

Influence of DFT functionals in the molecular structure and thermodynamic properties of the molybdenum oxodiperoxo complexes.

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INTRODUCTION

Metal transition oxodiperoxo complexes of type $[MO(O_2)_2L_1L_2]$, $M = Mo$ e W , $L_1 =$ pyrazole, N-oxo of pyridine, $L_2 = H_2O$, silica, are used in several selective oxidation reaction, e.g., of olefins and sulfides, in which the active species transfer oxygen and after can be regenerated, but these active species are not well established yet.

The use of quantum chemical computational methods to obtain the molecular and electronic structures of complexes of these kind and similar ones should be useful in understanding their behavior in oxygen transfer reactions and in proposing mechanisms which can also explain the observed chemoselectivity. For this purpose, in this work, ground state molecular and electronic structure calculations of some compounds with the general formula $[MoO(O_2)_2L_1L_2]$ with $L_1 =$ none, HMPA, OPH_3 , N-oxo of pyridine, pyrazole, silica, and $L_2 =$ none or H_2O .

METHODS

We have calculated all molecular and electronic structures of these complexes considered in this work and all critical points of the potential energy surface have been characterized by Hessian matrix. 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 the LanL2DZ (basis set and effective core potential) applied for molybdenum.

RESULTS AND DISCUSSION

In terms of geometry parameters, functionals B3LYP, M062X and PBE1PBE presents same Mo-L bond distances. In addition, these values keep the same for heptacoordinated complexes with water in the axial position. These results corroborate with the experimental observation that

in this position, the ligand has a weaker coordination. Effects such inclusion interval correction and dispersion correction (via functional WB97XD) are not essential for describing these structures. Instead, they overestimate interactions. Nevertheless, B3LYP functional presented the closest results in comparison to X-ray crystallography¹ results. Using B3LYP, it easier to keep the Cs-asymmetric structure of pentacoordinated moieties, since previous experimental studies have reported that this symmetry is substantially maintained even in the presence of ligands L_1 and/or L_2 . However, for heptacoordinated complexes with the water ligand in the axial position, the bond distance Mo-OH₂ is not well described, since its coordinate at this position is weaker. This discrepancy between the calculated and experimental results was previously attributed,¹ at least partially, solid-state effects and these differences become larger when the ligand is weaker. Unlikely the results obtained for the geometrical parameters, it seems that the inclusion of dispersion and correction range are important for achieving stabilization energies results obtained for by other groups. However, it is needed further investigation to acquire quantitative information.

CONCLUSIONS

The results show that the methodology is suitable for the study of molybdenum oxodiperoxo complexes, since the values of the geometric parameters of the studied complexes are in good agreement with literature data. Our results may help in the investigation of their reactivities and chemoselectivities in order to determine the mechanisms involved in such reactions.

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