Synthesis and characterization of transition metal complexes of dimeric N-confused porphyrin linked by an *o*-xylene fragment.

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Rok wydania

2009

Czasopismo

Inorganic Chemistry

Numer woluminu

48

Strony

432-445

DOI

10.1021/ic800591n

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Insertion of nickel(II), zinc, cadmium, or silver(III) into both macrocyclic crevices of 2,2′-*o*-xylene-bis(5,10,15,20-tetrakis(*p*-tolyl)-2-aza-21-carbaporphyrin) results in homometallic dimeric complexes which were isolated and characterized by NMR, UV−vis, mass spectrometry, and cyclic voltammetry. The ^{1}H NMR study of these systems at low temperatures (203−233 K) allowed determination of most stable conformers with respect to a rotational freedom around the xylene bridge. An unfolded conformation for the dicationic bis(silver(III)) complex was determined on the basis of 2D nuclear Overhauser effect spectrometry experimentation. A mixture of nonequally populated diastereomers is observed for bis(zinc) and bis(cadmium) complexes due to a possibility of two different orientations of the apical anionic ligands with respect to the bridge. In a reaction of 5,10,15,20-tetrakis(*p*-tolyl)-2-aza-21-carbaporphyrinato nickel(II) with 2-(*o*-bromoxylene)-5,10,15,20-tetrakis(*p*-tolyl)-2-aza-21-carbaporphyrin in the presence of a proton scavenger, two isomeric bis(N-confused porphyrin) complexes with one subunit “empty” and the other metalated by nickel(II) were obtained. In the product **10**, the *o*-xylene links external nitrogens of the subunits while product **11** consists of the xylene bridge between external nitrogen of the nonmetalated subunit and internal carbon of the fragment containing a nickel(II) ion. The products were characterized by mass spectrometry, UV−vis, NMR, and, in the case of complex **11**, also by X-ray crystallographic analysis (space group $P\bar{1}$, a =17.007(3), b = 18.130(3), c = 18.797(2) Å, α = 105.856(13)°, β = 107.447(13)°, γ = 98.818(15)°, V = 5141.1(15) Å^3, Z = 2). Insertion of zinc or silver(III) into an empty crevice of **10** resulted in heterometallic zinc−nickel(II) or silver(III)−nickel(II) complexes **12** or **13**, respectively, which were characterized by NMR, UV−vis, and cyclic voltammetry. The subunits in the bis(porphyrin) systems retain spectroscopic and redox properties typical for monomeric complexes.

Adres publiczny

https://doi.org/10.1021/ic800591n

Strona internetowa wydawcy

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