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The influence of deformation of the Zn-porphyrin macrocycle on its binding ability towards to small organic molecules of different nature

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Abstract

Using the method of spectrophotometric titration an axial coordination of small organic molecules by Zn(II)-porphyrins with different number of alkyl and aryl substituents on the periphery of the macrocycle have been studied in toluene. The processes of the Zn-5,15-diphenylporphyrin, Zn-5,10,15-triphenylporphyrin, Zn-5,10,15,20-tetraphenyl-porphyrin, Zn-2,3,7,8,12,13,17,18-octaethylporphyrin, Zn-5-phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin and Zn-2,3,7,8,12,13,17,18-5-octaethyl,10,15,20-tetraphenyl-porphyrin complexation with imidazole (L1), 1-methyl-imidazole (L2), propylamine (L3) and triethylenediamine (L4) have been investigated. The stability constants of the complexes have been calculated and found a good correspondence between the calculated values of the enthalpies of the ZnP-L complexes formation in the gas phase and the experimental thermodynamic data. By means of the methods of quantum-chemical calculations the degree of the porphyrin macrocycle distortion has been identified in connection with the introduction in the macrocycle of the alkyl and aryl functional groups. It was found that the distortion of the porphyrin macrocycle due to the simultaneous substitution of the meso-and β-position by the alkyl and aryl groups is very significant impact on the stability of the 1:1 (ZnP-L) and 1:2 (ZnP-L-ZnP) complexes between the porphyrins and the monodentate extra-ligands. It is shown that the distortion of the macrocycle core due to the *meso*-substitution leads to a reduction of excess positive charge on the Zn^{2+} cation and the appearance of "intramolecular" cavity in the macrocycle. As a result, the binding ability of the deformed porphyrins toward the axial ligands decreases due to a weaker Zn-L interaction, except for those cases when the geometric parameters of the ligand and the "cavity" are in a good correspondence. In this case, the resulting ZnP-L complexes are the supramolecular "guest-host" complexes formed according to the "nest" type.

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