Cadmium (II), nickel(II), and zinc(II) complexes of vacataporphyrin: a variable annulene conformation inside a standard porphyrin frame.

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Streszczenie

5,10,15,20-Tetraaryl-21-vacataporphyrin, **1** (butadieneporphyrin, annulene−porphyrin hybrid), which contains a vacant space instead of heteroatomic bridge, gives diamagnetic zinc(II) **1**-ZnCl and cadmium(II) **1**-CdCl and paramagnetic nickel(II) **1**-NiCl complexes. A metal ion is bound in the macrocyclic cavity by three pyrrolic nitrogens. Coordination imposes a steric constraint on the geometry of the ligand and leads to two stereoisomers with a butadiene fragment oriented toward **1**-MCl-i or outward **1**-MCl-o of the macrocyclic center. **1**-CdCl-o, **1**-ZnCl-o, and the free base share a common ^{1}H NMR spectral pattern as the basic structural features of **1** are preserved after metal ion insertion. The ^{1}H NMR spectra of **1**-CdCl-i and **1**-ZnCl-i reflect a decrease of aromaticity accounted for by the inverted butadiene geometry. The proximity of the butadiene fragment to the metal ion induces direct couplings between the spin-active nucleus of the metal ($^{111/113}$Cd) and the adjacent ^{1}H nuclei of butadiene. The pattern of chemical shifts detected for isomeric **1**-NiCl-i and **1**-NiCl-o is typical for high-spin nickel(II) complexes of porphyrin analogues. Resonances 2,3-H of **1**-NiCl-o or **1**-NiCl-i present the chemical shift typical for the β-H pyrrolic position despite the vacancy in the location of nitrogen-21. Coordination of imidazole, methanol-d_4, acetonitrile-d_3, or chloride converts **1**-NiCl-i and **1**-NiCl-o into distinct species which contain two axial ligands: **1**-Ni(Im)$_2^+$; **1**-Ni(CD$_3$OD)$_2^+$; **1**-Ni(CD$_3$CN)$_2^+$; **1**-Ni(Cl)$_2^-$. The density functional theory (DFT) has been applied to model the molecular and electronic structure of feasible **1**-CdCl stereoisomers. The total energies calculated using the B3LYP/LANL2DZ approach demonstrate a very small energy difference (2.3 kcal/mol) between **1**-CdCl-o and **1**-CdCl-i stereoisomers consistent with their concurrent formation.