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Computational study of standard reduction potential of osmium(III) complexes

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Osmium (Os) complexes have attracted great interest due to their large number of applications, considering the anticancer applications of Os(III) complexes, the reduction potential is an important property to be evaluated, since the potential mechanism of action of these complexes involves reduction to Os(II)[1]. The present study aims to build a computational protocol for predicting the standard reduction potential (ε^0)[2] of Os(III/II) complexes using the new light atoms basis sets nqtcm-VDZP. Initially, the redox system $[Os(NH_3)_6]^{+3/+2}$, which has experimental data for the ε^0 of -0,749 V in relation to the standard hydrogen electrode (SHE) was selected. Computational protocols assessing the role of the solvent effects, DFT functionals, ligands basis sets (LBS), and osmium basis sets (OSBS) were proposed. The calculations were performed in GAUSSIAN 16 Rev. C. 01 program. The calculated results showed that the inclusion of solvent effects and the LBS presented a fundamental role in predicting the ε^0, while OSBS played an important role when LBS=def2-SVP was considered. The best computational protocols mPW1LYP/def2-SVP/nqtcm-VDZP//IEF-PCM(Bondi) and BLYP/def2-TZVPP/def2-SVP//IEF-PCM(Bondi) presented a relative deviation (RD) in relation to the experimental value of 0.4% and 0.1%, respectively. Subsequently, the best computational protocols will be applied in a set of 40 osmium complexes, that presented experimental data of ε^0 available in the literature, aiming to validate the protocols.

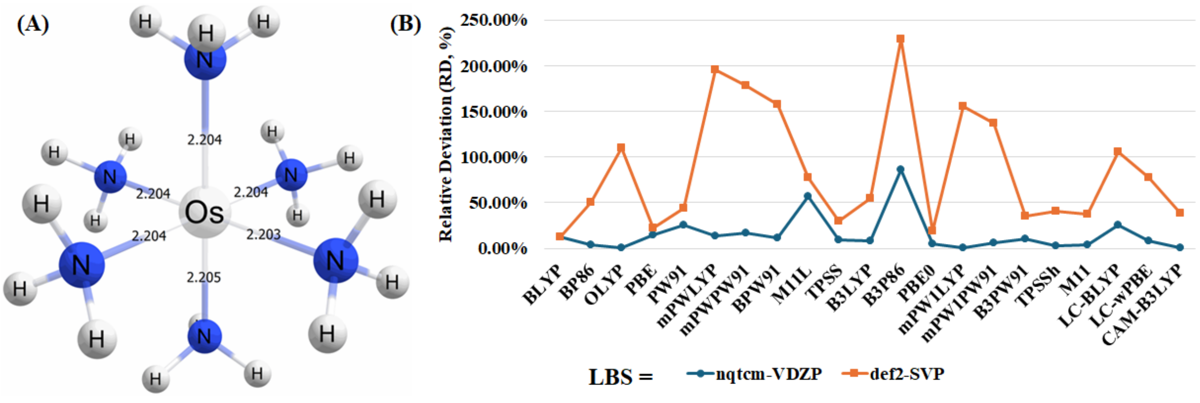

Figure 1. (A) $[Os(NH_3)_6]^{+3/+2}$ redox system considered in the construction of computational protocol; (B) Calculated relative deviation for the ε^0 at DFT-Functional/def2-SVP(Os)/LBS//IEF-PCM(Bondi) level.

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