A novel o-vanillin Fe(III) complex catalytically active in C–H oxidation: exploring the magnetic exchange interactions and spectroscopic properties with different DFT functionals.

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Streszczenie

The novel complex [$Fe^{III}Cl(L)_2(H_2O)$] (**1**) was synthesized by interaction of iron(III) chloride with ethanol solution of *o*-vanillin (HL) and characterized by IR, UV/Vis spectroscopy, thermogravimetry and single crystal X-ray diffraction analysis. The molecules of **1** in the solid state are joined into supramolecular dimeric units, where a set of strong hydrogen bonds predefines the structure of the dimer according to the "key-lock" principle. From the Hirshfield surface analysis the contribution of π···π stacking to the overall stabilization of the dimer was found to be negligible. Broken symmetry DFT calculations suggested the presence of long-range antiferromagnetic interactions (J = −0.12 cm^{-1} for $H = -JS_1S_2$ formalism) occurring through the Fe–O···O–Fe pathway, as evidenced by the studies of the model dimers where the water molecules were substituted by acetonitrile and acetone ones. The benchmark studies using a set of literature examples and various DFT functionals revealed the hybrid-GGA B3LYP as the best one for prediction of $Fe^{III}\cdots Fe^{III}$ antiferromagnetic exchange couplings of small magnitude. Magnetic susceptibility measurements confirmed antiferromagnetic coupling between the metal atoms in **1** with a coupling constant of −0.35 cm^{-1}. Catalytic studies demonstrated that **1** acts as an efficient catalyst in the oxidation of cyclohexane with hydrogen peroxide in the presence of nitric acid promoter and under mild conditions (yield up to 37% based on the substrate), while *tert*-butylhydroperoxide (TBHP) and *m*-chloroperoxybenzoic acid (*m*-CPBA) as oxidants exhibit less efficiency. Combined UV/TDDFT studies evidence the structural rearrangement of **1** in acetonitrile with the formation of [$Fe^{III}Cl(L)_2(CH_3CN)$] species. The TDDFT benchmark using nine common DFT functionals and two model compounds (*o*-vanillin and $[Fe^{III}(H_2O)_6]^{3+}$ ion) support the hybrid meta-GGA M06-2X functional as the one most correctly predicting the excited state structure for the Fe(III) complexes, under the conditions studied.

Adres publiczny

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