Helical Structures

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Helicity Inversion in Lanthanide(III) Complexes with Chiral Nonaaza Macrocyclic Ligands**

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Controlling the chirality of metal complexes or supramolecular assemblies continues to be a challenging and fascinating area of research.[1] The chirality of these systems may be related, for example, to the spatial disposition of chelating ligands around a metal ion,[1a] to the formation of double or triple helices,[2] to the helical twist of a macrocyclic ligand,[3] or to the rotation of the side arms of a macrocyclic ligand.[4] In favorable cases, these chiral compounds can be separated into enantiopure forms.[2c,5] Alternatively, the enantiopure supramolecular assemblies and metal complexes can be obtained by diastereoselective synthesis from nonracemic chiral organic building blocks, which may determine the chirality of the assembly or complex (for example, the handedness of a helical structure). Generally, this strategy is successful when one of the possible diastereoisomers is thermodynamically favored.[6] In the case of DNA, however, diastereoisomeric structures of opposite helicity can be obtained from sugar

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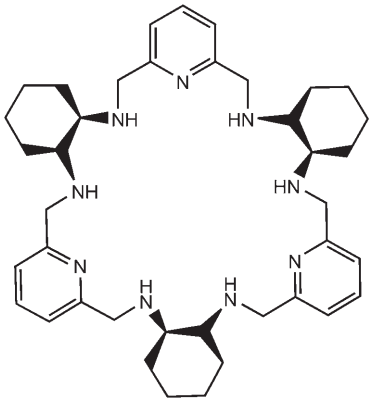
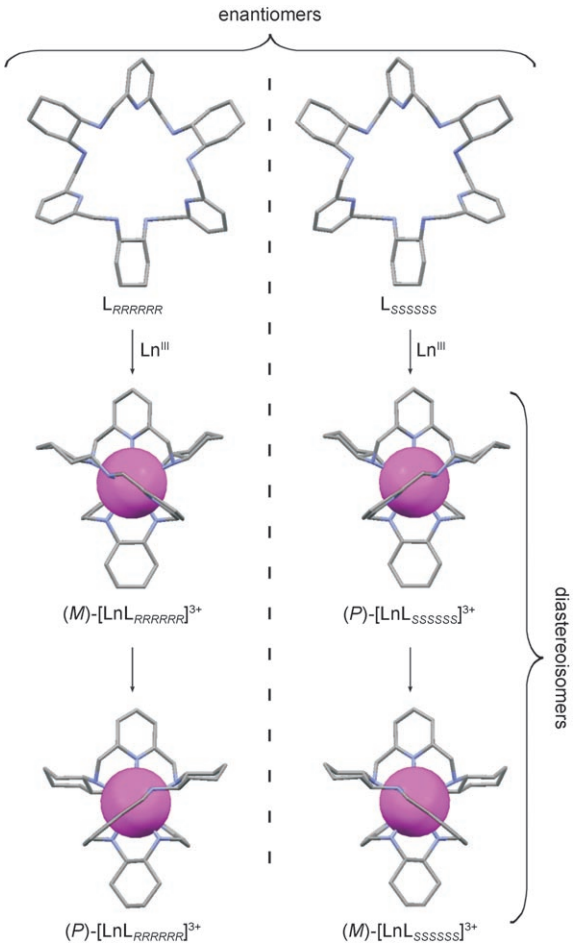
building blocks of the same chirality. Furthermore, the normal right-handed helix of the B form of DNA can be inverted (for example, by increasing the salt concentration) to the left-handed helix of the Z form.[7] Similar controlled helicity inversion is very rare for artificial systems.[8] Herein, we report a unique example of helicity inversion between the kinetic and thermodynamic complexation products of a macrocyclic ligand, as well as the isolation of both products in enantiopure form. We describe diastereoisomeric lanthanide(III) (Ln^{III}) complexes with the nonaaza macrocycle L (Scheme 1), which have the same configuration at all stereogenic carbon atoms, yet opposite helicity (Scheme 2).



Scheme 1. The L_{RRRRRR} macrocycle.

