Enantiopure Zn(II) and Cu(II) complexes of hexaazatetracyclomacrocycles based on cyclohexane moiety.

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Streszczenie

The template condensation of (1*R*,2*R*)- or (1*S*,2*S*)-1,2-diaminocyclohexane, N,N′-bis(3-aminopropyl)ethylenediamine and paraformaldehyde in the presence of zinc(II) chloride or copper(II) chloride, followed by the metathesis with hexafluorophosphate or tetraphenylborate, afforded chiral, enantiopure Zn(II) complexes (*R*,*R*)-[ZnL^{1}Cl](PF_6), (*S*,*S*)-[ZnL^{1}Cl](PF_6), (*R*,*R*)-[ZnL^{1}Cl](BPh_4) (*R*,*R*)-[CuL^{1}Cl](BPh_4) and (*S*,*S*)-[CuL^{1}Cl](BPh_4) of the chiral macrocyle L^1 (1,3,10,12,16,19-hexaazatetracyclo[17,3,1,1^{12,16},0^{4,9}]tetracosane). Similar condensation of (1*R*,2*R*)-1,2-diaminocyclohexane, N,N′-bis(2-aminoethyl)ethylenediamine and paraformaldehyde in the presence of zinc(II) chloride afforded the enantiopure complex (*R*,*R*)-[ZnL^{2}Cl](BPh_4) of the chiral macrocyle L^2 (1,3,10,12,15,18-hexaazatetracyclo[16,2,1,1^{12,15},0^{4,9}]docosane). The complexes have been characterised on the basis of NMR, CD and ESI MS spectra and elemental analyses. In these complexes the chirality at the carbon atoms of the cyclohexyl fragment determines the chirality at the coordinated nitrogen atoms. The X-ray crystal structures of the (*R*,*R*)-[ZnL^{1}Cl](PF_6), (*R*,*R*)-[ZnL^{1}Cl](BPh_4) and (*R*,*R*)-[CuL^{1}Cl](BPh_4) complexes indicate the untypical for this class of complexes (R,S,R,S) configuration at the coordinated nitrogen atoms. The 1,3-diazacyclohexane rings fused to the two six-membered chelate rings are both bend towards the apical chloride anion. The 2D NMR spectra confirm the presence of single conformation of the complex present in acetone solution, in particular the ROESY spectrum confirms the characteristic bending of the 1,3-diazacyclohexane rings towards the same side of the macrocyle, observed in the crystal structure. On the other hand the crystal structure of the (*R*,*R*)-[ZnL^{2}Cl](BPh_4) complex indicate more common (R,R,S,S) configuration at the coordinated nitrogen atoms, accompanied by bending of the two fused 1,3-diazacyclopentane rings towards the opposite sides of the macrocycle.

Słowa kluczowe

Chral ligands, macrocyclic complexes, zinc, copper, Amines, crystal structure