Unsymmetrical Dinuclear [Fe^{III}(μ-OH)M^{II}] (M^{II} = Zn, Cu) Complexes as Artificial Metallohydrolases

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In developing dinuclear artificial phosphohydrolytic systems, with a biomimetic approach, some characteristics must be followed such as metal-metal distance, orientation and dissociation constants of metal coordinated water molecules at pH values near to neutrality. Furthermore, since in dinuclear metalloenzymes the two metal centers usually reside in chemically distinct environments, even in homodinuclear species, the use of unsymmetrical dinucleating ligands is also of crucial importance. As part of our effort to obtaining structural and functional models for metalloenzymes, we present here the X-structures and some physico-chemical properties of the $[L(OH_2)Fe^{III}(\mu\text{-}OH)Zn^{II}]^{2+}$ (**1**) and $[L(OH)Fe^{III}(\mu\text{-}OH)Cu^{II}]^{+}$ (**2**) complexes (L= 2-bis[{(2-pyridylmethyl)-aminomethyl}-6-{(2-hydroxybenzyl)(2-pyridylmethyl)}-aminomethyl]-4-methyl-phenol) in which the Fe$^{III}\cdots$M^{II} are ~ 3.0 Å apart and contain terminally coordinated Fe^{III}-OH/OH_2 molecules. Detailed kinetic studies for the hydrolysis of the model substrates bis(2,4-dinitrophenyl) phosphate (2,4-BDNPP) and diethyl 2,4-dinitrophenyl phosphate (DEDNP) promoted by **1** and **2** and their interaction with plasmid DNA will also be presented. The interaction of **1** and **2** with DNA is of interest since the complexes show a decrease in the dissociation constants for coordinated water molecules producing good nucleophiles at neutral pH. A plausible mechanism based on intramolecular Fe^{III}-OH attack on the M^{II}-coordinated phosphate is proposed for (**1**) and (**2**).

Complex **1**