$ enantiomers with NaOH resulted in formation of dimers that give NMR spectra identical to those generated from the corresponding $[LnL^{RRRR}]^{3+}$ enantiomers discussed above. Similarly, the dinuclear complexes prepared from the racemic monomeric complexes $[LnL^{rac}]^{3+}$ possess the same NMR spectra as the dimers obtained from enantiopure complexes. This may indicate that only one homochiral diastereomer of the dinuclear complex is formed. The observation of a single set of signals obtained from a racemic mixture of aggregating components is often invoked as a proof for diastereoselectivity and a complete homo- or heterochiral recognition operating in solution. However, this argument should be treated with caution. For instance, the two diastereomers may have very similar structures and their signals may coincidentally overlap. This situation is very unlikely in the studied case, since the NMR signals of the paramagnetic macrocyclic Ln(III) complexes are extremely sensitive to any structural modifications. More importantly, the single set of resonances would be observed in the case of fast (on the NMR time scale) chemical exchange between the homochiral and heterochiral species leading to signal averaging. In a general case of racemic chiral molecular building block (*R*)-X and (*S*)-X forming a dimer (or higher aggregates), a fast chemical exchange between the possible diastereomers $[(R)\text{-X}]_2/[(S)\text{-X}]_2$ and $[(R)\text{-X}(S)\text{-X}]$ will average the two distinct chemical shifts of these diastereomers. A given signal of the chiral (*R*)-X unit will exhibit a chemical shift that is a weighted average of the relevant shifts of the homochiral dimer $[(R)\text{-X}]_2$ and heterochiral dimer $[(R)\text{-X}(S)\text{-X}]$. An identical weighted average of the relevant shifts of the homochiral dimer $[(S)\text{-X}]_2$ and heterochiral dimer $[(R)\text{-X}(S)\text{-X}]$ will be observed for the corresponding signal of the chiral (*S*)-X enantiomer. In this situation, in contrast to the case of a slow chemical exchange, a single set of resonances will be observed for the racemic mixture of isomers $[(R)\text{-X}]_2/[(S)\text{-X}]_2$ and $[(R)\text{-X}(S)\text{-X}]$ (although two sets of resonances will be observed for the nonracemic mixtures[13a]). Thus, the observation of a single set of resonances for a self-aggregating racemic mixture is not an absolute proof of enantiomeric self-recognition. To confirm the selective formation of homochiral dinuclear species $[Ln_2L^{RRRR}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}/[Ln_2L^{SSSS}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$, the exchange of macrocyclic units between different dinuclear complexes as well as the formation of dimers composed of monomeric units differing both in chirality and in the kind of lanthanide(III) ion has been investigated.

The axial anion exchange between various $[LnLX_2]^+$ complexes (where X is an anion such as chloride, nitrate, acetate, or diphenyl phosphate) is relatively fast, and the corresponding exchange cross-peaks are readily observed in the EXSY spectra.[3d] On the contrary, in the case of the discussed dimers, no EXSY correlations are observed between the signals of the starting complexes and the signals of the hydroxo derivatives, in accord with a much slower exchange rate. The fact that the dinuclear $[Ln_2L_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$ complexes are relatively inert toward dissociation is also evident from the results of scrambling experiments. When two different homodinuclear $[Ln_2L^{RRRR}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$ complexes are generated in separate solutions and subsequently mixed, the immediately taken ^{1}H NMR spectra of the resulting solutions indicate the presence of homodinuclear complexes only, with no indication of heterodinuclear species. The traces of heterodinuclear complexes appear in the ^{1}H NMR spectra taken after 1 h, and they are clearly visible after 24 h. These results point to slow dissociation of homodinuclear μ-hydroxo-bridged complexes into mononuclear fragments and subsequent recombination of mononuclear subunits containing two different lanthanide ions into heterodinuclear complexes. Since the exchange of macrocyclic units containing different Ln(III) ions is slow in the discussed dinuclear complexes, the exchange of macrocyclic units of different chirality should also be slow. Hence, the observation of a single set of resonances of the dimeric complexes obtained from the racemic macrocyclic precursors cannot be caused by the fast chemical exchange.