Depending on the reaction conditions, the condensation of 2,6-diformylpyridine and *trans*-1,2-diaminocyclohexane leads to various 2+2, 3+3, and 4+4 macrocyclic Schiff bases, which can be easily converted into the corresponding macrocyclic amines.[9] While the 2+2 macrocycles form complexes with transition-metal and Ln^{III} ions,[3] the coordination properties of the chiral 3+3 macrocyclic amine L have not yet been explored, with the exception of the electrospray ionization mass spectrometry (ESI MS) characterization of a dinuclear $[Cd_2L]^{6+}$ complex generated in solution.[9b] The chiral ligand L can be obtained in the enantiopure forms L_{RRRRRR} and L_{SSSSSS}, which correspond to all-*R* or all-*S* configurations of the diaminocyclohexane carbon atoms, respectively.[9b,c]

The addition of Ln^{III} nitrate or chloride salts to solutions of the free L_{RRRRRR} macrocycle results in smooth complex formation, as indicated by ^{1}H NMR spectroscopy. Depending on the metal/ligand ratio and the reaction conditions, the complexes formed can be isolated as enantiopure nitrate salts ((*M*)-$[EuL_{RRRRRR}](NO_3)_3\cdot CHCl_3\cdot 2H_2O$, (*M*)-$[TbL_{RRRRRR}](NO_3)_3$sdot;$0.5\,CHCl_3\cdot 1.5\,H_2O$, and (*M*)-$[YbL_{RRRRRR}](NO_3)_3\cdot CHCl_3\cdot H_2O$) or as derivatives containing an additional complex $[Ln(NO_3)_5]^{2-}$ counterion ((*M*)-$[EuL_{RRRRRR}]_2[Eu(NO_3)_5](NO_3)_4\cdot 2H_2O$ and (*M*)-$[YbL_{RRRRRR}]_2[Yb(NO_3)_5](NO_3)_4\cdot 4H_2O$; see Supporting Information for experimental details and characterization of the compounds). For a given Ln^{III} ion, both types of derivatives, as well as the species generated in solution, give rise to very similar NMR spectra, indicating that, in each case, the same type of $[LnL]^{3+}$ complex is present. The presence of this type of cationic complex is also supported by the ESI mass spectra (see Supporting Information). The ^{1}H NMR spectra of the $[LnL]^{3+}$ complexes consist of 29 lines, most of which are well resolved for the paramagnetic Eu^{III}, Tb^{III}, and Yb^{III} derivatives (see Supporting Information). In the case of the $[EuL]^{3+}$ complex, the combination of correlation spectroscopy (COSY), total correlation spectroscopy (TOCSY), nuclear Overhauser effect spectroscopy (NOESY), rotational Overhauser effect spectroscopy (ROESY), and heteronuclear multiple quantum correlation (HMQC) data allowed a complete assignment of all resonances (see Supporting Information). The TOCSY spectrum of (*M*)-$[EuL_{RRRRRR}](NO_3)_3\cdot CHCl_3\cdot 2H_2O$ clearly indicates that the only symmetry element of the complex is a C_2 axis that passes through one of the pyridine rings and bisects the opposite cyclohexane ring.



Scheme 2. Preparation and transformation of the $[LnL]^{3+}$ diastereoisomers. The conformations of the free ligand L (based on the molecular structure of the protonated form $H_6L_{RRRRRR}{}^{6+}$[9b]) and the complex cations $[LnL]^{3+}$ (based on the molecular structures of (*M*)-$[YbL_{RRRRRR}]^{3+}$ and (*P*)-$[YbL_{RRRRRR}]^{3+}$) are shown. Yb pink, C gray, N blue; H omitted.

The X-ray crystal structure of (*M*)-$[EuL_{RRRRRR}]_2[Eu(NO_3)_5](NO_3)_4\cdot 2H_2O$ reveals that the nonaaza macrocyclic $[EuL_{RRRRRR}]^{3+}$ complex adopts a new type of geometry (Figure 1).[10] Because the cavity radius of the "open" form of the ligand (2.55 Å)[9b] is far too large to accommodate a

