

Understanding the molybdenum oxodiperoxo complexes reactivities through of the IR and ^{17}O -NMR DFT calculations

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INTRODUCTION

Molybdenum oxodiperoxo complexes of type $[\text{MoO}(\text{O}_2)_2\text{L}_1\text{L}_2]$, $\text{L}_1 =$ pyrazole, N-oxo of pyridine, $\text{L}_2 = \text{H}_2\text{O}$, silica, are used in selective sulfide oxidation reactions, whereas active species transfer oxygen and it will be regenerated later. Albeit, there are some questions about how their reactivities are affected by different ligands (L_1 and/or L_2) effects. Quantum chemical (QC) methods can be useful to understand the behavior in oxygen transfer reactions, also in proposing mechanisms, which can explain the observed chemoselectivity and stereoselectivity, e.g., in case of chiral sulfoxides formation. In order to elucidate the mechanism of oxidation reactions, some NMR and IR spectroscopic properties were evaluated. The following complexes were chosen $[\text{Mo}(\text{O}_2)_2\text{L}_1\text{L}_2]$, with $\text{L}_1 =$ HMPA, OPH_3 , N-oxo of pyridine, pyrazole, and $\text{L}_2 =$ none or H_2O .

METHODS

All calculations were performed with Gaussian 09 program (Rev. D.01). We applied four DFT functionals in this study: B3LYP, PBE1PBE, WB97XD and M062X. These functionals were used associated with the 6-31G(d) basis set for all atoms, except LanL2DZ applied for molybdenum (also effective core potential). For ^{17}O -NMR chemical shifts $\delta(^{17}\text{O})$, the DFT/LANL2DZ/IGLO3 was applied for all systems.

RESULTS AND DISCUSSION

The vibrational analysis showed invariance in the Mo-O(oxo) stretch (oxo) between the different ligands in the hexacoordinated (with $\text{L}_2 =$ none) and heptacoordinated complexes. In particular, for the complex $[\text{MoO}(\text{O}_2)_2(\text{pyrazole})(\text{H}_2\text{O})]$, our results are in good agreement with the experimental frequencies (errors $\sim 10\%$ - B3LYP).¹ For other functionals, the errors are higher. The order errors associated with vibrational frequencies values are: B3LYP < PBE1PBE < WB97XD < M062X, in special, for stretching modes

For ^{17}O -NMR chemical shifts suggest that the oxygen atom present in the oxo group is less susceptible to the different ligands than peroxo group. For oxygen atoms in peroxo group, $\delta(^{17}\text{O})$ shifts decrease in those oxygen that are in the same side of ligand (*syn*). This result is explained in terms of increased electron density due to the coordination ligands.

The presence of another ligand heptacoordinated complexes ligands enhances the chemical shifts for oxygen (oxo) in relation to the hexacoordinated complexes. This result shows that the introduction of one more ligand at the axial position decreases the electron density and thus shielding of those oxygen atoms. In particular, ^{17}O -NMR chemical shifts $\delta(^{17}\text{O})$ of the oxygen atom (oxo) in the complex $[\text{MoO}(\text{O}_2)_2(\text{HMPA})]$ is 916ppm (B3LYP), whereas the experimental value (obtained by Postel *et al.*²) is 863ppm, a 6.1% error, suggesting B3LYP is the most suitable DFT functional to apply in order to obtain this kind of NMR properties.

CONCLUSIONS

The calculated vibrational frequencies of $[\text{MoO}(\text{O}_2)_2(\text{pyrazole})(\text{H}_2\text{O})]$ were used to assign the experimental vibrational spectrum. The spectroscopic analysis shows correlation of the vibrational frequencies and chemical shifts with the strengths of the ligands and the reactivity of the complexes. The oxo group is less susceptible to the presence of different ligands than the peroxo oxygen atoms.

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