Intramolecular rotation of iron (II) dithiaethyneporphyrin double-decker complex: ^{1}H NMR studies.

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Streszczenie

The paramagnetic six-coordinated iron(II) 3,8,13,18-tetraaryldithiaethyneporphyrin $(ES_2P)_2Fe^{II}$ complexes of the double-decker type have been synthesized using iron pentacarbonyl as the metal source. The complex contains two porphyrinic macrocycles coordinated to the iron(II) in the sandwich-like fashion as determined by ^{1}H NMR. The ^{1}H NMR spectra of $(ES_2P)_2Fe^{II}$ have been examined in detail in the 180 − 366 K temperature range. Functional group assignments based on the selective deuteration, analysis of T_1 relaxation times and the NOESY experiment have been made at 313 and 210 K. The variable temperature ^{1}H NMR studies allowed to elucidate the dynamic behavior of $(ES_2P)_2Fe^{II}$ which involves rotation of dithiaethyneporphyrin rings around the metal ion. To account for the observed conformational rearrangements a cube, a square antiprism or a distorted triangular dodecahedron structure of $(ES_2P)_2Fe^{II}$ defined by the mutual orientation of two macrocyclic ligands have been considered. The six vertexes of a polyhedron are occupied by two pyrrolic nitrogens and four sulfur atoms, while two remaining vertexes are filled with two ethyne moieties. The dynamic rearrangements of $(ES_2P)_2Fe^{II}$ involve two enantiomeric couples of four fundamental staggered rotamers. The fast dynamic process engaging rotation of two dithiaethyneporphyrin ligands has been detected at 298 K. At low temperature range two rotamers have been identified as they presented the individual spectroscopic patterns. Considering the multiplicity of resonances the fast rotational oscillation involving one enantiomeric pair has been observed at 210 K, while all other processes are slow. The exchange between diastereomers has been confirmed at 210 K as the EXSY correlations linking diastereomeric resonances have been detected at the NOESY map.

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