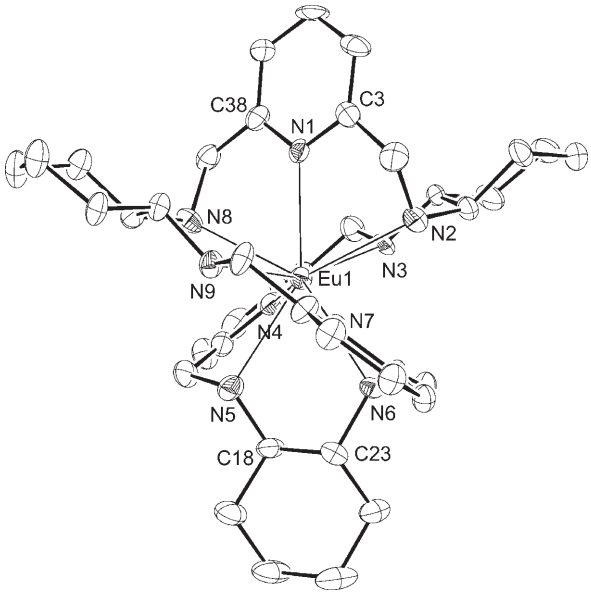


Figure 1. Molecular structure of the (*M*)-$[EuL_{RRRRRR}]^{3+}$ complex cation; H omitted.

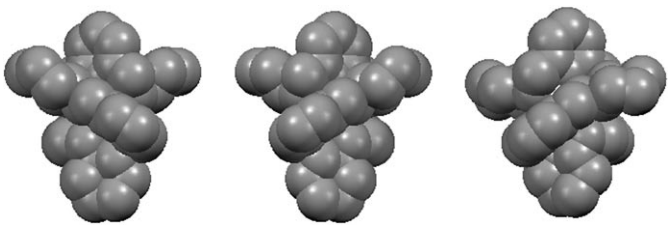


Figure 2. Molecular structures of the (*M*)-$[YbL_{RRRRRR}]^{3+}$ (left) and (*P*)-$[YbL_{RRRRRR}]^{3+}$ (right) complex cations. The mirror image of (*M*)-$[YbL_{RRRRRR}]^{3+}$, that is, (*P*)-$[YbL_{SSSSSS}]^{3+}$ (middle) is presented for comparison.

single Eu^{III} ion, the ligand wraps around the cation in a helical fashion, leading to the generation of a new element of chirality: a left-handed *M* double helix (Figure 1). The helical twist of the macrocycle is determined by the mutual orientation of the pyridine and cyclohexane rings positioned on the (noncrystallographic) C_2 axis. For the (*M*)-$[EuL_{RRRRRR}]^{3+}$ molecule shown in Figure 1, the helical twist, which corresponds to the improper torsion angle C3-C38-C18-C23, is −186.8°; for the second independent molecule in the crystal structure, the twist is −185.5°. These values are among the largest reported for macrocyclic complexes and are much larger than those observed for Ln^{III} complexes with related 2+2 macrocycles.[3] In accord with the spin systems observed in the TOCSY spectrum, the pyridine and cyclohexane rings positioned on the (noncrystallographic) C_2 axis are different from the remaining pairs of pyridine and cyclohexane rings, which are each related by (noncrystallographic) C_2 symmetry. All nine nitrogen atoms of the macrocycle [27]trieneN$_9$ core coordinate to the metal ion, which is the first example of this type of coordination for a nonaaza macrocycle. The donor atoms of L satisfy the coordination sphere of the Eu^{III} ion; unlike most of the known macrocyclic Ln^{III} complexes, no other ligand, such as a counteranion or solvent molecule, is coordinated to the metal ion. The helical twist of the macrocycle imposes the *S*,*S* chirality at the nitrogen atoms attached to the unique axial cyclohexane ring and the *R*,*S* chirality at the nitrogen atoms attached to the two nearly equivalent cyclohexane rings. The structure of the (*M*)-$[EuL_{RRRRRR}]^{3+}$ complex is completely different from that of the Eu^{III} complex of an analogous 3+3 macrocycle derived from 2,6-diformylphenol.[11].

The X-ray crystal structure of (*M*)-$[YbL_{RRRRRR}]$-$(NO_3)_3 \cdot 2.33\,CH_3CN \cdot 2\,H_2O$ reveals the presence of a similar complex cation (Figure 2; Scheme 2).[12] The helical twists of the macrocycles in the two independent (*M*)-$[YbL_{RRRRRR}]^{3+}$ molecules are −192.5° and −193.8°, which are even greater than those of the (*M*)-$[EuL_{RRRRRR}]^{3+}$ complex. This difference reflects the tighter wrapping of the macrocycle around the smaller Yb^{III} ion.

