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Kinetic investigation of the formation of neodymium(III) porphyrin complexes

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Lanthanide(III) ions offer good opportunities to examine the special properties of out-of-plane (OOP or sitting-atop=SAT) metalloporphyrins, utilizing the well-known lanthanide contraction. Their insertion into the coordination cavity of porphyrin ligand is a slow and complicated process in aqueous solution, originating from the high stability of their aqua complexes and oligomer forms. As a consequence of the lanthanide(III) ions' Pearson-type hard character, they can coordinate rather to the peripheral substituent of porphyrin, if it possesses similarly hard O-donor atom (e.g. carboxy-, sulfonato-phenyl). Only under thermodynamic control, at higher temperatures, can coordinate the metal ion also, or rather, to the four pyrrolic nitrogens; resulting in the formation of typical metalloporphyrin complexes. 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 the neodymium(III) ion, 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 don't dissociate from the metal ion, only monoporphyrin can form. 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, 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 Patricia 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 7 years.

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