

DFT study of spin state preferences in substituted polypyrazolylborato transition metal complexes

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Density Functional Theory (DFT) at OPBE/TZP level of theory, that proved to be accurate for spin states, was used to analyse and explain spin state energetics of first-row transition metals (Mn^{II} , Fe^{II} , Co^{II} ; Cr^{III} , Mn^{III} , Fe^{III} , Co^{III} ; Mn^{IV}) in substituted polypyrazolylborato complexes. We explored the effects of substitutions at the 3 and 5 positions of the pyrazolyl rings, as well as the influence of Jahn–Teller (JT) distortions on spin-state switching.

Although the stabilizations due to JT distortion are sometimes substantial, this does not lead to switching of the spin ground-state. Detailed analysis indicated that electron withdrawing groups in position 5 enhance π -acceptor properties of the ligands, while electron donating groups intensify their π -donor properties, and thus affect only the energy separation but not the spin ground state. On the other hand, the substituents in position 3 are mainly demonstrating the steric influence, and thus always tend to favor the longer metal-ligand bonds and high spin state. These findings pave the way for a rational design of transition-metal compounds with spin-crossover properties.