The ^1H NMR spectra of the (*M*)-$[LnL_{RRRRRR}]^{3+}$ complexes reflect their relatively high stability in solution. For instance, the ^1H NMR spectrum of a water solution of (*M*)-$[EuL_{RRRRRR}]^{3+}$ shows only traces of a new complex after 3 weeks. The (*M*)-$[YbL_{RRRRRR}]^{3+}$ complex is somewhat less stable. In water, it gradually converts into a new paramagnetic complex (see Supporting Information). After heating at 238 K for 339 h, equilibrium is reached, with 95% conversion into the new form. The process can also be observed by circular dichroism (CD) spectroscopy, which reveals profound differences between the two forms (Figure 3).

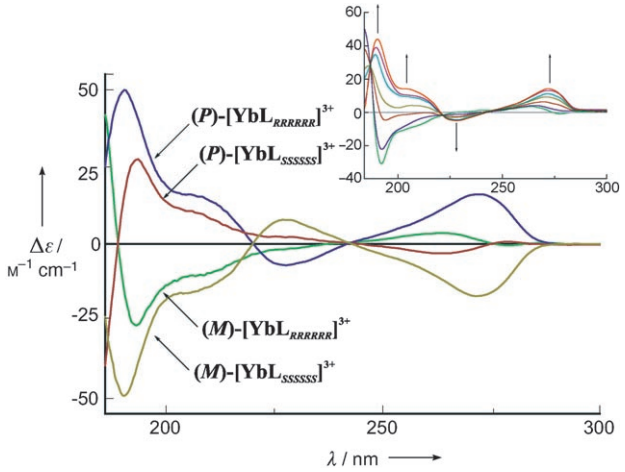


Figure 3. CD spectra of the $[YbL]^{3+}$ diastereoisomers. Inset: CD spectra recorded during the conversion of the starting (*M*)-$[YbL_{RRRRRR}]^{3+}$ complex cation into (*P*)-$[YbL_{RRRRRR}]^{3+}$, after heating in water solution at 238 K for 0, 5, 29, 50, 74, 171, and 339 h; arrows indicate changes on increasing heating time.

The new enantiopure complex (*P*)-$[YbL_{RRRRRR}]^{3+}$ can be isolated from solutions of enantiopure (*M*)-$[YbL_{RRRRRR}]^{3+}$ upon long standing; however, synthesis of the (*P*)-$[YbL_{RRRRRR}]^{3+}$ complex from the free ligand, using modified reaction conditions, is more practical (see Supporting Information).[13] Although the NMR spectra of the new form clearly differ from those of (*M*)-$[YbL_{RRRRRR}]^{3+}$, the ESI mass

spectrum of (*P*)-$[YbL_{RRRRRR}]^{3+}$ contains the same signals as that of the starting complex, indicating the formation of an isomeric complex (see Supporting Information). The ^{1}H NMR spectrum of (*P*)-$[YbL_{RRRRRR}]^{3+}$ consists of 29 signals, which indicates that the new form also has C_2 symmetry. Note that ^{1}H NMR spectra of paramagnetic Yb^{III} complexes with macrocyclic ligands are very sensitive to any structural changes.[3a,14] In contrast, the UV/Vis spectra of both forms are nearly identical (see Supporting Information), reflecting the similar chemical character of the isomers.

The formation of the isomeric complex was confirmed by the X-ray crystal structure of (*P*)-$[YbL_{RRRRRR}](NO_3)_3{\cdot}2\,CH_3CN{\cdot}0.5\,H_2O$, which reveals the presence of the *P*-helical complex cation (*P*)-$[YbL_{RRRRRR}]^{3+}$ (Figure 2; Scheme 2).[15] In this cation, the twist of the macrocycle +255.6°, even greater than that of the starting *M* form. More importantly, the direction of the twist is opposite (see Supporting Information), which imposes a different chirality at the donor nitrogen atoms; the two nitrogen atoms attached to the unique cyclohexane ring positioned on the (non-crystallographic) C_2 symmetry axis have an *R* configuration, while the four remaining amine nitrogen atoms have an *S* configuration.

