Dendrimers with a copper(I) bis(phenanthroline) core: synthesis, electronic properties, and kinetics.

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Streszczenie

The copper(I) bis(chelate) complex **Cu(L^0)$_2$** has been prepared from 2,9-diphenethyl-1,10-phenanthroline and Cu(CH$_3$CN)$_4$BF$_4$. Derivative **Cu(L^0)$_2$** has been characterized by NMR, UV−vis spectroscopy, and X-ray crystallography. Interestingly, owing to the presence of the ethylene linker, the interligand π−π stacking interactions between the phenyl rings and the phenanthroline subunits in **Cu(L^0)$_2$** do not induce significant distortions of the pseudotetrahedral symmetry around the Cu(I) center in the solid state or in solution. Following the synthesis of **Cu(L^0)$_2$**, dendrimers **Cu(L$^{1-4}$)$_2$** with a Cu(I) bis(2,9-diphenethyl-1,10-phenanthroline) core surrounded by Fréchet type dendritic branches have been prepared and the kinetics of their cyanide-assisted demetalation studied. Importantly, the surrounding dendritic wedges have no significant influence on the coordination geometry of the Cu(I) center, as deduced from their absorption spectra. Therefore, the variations of the rate constants only reflect changes resulting from the presence of the dendritic branches. The kinetics of the cyanide-mediated demetalation reaction indeed revealed that cyanide diffusion through the dendritic shell is slightly influenced by the size of the branches. Significant effects were observed in the kinetics when going from the third to the fourth generation and have been ascribed to changes in the lipophilicity around the metallic core as a result of dendritic encapsulation.

Słowa kluczowe

Cations, Dendrons, Kinetic parameters, Ligands, Phenyls

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