

Paramagnetic Cage-Type Co(II) Complexes of Chiral Macrocycles: Enantio- and Size-Selective Binding of Guest Molecules

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Two enantiomers of the cage-type complex, $[\text{Co}_3\text{L}^R_2]$ and $[\text{Co}_3\text{L}^S_2]$ of a large hexaazatriphenolic [3 + 3] macrocyclic imine **L**, have been synthesized and characterized on the basis of NMR, CD, and ESI MS spectra. The X-ray crystal structures of $[\text{Co}_3\text{L}_2]$ crystalline forms reveal two macrocycles of cone shape stitched together by three Co(II) ions, forming a barrel-shaped molecule with a central void. Because of the limited size of the $[\text{Co}_3\text{L}_2]$ cavity and the enantiopure nature of these enantiomeric complexes, both size-selective and enantioselective binding of guest molecules are observed. In the case of chiral guests, the interaction with paramagnetic Co(II) centers leads to an effective NMR enantiodifferentiation of the signals of guest molecules, even at host:guest ratios as low as 1:200. The tight binding of prochiral guest molecules such as ethanol and isopropanol within the chiral cavity results in the splitting of enantiotopic methylene and methyl signals. The *dc* magnetic data for $[\text{Co}_3\text{L}_2]$ are in accord with the presence of high-spin Co(II) ions, and the *ac* susceptibility data of this complex indicate field-induced single molecule magnet (SMM) behavior. In contrast to the reaction with Co(II), the reaction of the macrocyclic ligand **H₃L** with Ni(II) or Cu(II) salts results in the contraction of this [3 + 3] macrocycle and the formation of complexes of a smaller [2 + 2] macrocycle.

Słowa kluczowe

Ions, Ligands, Macrocycles, Magnetic properties, Molecular structure

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