Reversible O–O Bond Cleavage and Reformation of a Peroxo Group of a Peroxocarbonate Ligand of an Iron(III) Complex

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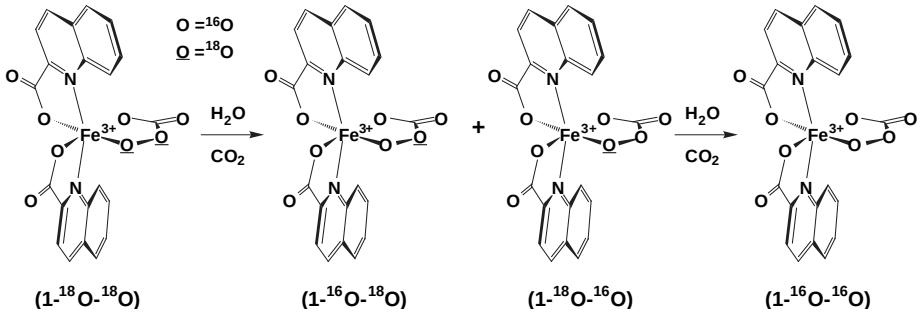
Reversible cleavage and formation of the peroxo O–O bond catalyzed by transition metal centers is of great importance for understanding the reaction mechanisms of dioxygen activating and dioxygen evolving metalloproteins such as methane monooxygenase and photosystem II. Herein, we report evidence for a reversible cleavage and formation of the peroxo O–O bond of a mononuclear peroxocarbonate iron(III) complex $[Fe(qn)_2(O_2C(O)O)]^-$ (**1**), where Hqn = quinaldic acid.

Complex **1** is stable at –40 ℃ in acetonitrile, whereas it decomposes at 20℃. Thermal decomposition of an ^{18}O-labeled complex $[Fe(qn)_2(^{18}O–^{18}O(O)O)]^-$ (**1-^{18}O–^{18}O**) at 20℃ in acetonitrile was investigated by resonance Raman and ESI-MS spectroscopy. The $^{18}O–^{18}O$ of the peroxocarboante ligand is converted through $^{18}O–^{16}OC(O)O$ and $^{16}O–^{18}OC(O)O$ to $^{16}O–^{16}OC(O)O$ during thermal decomposition as shown in the following scheme.



The results suggest that the reversible O–O bond cleavage and formation process of the peroxo moiety of the peroxocarbonate group includes the formation of a high-valent ion-oxo species (Fe^{IV}=O or Fe^{V}=O), where the conversion of **1-^{18}O–^{18}O** into **1-^{16}O–^{16}O** proceeds by stepwise through the mixture of 16/18 peroxo species **1-^{18}O–^{16}O** and **1-^{16}O–^{18}O**.