

High resolution crystal structures of two of the intermediates in the myoglobin peroxide reaction.

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The biological conversions of O₂ and peroxides to water as well as certain incorporations of oxygen atoms into small organic molecules can be catalyzed by metal-ions in different clusters or cofactors. The catalytic cycles of these reactions pass through similar metal-based complexes. We have previously reported high resolution structure (1.35 Å) of the myoglobin compound II intermediate at pH 5.2 [1], and the state has been confirmed by microspectrophotometry in the pH range 5.2 to 8.7. These structures show a relatively long Fe...O distance of 1.9 Å compared to the 1.6 Å distance of the commonly proposed oxo-ferryl [Fe^{IV}=O] species. This long Fe...O bond is supported by the newly observed resonance Raman Fe-¹⁸O mode below 700 cm⁻¹. Quantum refinement best fit either a Fe^{III}OH⁻ or a Fe^{IV}OH state [2], while the Mössbauer spectroscopy indicates a Fe^{IV}-state. From compound II we were able to generate compound III (an oxy-complex). This intermediate was reduced by the synchrotron radiation giving an equivalent of compound 0 (Fe^{III}-peroxide) for which we have solved the 1.25 Å resolution structure. The different states were confirmed by microspectrophotometry, which also indicated that the normal high spin ferric state can be reduced by the synchrotron radiation.

- [1] Hersleth, H.-P., Dalhus, B., Görbitz, C.H. and Andersson, K.K. (2002) *J. Biol. Inorg. Chem.* **7**, 299-304.
[2] Nilsson, K., Hersleth, H.-P., Rod, T.H., Andersson, K.K. and Ryde, U. (2004) *Biophys. J.* **87**, 3437-3447.

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