The final confirmation of the selective formation of homochiral dimers is based on an NMR titration experiment, in which mixtures of two monomeric complexes, differing both in chirality and in the kind of lanthanide(III) ion, were reacted with NaOH. In these reactions the homochiral, homodinuclear complexes are solely formed, while the NMR signals of the heterodinuclear species are missing (Figures 2 and 7; Figures S13, S15, and S16, Supporting Information). For instance, the reaction of a mixture of the $[YbL^{SSSS}(NO_3)_2](NO_3)$ and $[TmL^{RRRR}(NO_3)_2](NO_3)$ complexes with NaOH results in a ^{1}H NMR spectrum consisting of the 15 signals of the homodinuclear complex $[Yb_2L^{SSSS}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$ and 15 signals of the homodinuclear complex $[Tm_2L^{RRRR}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$. On the other hand, the signals of the heterodinuclear, and hence necessary heterochiral, complex $[YbL^{SSSS}TmL^{RRRR}(\mu\text{-OH})_2(H_2O)_2]^{4+}$ are not observed (Figure 7C; Figure S13). This absence of heterodinuclear, heterochiral complex is in sharp contrast to the formation of analogous heterodinuclear, homochiral complex $[YbTmL^{RRRR}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$ (Figure 7D) discussed in the previous section. Similarly, heterochiral complexes were not observed for the reactions of other pairs of macrocyclic monomeric complexes of opposite chirality containing different lanthanide ions, such as Eu(III) and Lu(III) (Figure 2) or Yb(III) and Lu(III) (Figures S15 and S16). The above observations prove the enantiomeric self-recognition of the chiral mononuclear units and the selective formation of homochiral hydroxo-bridged dinuclear lanthanide(III) (Scheme 2).

Scheme 2. Enantiomeric Self-Recognition of the Macrocyclic $[LnL]^{3+}$ Units



The chiral discrimination accompanying the formation of the discussed dimers most likely arises from the steric interaction between the two macrocyclic ligands within the dinuclear complex as well as between the bridging hydroxo groups and the ligands. The two macrocycles have to adjust their conformation to minimize the steric hindrance. Apparently, there are fewer steric interactions between the two macrocycles of the same helicity in the observed $[Ln_2L^{RRRR}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$ or $[Ln_2L^{SSSS}{}_2(\mu\text{-OH})_2(H_2O)_2]^{4+}$ complexes than between the macrocycles of the opposite helicity in the putative $[Ln_2L^{SSSS}L^{RRRR}(\mu\text{-OH})_2(H_2O)_2]^{4+}$ complexes. Indeed, the estimated energy of the MM+-modeled structure of the putative heterochiral dimer $[Y_2L^{SSSS}L^{RRRR}(\mu\text{-OH})_2(H_2O)_2]^{4+}$ is ca. 12 kcal/mol higher than that of the homochiral dimer. In comparison, two types of dimeric hydroxo-bridged complexes can be generated from the monomeric Yb(III) complex of the less bulky macrocycle L1 (Scheme 1). Although this macrocycle lacks stereogenic centers, it forms chiral racemic Ln(III) complexes because of the helical twist of the ligand. NMR titration of the mononuclear Yb(III) complex of this ligand with NaOH indicates formation of two C_2-symmetric hydroxo-bridged complexes after addition of NaOH

(Figure S24, Supporting Information). Likely, the major form corresponds to a homochiral dimer $[Yb_2L1_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ with identical sense of helical twist of the macrocycle L1 in both macrocyclic units, while the minor form corresponds to the heterochiral dimer with the two macrocycles L1 of opposite helicity. In this case, the partial homochiral recognition reflects the smaller steric hindrance between the macrocyclic subunits.

CONCLUSIONS

Addition of NaOH to the mononuclear $[LnLX_n]^{3+}$ complexes results in a clean formation of di-μ-hydroxo-bridged dimers $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$. The NOESY data prove that the structure of these complexes in solution corresponds to that observed for the solid state, including subtle conformation features of the macrocycles. In addition to the homodinuclear $[Ln_2L_2(\mu\text{-}OH)_2X_2]^{n+}$ complexes, the heterodinuclear complexes $[Ln^1Ln^2L_2(\mu\text{-}OH)_2X_2]^{n+}$ can be obtained in solution using two different starting mononuclear complexes. The formation of such species is directly confirmed by the observation of NOE cross-peaks between the signals of macrocyclic units containing two different Ln(III) ions. The formation of heterodinuclear species $[Ln^1Ln^2L_2(\mu\text{-}OH)_2X_2]^{n+}$ is partially selective when the difference in the radii of the two Ln^1(III) and Ln^2(III) ions is relatively large. While the reaction of NaOH with a mixture of two different monomeric $[LnL(H_2O)_2]^{3+}$ complexes of the same chirality leads to formation of heterodinuclear complexes containing two different Ln(III) ions, $[Ln^1Ln^2L^{RRRR}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ or $[Ln^1Ln^2L^{SSSS}{}_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$, the analogous experiment with two different complexes of opposite helicity does not lead to heterodinuclear complexes. This effect results from a complete enantioselective self-recognition of macrocyclic subunits accompanying the formation of the hydroxo-bridged dimer. In contrast, for a less bulky macrocycle L1 only a partial homochiral self-recognition is observed.

ASSOCIATED CONTENT

Ⓢ Supporting Information. ^1H and ^{13}C NMR signal assignment and Figures S1−S24 showing 2D NMR, ^1H NMR, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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