

Calculating the structures and NMR chemical shifts of octahedral platinum and iridium complexes: calibration of DFT methods

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Abstract:

A methodology for optimizing the geometry and calculating the NMR shielding constants is calibrated for octahedral complexes of Pt(IV) and Ir(III) with modified nucleic acid bases. The performance of seven different functionals (BLYP, B3LYP, BHLYP, BP86, TPSS, PBE and PBE0) in optimizing the geometry of transition-metal complexes is evaluated using supramolecular clusters derived from X-ray data, as well as the effect of the basis set and dispersion correction. The PBE0/def2-TZVPP approach provides excellent results and it is used in subsequent step to optimize the geometry of single molecules for the calculation of the NMR shielding constants. In order to account for relativistic shielding contribution from heavy atom, the two-component zeroth-order relativistic approximation (SO-ZORA) is used for NMR shielding calculations. Additionally, the amount of exact exchange in functional (PBE0) is calibrated vs. experimental results. The influence of incorrect structural parameters to NMR chemical shift is illustrated on the amount of exact exchange required to obtain the correct value.