Cadmium(II) and zinc(II) complexes of *S*-confused thiaporphyrin.

Autorzy

Michał J. Chmielewski

Miłosz Pawlicki

Natasza Sprutta

Ludmiła Szterenberg

Lechosław Latos-Grażyński

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Streszczenie

The synthesis of 5,10,15,20-tetraphenyl-2-thia-21-carbaporphyrin [*S*-confused thiaporphyrin, (*SCPH*)H] was optimized. The formation of the phlorin was detected, which was saturated at the meso carbon adjacent to thiophene. Phlorin converted readily to (*SCPH*)H in the final oxidation process. Insertion of cadmium(II) and zinc(II) into *S*-confused thiaporphyrin yielded (*SCPH*)$Cd^{II}Cl$ and (*SCPH*)$Zn^{II}Cl$ complexes. The macrocycle acted as a monoanionic ligand. Three nitrogen atoms and the C(21)H fragment of the inverted thiophene occupied equatorial positions. The compensation of the metal charge required the apical chloride coordination. The characteristic C(21)H resonances of the inverted thiophene ring were located at 1.71 and 1.86 ppm in the ^{1}H NMR spectra of (*SCPH*)$Cd^{II}Cl$ and (*SCPH*)$Zn^{II}Cl$, respectively. The proximity of the thiophene fragment to the metal ion induced direct scalar couplings between the spin-active nucleus of the metal ($^{111/113}Cd$) and the adjacent ^{1}H nucleus (J_{CdH} = 8.97 Hz). The interaction of the metal ion and C(21)H also was reflected by significant changes of C(21) chemical shifts: (*SCPH*)$Zn^{II}Cl$, 92.9 ppm and (*SCPH*)$Cd^{II}Cl$, 88.2 ppm (free ligand (*SCPH*)H, 123.7 ppm). The X-ray analysis performed for (*SCPH*)$Cd^{II}Cl$ confirmed the side-on cadmium−thiophene interaction. The Cd···C(21) distance (2.615(7) Å) exceeded the typical Cd−C bond lengths, but was much shorter than the corresponding van der Waals contact. The density functional theory (DFT) was applied to model the molecular structures of zinc(II) and cadmium(II) complexes of *S*-confused thiaporphyrin. Subsequent AIM analysis demonstrated that the accumulation of electron density between the metal and thiophene, which is necessary to induce these couplings, was fairly small. A bond path linked the cadmium(II) ion to the proximate C(22) carbon of the thiophene.