

Cadmium(II) and nickel(II) complexes of benziporphyrins. A study of weak intramolecular metal-arene interactions.

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Rok wydania

2004

Czasopismo

Journal of the American
Chemical Society

Numer woluminu

126

Strony

4566-4580

DOI

10.1021/ja039384u

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Weak metal-arene interactions have been investigated in Zn, Cd, Hg, and Ni complexes of *meso*-tetraaryl *m*- and *p*-benziporphyrin (**1** and **2**) and of the new compound, *m*-benziporphodimethene (**3**). Compounds **1–3** incorporate the phenylene moiety into a macrocyclic structure so as to facilitate the interaction between the arene and coordinated metal ion. X-ray studies performed on Cd(II) and Ni(II) complexes show that the arene fragment approaches the ion at a distance much shorter than the sum of van der Waals radii. In chloronickel(II) *m*-benziporphyrin, a weak agostic bond is actually formed. In the NMR spectra of the Cd(II) and Hg(II) species, unusual $^1\text{H-M}$ and $^{13}\text{C-M}$ scalar couplings have been observed that are transmitted directly between the metal and the arene. DFT calculations performed for two Cd(II) species and subsequent AIM analysis show that the accumulation of electron density between the metal and arene necessary to induce these couplings is fairly small and the interaction is steric in nature. In the paramagnetic Ni(II) complexes of **1** and **3**, the agostic proton of the *m*-phenylene exhibits large downfield ^1H NMR shifts (386 and 208 ppm at 298 K, respectively). An agostic mechanism of spin density transfer is proposed to explain these shifts as resulting from electron donation from the CH bond to the metal. In chloronickel(II) *p*-benziporphyrin, the inner protons of the *p*-phenylene have a contrastingly small shift (0.0 ppm at 298 K), indicating that in this case the agostic interaction is inefficient, in agreement with the X-ray data.

Adres publiczny

<https://doi.org/10.1021/ja039384u>

Strona internetowa wydawcy

<https://www.acs.org/content/acs/en.html>

