Spectrochemical and electrochemical studies of 21-thiatetra(*p*-tolyl)porphyrin and its copper(II) complexes.

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Streszczenie

Electrochemistry, NMR, ESR and UV-Vis spectroscopy of 21-thiatetra(*p*-tolyl)porphyrin (STpTPH) and respective copper(II) (21-tiatetra(*p*-tolyl)porphyrin) X Cu(STpTP)X (X=Cl^-, Br^-, HCO_3^-, ClO_4^-, PPh_3) complexes have been investigated.Monothiaporphyrin is an analogue of widely studied tetraphenylporphyrin, where one of the pyrrole rings has been replaced by a thiophene moiety. The impact of the replacement and the coordinating abilities of thiophene sulfur have been studied. STpTPH undergoes a two step proton addition in dichloromethane. Mono- and dication formations result in distorting the planar thiaporphyrin structure as confirmed by NMR and UV-Vis data. The electronic spectra of Cu(STpTP)X have a similar pattern to the monocation form but the pronounced dependence of the band positions on the ligand character has been established. An ESR spectrum pattern is typical for quasi-tetragonal Cu(II)systems. Parallel features show well resolved seven lines associated with coordination of three nearly equivalent nitrogens. The ESR parameters, particularly hyperfine coupling constant *A*, have been correlated with the geometry of Cu(II) porphyrins or porphyrin- like ligands. The influence of the axial ligand on the ESR parameters has also been discussed. Cyclic voltammetry studies show that Cu(STpTP)X exhibits a well defined Cu(II)/Cu(I) reduction ($E_{1/2}$= −0.14 ±0.03 V depending on the axial ligand), reported previously only for Cu(II) N-substituted porphyrins but not for Cu(II) porphyrins. The second reduction step results in demetalation. The physicochemcial properties of Cu(STpTP)X are considerably different from Cu(TTP) and closely resemble those of Cu(II) N-substituted porphyrin. Comparison between the electrochemical and spectroscopical properties has been discussed in terms of the general stability of a Cu(II)-axial ligand bond.

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