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Lanthanide complexes of the heterochiral nonaaza macrocycle: switching the orientation of the helix axis.

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Streszczenie

The La(III), Ce(III), Pr(III), Nd(III), Sm(III), and Eu(III) complexes of the racemic heterochiral nonaaza macrocyclic amine L have been synthesized and characterized by spectroscopic methods. The X-ray crystal structures of the $[PrL][Pr(NO_3)_6]\cdot CH_3OH$ and the isomorphic $[NdL][Nd(NO_3)_6]\cdot CH_3OH$ complexes show that all nine nitrogen atoms of the macrocycle coordinate to the Ln^{3+} ion, completing its coordination sphere. The macrocycle wraps tightly around the metal ion in double-helical fashion. The structures reveal the *RRRRSS*/*SSSSRR* configuration at the stereogenic carbon atoms of the three cyclohexane rings, confirming the heterochiral nature of the parent 3 + 3 macrocycle obtained in the condensation of racemic *trans*-1,2-diaminocyclohexane and 2,6-diformylpyridine. The NMR spectra of the isolated complexes indicate the presence of low C_1 symmetry $[LnL]^{3+}$ complexes. The same symmetry is indicated by the X-ray crystal structures of Pr(III) and Nd(III) complexes, which show that for the *RRRRSS* enantiomer of the macrocycle L, the helix axis passes through the cyclohexane ring of *RR* chirality and the opposite pyridine ring. The NMR studies of complex formation in solution by the paramagnetic Pr^{3+} and Eu^{3+} ions indicate that the initially formed $[LnL]^{3+}$ complexes are of C_2 symmetry. For the *RRRRSS* enantiomer of the macrocycle L in the C_2-symmetric species, the helix axis passes through the cyclohexane ring of *SS* chirality and the opposite pyridine ring. The C_1-symmetric and C_2-symmetric forms of the $[LnL]^{3+}$ complexes constitute a new kind of isomers and the conversion of the kinetic complexation product of C_2 symmetry into the thermodynamic product of C_1 symmetry corresponds to an unprecedented switching of the orientation of the helix axis within the macrocycle framework.

Słowa kluczowe

Thermodynamics, Molecular structure, Kinetics, Macrocycles, Ions

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