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Spectrophotometric investigation of early lanthanide(III) porphyrin complexes

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Larger-sized metal ions are not able to coplanarly fit into the cavity of the porphyrin ring; they are located out of the ligand plane, resulting in out-of-plane (OOP or sitting-atop=SAT) complexes. OOP position promotes the formation of bis- or oligoporphyrins, so-called sandwich complexes. Lanthanide(III) ions offer good opportunities to fine tune the out-of-plane distances, utilizing the well-known lanthanide contraction. The UV-Vis absorption bands of SAT complexes represent redshift compared to the free-base ligand. SAT complexes can be used as photocatalysts in redox reactions, as photosensors in the medical science in luminescence imaging and as polymer diodes in cancer treatment. We investigated the reaction between the 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and early lanthanide(III) ions (La-Gd), as well as the effect of the ionic strength, the temperature and the potential axial ligands on these processes. The structures of different complexes were identified on the basis of their UV-Vis absorption spectra. The bidentate O-donor acetate and glycol, as well as the monodentate ethanol and chloride can enhance the coordination of the first porphyrin ligand, due to their axial effect, but they can hinder the connection of an additional porphyrin. In the presence of non-coordinating perchlorate anion, bisporphyrins can form, too. At lower temperatures, the lanthanide(III) ions were not able to coordinate into the cavity of the macrocycle, to the softer pyrrolic nitrogens, rather to the sulfonato groups, to the harder oxygens; resulting in the formation of the free-base ligands' tail-to-tail dimer. So the coordination position of metal ion can be influenced by temperature.

Biography

Melitta Patrícia Kiss got her MSc degree in Chemistry at University of Pannonia, Veszprém, Hungary. Now, she is a PhD student at the Department of General and Inorganic Chemistry at the same university. In her research work, she studies the formation of lanthanide porphyrin complexes from equilibrium and kinetic aspects since 6 years.

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