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Cr(V)-oxo and Cr(IV)-peroxo complexes can be made from a surprisingly labile Cr(III) complex

David P. de Sousa, Jonas Sundberg, Christine J. McKenzie
Department of Physics, Chemistry and Pharmacy. University of Southern Denmark. desousa@sdu.dk

Early first row metal-oxygen adducts are useful as mimics of their more elusive iron- and manganese counterparts [1,2]. We have exploited the reactivity of the coordinatively saturated, but highly strained, [CrIII(tpena)]2+ to react it with organic oxidants:

\[ \text{[CrIII(tpena)]}^2+ + \text{H}_2\text{O}_2 \rightarrow \text{[CrIV(\eta_2-O_2)(tpenaH)]}^2+ \]

[CrIII(tpena)]2+  \[ \rightarrow \]
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\[ \rightarrow \]
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Crystal Trapping of a Cr(IV)-Peroxo Intermediate

When [CrIII(tpena)]2+ is exposed to 33% aqueous H2O2, a moderate O2 gas production due to H2O2 disproportionation is observed. [CrIV(\eta_2-O_2)(tpenaH)][ClO4]2·4H2O crystallizes under these working conditions. Because excess substrate is trapped in channels in the crystals we believe we have crystallized a catalytically competent intermediate.

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} \]

\[ \text{H}_2\text{O}_2 \text{ and } \text{ClO}_4^- \text{ removed in-silico. Coordinated peroxides depicted as spacefills.} \]

Catalytic Sulfoxidations with Cr(V)-Oxo

[CrIII(tpena)]2+ catalyzes the monooxygenation of thioanisole and diphenyl sulfide using PhIO as terminal oxidant with TONs up to 100.

The proposed [CrIV(\eta_2-O_2)(tpena)]2+ intermediate with a characteristic d1 EPR spectrum and an intense ESI-MS signal at m/z = 229.1 can be detected by reacting [CrIII(tpena)]2+ with excess PhIO when no substrates are present.


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