Cadmium(II) and zinc(II) complexes of pyrrole-appended oxacarbaporphyrin: a side-on coordination mode of *O*-confused carbaporphyrin.

Autorzy

Miłosz Pawlicki

Lechosław Latos-Grażyński

Ludmiła Szterenberg

Rok wydania

2005

Czasopismo

Inorganic Chemistry

Numer woluminu

44

Strony

9779-9786

DOI

10.1021/ic051238x

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A pyrrole adduct of 5,20-diphenyl-10,15-di(*p*-tolyl)-2-oxa-21-carbaporphyrin [(H,pyr)*OC*P*H*]H_2 reacted with sodium ethanolate to yield 5,20-diphenyl-10,15-di(*p*-tolyl)-3-ethoxy-3-(2‘-pyrrol)-2-oxa-21-carbaporphyrin [(EtO,pyr)*OC*P*H*]H_2. Subsequently, “true” *O*-confused oxaporphyrin with a pendant pyrrole ring [(pyr)*OC*P*H*]H was formed by the addition of acid to [(EtO,pyr)*OC*P*H*]H_2, which triggered an ethanol elimination. In the course of this process, the tetrahedral−trigonal rearrangements originated at the C(3) atom. Insertion of zinc(II), cadmium(II), and nickel(II) into [(pyr)*OC*P*H*]H yielded [(pyr)*OC*P*H*]$Zn^{II}Cl$, [(pyr)*OC*P*H*]$Cd^{II}Cl$, and [(pyr)*OC*P]Ni^{II}. The formation of [(pyr)*OC*P]Ni^{II} was accompanied by the C(21)H dehydrogenation step. The nickel(II) ion of [(pyr)*OC*P]Ni^{II}, coordinated to a dianionic macrocyclic ligand, is bound by three pyrrolic nitrogens and a trigonally hybridized C(21) atom of the inverted furan. The pyrrole-appended *O*-confused carbaporphyrin acts as a monoanionic ligand toward zinc(II) and cadmium(II) cations. Three nitrogen atoms and the C(21)H fragment of the inverted furan occupy equatorial positions. In ^{1}H NMR spectra, the unique inner C(21)H resonances of the inverted furan ring are located at 0.15 ppm for [(pyr)*OC*P*H*]$Zn^{II}Cl$, and at 0.21 ppm for [(pyr)*OC*P*H*]$Cd^{II}Cl$. The proximity of the furan fragment to the metal ion induces direct scalar couplings between the spin-active nucleus of the metal ($^{111/113}Cd$) and the adjacent ^{1}H nucleus. The interaction of the metal ion and C(21)H was also reflected by significant changes in carbon chemical shifts ([(pyr)*OC*P*H*]$Zn^{II}Cl$, 78.3 ppm; [(pyr)*OC*PH]$Cd^{II}Cl$, 81.4 ppm; the free base, 101.3 ppm). The density functional theory (DFT) has been applied to model the molecular structures of zinc(II) and cadmium(II) complexes of *O*-confused oxaporphyrin with an appended pyrrole ring. The Cd···C(21) distance in the optimized structure exceeds the typical Cd−C bond lengths, but is much shorter than the corresponding van der Waals contact.

Słowa kluczowe

Coupling reactions, Ions, Macrocycles, Metals, pyrroles

Adres publiczny

https://doi.org/10.1021/ic051238x