Theoretical insights on the unexpected lability of Ru(III)(phtpy)Cl3: ligand-metal interactions through the lenses of DFT and TD-DFT

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Even though Ruthenium(III) complexes are widely known for being stable and inert, experiments carried out by Benavides et al. provided evidence for the lability of the Ru(III)(phtpy)Cl3 complex[1], a well-established synthetic precursor of water-splitting catalysts. By monitoring changes in the complex UV-vis spectrum during reduction and subsequent oxidation, they were able to show the dissociation of the phenyl-terpyridine ligand from the Ru(III) complex. At the same time, the Ru(II)-phtpy interaction is strong enough to form the [Ru(II)(phtpy)2]2+ specimen in solution, regardless of the solvent.

In this work, we apply Density Functional Theory to study the ligand dissociation process, in order to shed light on the nature of the phenyl-terpyridine lability in this complex. Gibbs free energies of ligand release and formation of [Ru(II)(phtpy)2]2+ were computed at the ωB97XD/def2-TZVP level of theory. Natural Bond Orbital (NBO) and Quantum Theory of Atoms in Molecules (QTAIM) analyses were performed in order to understand the covalent/ionic nature of Ru-phtpy bonds, making comparisons between the Ru(II) and Ru(III) species. Ligand orbitals and π-backbonding effects were also compared. MLCT bands and their bathochromic shifts were calculated through Time-Dependent Density Functional Theory calculations.

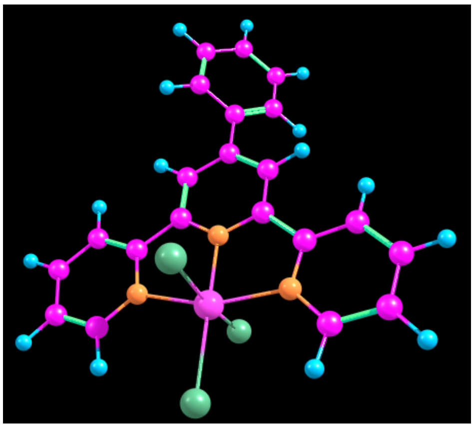

Figure 1. Ru(III)(phtpy)Cl3 complex visualized with Chemcraft.

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References

[1] P. A. Benavides, T. Matias, K. Araki, Dalton Trans, **46**, 15567-15572 (2017).