

MN-OXO PORPHYRINS: SPIN STATE ENERGETICS AND OXYL CHARACTER AS KEY FACTORS TO REACTIVITY

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The electronic structure and relative energy of important electromeric states in manganese-oxo porphyrins MnO(L)^+ (L being P=porphyrinato or PF_4 =meso-tetrafluoroporphyrinato) have been investigated with correlated ab initio methods (CASPT2, RASPT2), focusing on their possible role in multi-state reactivity patterns in oxygen transfer (OAT) reactions. Due to the lack of oxyl character, the $\text{Mn}^{\text{V}} \ ^1\text{A}_1$ ground state is unreactive. OAT reactions should therefore proceed through thermally accessible triplet and quintet states that have a more pronounced oxyl character. Two states have been identified as possible candidates: a Mn^{V} triplet state and a $\text{Mn}^{\text{IV}}\text{O(L}^{\cdot}\text{a}_{2u})^+$ quintet state.

The results were also used as a benchmark for the description of excited state energetics and Mn–O oxyl character with a wide range of GGA and hybrid density functionals. With the latter functionals both the $\text{Mn}^{\text{V}} \rightarrow \text{Mn}^{\text{IV}}$ promotion energy and the diradical character of the Mn–O π bond in the Mn^{V} triplet state are found to be extremely dependent on the contribution of exact exchange. For this reason, GGA functionals are to be preferred for further reactivity studies.