Helicity inversion in lanthanide(III) complexes with chiral nonaaza macrocyclic ligands.

Autorzy

Janusz Gregoliński

Jerzy Lisowski

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Streszczenie

The chiral nonaaza macrocycle L wraps tightly around lanthanide(III) ions in a helical fashion (see picture). The all-*R* enantiomer of the macrocycle, L_{RRRRRR}, forms kinetically controlled complexation products of *M* helicity (100 % *de*), which undergo inversion to the *P* diastereomer (90 % *de*). Both products have been isolated in enantiopure form and structurally characterized. 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 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.

Adres publiczny

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