We have also synthesized the Yb^{III} complex of the all-*S* form of the ligand L, (*P*)-$[YbL_{SSSSSS}](NO_3)_3{\cdot}CHCl_3{\cdot}H_2O$, and its inversion product, (*M*)-$[YbL_{SSSSSS}](NO_3)_3{\cdot}0.5\,CH_3CN{\cdot}4\,H_2O$. As expected, the NMR spectra of the two complexes of each enantiomeric pair ((*M*)-$[YbL_{RRRRRR}]^{3+}$/(*P*)-$[YbL_{SSSSSS}]^{3+}$ and (*P*)-$[YbL_{RRRRRR}]^{3+}$/(*M*)-$[YbL_{SSSSSS}]^{3+}$) are identical, but their CD spectra are mirror images of one another (Figure 3; Scheme 2). Although the CD spectra of all four stereoisomers differ, the spectrum of (*P*)-$[YbL_{RRRRRR}]^{3+}$ somewhat resembles that of the (*P*)-$[YbL_{SSSSSS}]^{3+}$ diastereoisomer and is very different from that of the parent diastereoisomer (*M*)-$[YbL_{RRRRRR}]^{3+}$ (as is also true for the other pair of diastereoisomers). This observation is in accord with the fact that the overall shape of the (*P*)-$[YbL_{RRRRRR}]^{3+}$ complex is similar to that of the (*P*)-$[YbL_{SSSSSS}]^{3+}$ diastereoisomer (Figure 2; Scheme 2) and reflects that the *P*/*M* helicity has a stronger influence on the CD spectra of the complexes (for example, by an exciton-coupling mechanism) than does the *R*/*S* configuration at the cyclohexane fragments.

The conversion of (*M*)-$[YbL_{RRRRRR}]^{3+}$ into the (*P*)-$[YbL_{RRRRRR}]^{3+}$ isomer was rather unexpected. In principle, either the stability of two diastereoisomers derived from the same enantiopure form of a ligand are comparable, and a mixture of both forms is obtained, or one diastereoisomer exhibits a higher thermodynamic stability, leading to diastereoselection. In the present case, the less stable (*M*)-$[YbL_{RRRRRR}]^{3+}$ isomer is a kinetic product of the complexation of the free ligand (100% *de*), and the (*P*)-$[YbL_{RRRRRR}]^{3+}$ isomer is a thermodynamic product (90% *de*). Luckily, the conversion rate of the *M* form into the more stable *P* form is slow enough to allow the isolation and characterization of both enantiomers. The helicity-inversion process is dependent on the size of the Ln^{III} ion. Inversion is also observed for solutions of the $[TbL]^{3+}$ complex, while only traces of the inverted isomer are observed for $[EuL]^{3+}$.

In conclusion, we have demonstrated the formation of enantiopure complexes of opposite helicity with the same configuration at all stereogenic carbon centers from one enantiomer of a chiral ligand. The NMR, CD, ESI MS, and X-ray crystal-structure data confirm the isolation of the four enantiopure stereoisomers (*M*)-$[YbL_{RRRRRR}]^{3+}$, (*P*)-$[YbL_{RRRRRR}]^{3+}$, (*P*)-$[YbL_{SSSSSS}]^{3+}$, and (*M*)-$[YbL_{SSSSSS}]^{3+}$ and show that the kinetic complexation product slowly converts into the thermodynamic product of opposite helicity. Thus, helicity inversion corresponding to the conversion of the enantiopure complex (*M*)-$[YbL_{RRRRRR}]^{3+}$ into (*P*)-$[YbL_{RRRRRR}]^{3+}$ can be realized on a preparative scale. Note that the helicity inversion described herein differs from the inversion observed during the racemization of enantiopure helical structures and also from the inversion of helicity observed in polymeric systems,[16] as we observe a clear conversion of well-defined molecular compounds into their diastereoisomers. The properties of the complexes described are currently under investigation, in view of the many applications of enantiopure chiral lanthanide complexes, including macrocyclic derivatives, as enantioselective catalysts and spectroscopic probes.

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Keywords: chirality · diastereoselectivity · helical structures · lanthanides · macrocyclic ligands

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[6] For instance, the important magnetic resonance imaging (MRI) contrast-enhancing agent GdDOTA and related Ln^{III} complexes of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) can exist as four stereoisomers, the enantiomeric pairs Λ(δδδδ)/Δ(λλλλ) and Δ(λλλλ)/Λ(δδδδ), where Δ/Λ denote chirality related to the coordination around the Ln^{III} ion and the rotation of the coordinated side arms, while δ/λ denote chirality related to the conformation of the cyclene macrocycle. These complexes, which lack stereogenic carbon atoms, exist either as a mixture of all four stereoisomers, or as a mixture of just one of the two enantiomeric pairs. In contrast, the introduction of additional chiral centers into the system, as carbon atoms of defined *R* or *S* configuration, results in the preferential formation of only one of the four possible stereoisomers.[4]

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