

The influence of the metal-ligand charge transfer effects on the structural stability and the strength of the spin-orbit coupling in Ni(II)-based metal-ligand complexes

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The structural stability, charge transfer effects and the strength of the spin-orbit couplings in different Ni(II)-ligand complexes with square-pyramidal and octahedral coordination have been studied at M06/def2-TZVP level of theory. Accordingly, two different, porphyrin- and diketo-pyrphyrin-based four-coordination macrocycles as planar ligands as well as pyridine, pyrrole and mesylate anion molecular groups as vertical ligands were considered in order to build the square-pyramidal and octahedral coordination configurations. For each molecular system the identification of equilibrium geometries and the intersystem crossing (the minimum energy crossing point) between the potential energy surfaces of the singlet and triplet spin states is followed by computing the spin-orbit couplings between the two spin states. Structures, based on the diketo-pyrphyrin macrocycle as planar ligand, show stronger five- and six-coordination organometallic complexes due to the extra electrostatic interaction between the positively charged central metal cation and the negatively charged vertical ligands (See at Figure 1 the electrostatic potential map of the two macrocycles). The results also show that the magnitude of the spin-orbit coupling is strongly influenced by the atomic positions of deprotonations of the ligands and implicitly the direction of the charge transfer between the ligand and the central metal ion.

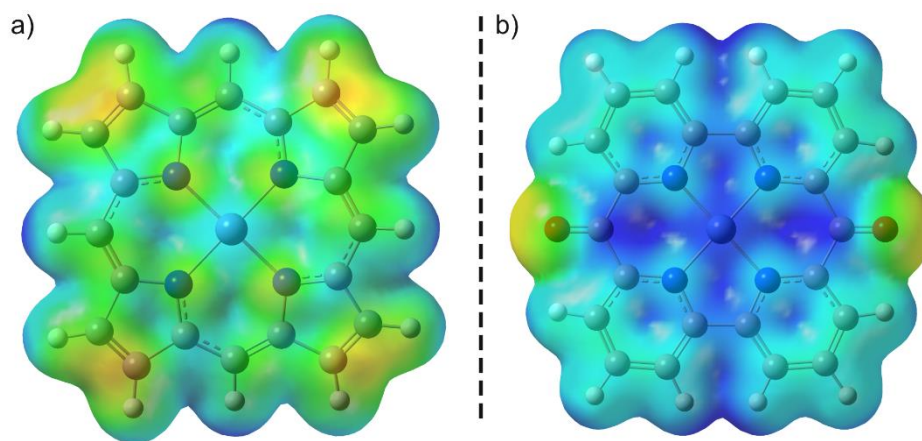


Figure 1. The two maps of the electrostatic potential ($e_{\min}=0.1e$ and $e_{\max}=0.3e$) for the Ni(II)²⁺-porphyrin²⁻ (a) and of Ni(II)²⁺-diketo-pyrphyrin (b) complexes.