Benchmarking dioxygen complexes: coupled cluster and density functional theory

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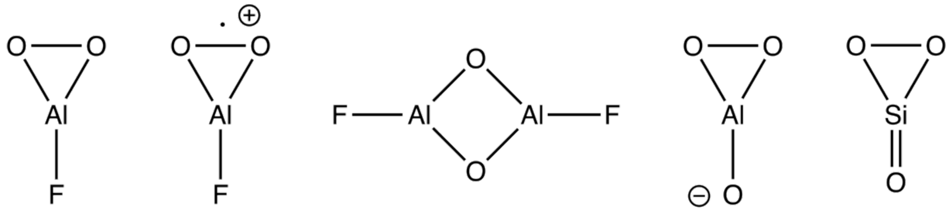
ABSTRACT

Dioxygen can coordinate to first-row transition metals (in different oxidation and spin states) with several protonation states, and hapticity, leading to e.g. peroxo, superoxo, hydroperoxo or bis-μ-oxo species. Although crystal structures exist for all of these species, the corresponding complexes are too large for treatment by accurate wavefunction methods like CCSD(T) with large basis sets (aug-cc-pVQZ or better). This prevents the systematic validation of more efficient yet less accurate quantum-chemistry methods, e.g. based on density functional theory, leading to uncertainty about the reliability and appropriateness of different density functionals for this metal-dioxygen chemistry. Here we report[1] a benchmark study on five dioxygen complexes (see Figure 1), for which many DFT functionals are less accurate than usual.



1 ^{2}**2** **3** **4** **5**

Figure 1. Metal-dioxygen complexes studied

Lessons learned from the benchmark study are applied in the design of new density functional approximations.

References

[1] Swart, M.; Reimann, M. A benchmark study of dioxygen complexes based on coupled cluster and density functional theory. *SciPost:Chem* **2024**, *submitted*.