Rare earth complexes of chiral unsymmetrical hexaazamacrocycles.

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Streszczenie

A step-by-step synthesis based on the application of monoprotected 2.6-diformylpyridine intermediate resulted in the formation of enantiopure Eu(III), Yb(III) and Y(III) complexes of unsymmetrical macrocycles L^3 and L^4 containing two pyridine units and two different diamine and diimine links. The final step in the formation of these mixed amine-imine hexaazamacrocycles was based on a templated condensation of ethylenediamine or enantiopure *trans*-1,2-diaminocyclohexane with a linear [2 + 1] amine intermediate bearing two pyridinecarboxaldehyde fragments. The identity of these unsymmetrical complexes have been determined on the basis of 2D NMR and ESI MS spectroscopy and confirmed by the X-ray crystal structures of Eu(III) and Yb(III) complexes of macrocycle L^3. In these complexes the macrocyclic ligand adopts twist-fold conformation and the twist of the achiral ethylene link is dictated by the conformation of the cyclohexane link. The ten-coordinate Ln(III) ions are bound in equatorial positions by the six nitrogen atoms of the macrocycle and their coordination spheres are completed by two axial bidentate nitrate anions. The luminescent properties of the Eu(III) complexes of L^3 and L^4 have been characterized.

Słowa kluczowe

Macrocyclic complexes, Lanthanides, Enantiopure ligands, Crystal structure, Luminescence

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