Oxygenation of Nucleosides by Peroxide Adduct of Binuclear Iron(III) Complex with a μ-Oxo Bridge

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The (μ-oxo)(μ-carbonato)diiron(III) complex with H_2(tfda) (H_2(tfda) = 2-aminomethyltetrahydrofuran-N,N-diacetic acid) exhibited high activity for hydroxylation of 2′-deoxyguanosine in the presence of hydrogen peroxide, giving 8-hydroxydeoxyguanosine, but its hydroxylation activity towards other nucleosides such as 2′-deoxyadenosine, adenosine or thymidine was found negligible. In the case of the Fe(III)-(eda) complex (H_2(eda) = 2-methoxyethylamine-N,N-diacetic acid), hydroxylation occurred mainly at the sugar site, converting 2′-deoxyguanosine to guanosine. Based on the spectroscopic and structural properties of these iron(III) compounds, it seems most likely that an intrinsic active species for hydroxylation should be an electrophilic peroxide adduct of the (μ-oxo)diiron(III) core with η^1-coordination mode, while the contribution of OH· to the hydroxylation reaction of nucleosides is ruled out.