UNDERSTANDING THE EFFECT OF INTERNAL ELECTROSTATIC FIELDS CREATED BY ALKALINE EARTH METAL IONS POISED OVER SECONDARY COORDINATION SPHERE OF MOLECULAR IRON COMPLEXES

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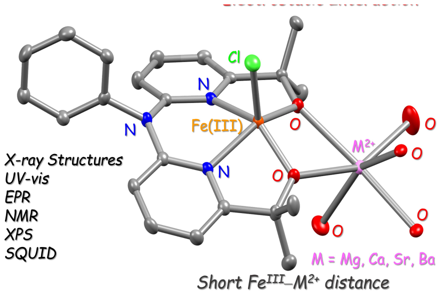
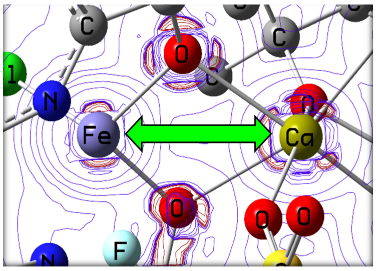
Understanding the effect of the local electrical field around the reaction centre in enzymes and molecular catalysis is a burgeoning research interest. It has been recognized that such a field can alter the stability of reaction intermediates, transition states, and product selectivity. [1,2] Herein, we explored the electrostatic field exerted by the alkaline earth metal ions (M^{2+}= Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) around iron in a Fe^{III}(Cl) complex (**1**) by experimental and computational investigations. M^{2+} coordinated dinuclear Fe^{III}(Cl) complexes (1_2M) were synthesized and characterized by X-ray crystallography and different spectroscopic techniques. X-ray structure of the 1_2M complexes revealed very short Fe–M distances, close to the theoretical distance expected for a high-spin Fe^{III} and M^{2+}. Electrochemical investigations revealed Fe^{III}/Fe^{II} reduction potential values shifted anodically in 1_2M complexes compared to **1**. Likewise, $2p_{3/2}$ and $2p_{1/2}$ peaks in the XPS data were found to shift positively in the 1_2M complexes, demonstrating that redox-inactive metal ions alter the electronic structure of Fe^{III}.





The first principle-based computational simulations further revealed the impact of M^{2+} on stabilizing 3d-orbitals of Fe. The distortion in Laplacian distribution ($\nabla^2\rho(r)$) of electron density around M^{2+} also indicates the possibility of having Fe–M interactions in these complexes. The absence of a bond critical point between Fe^{III} and M^{2+} ions in the 1_2M complexes indicates dominant through-space interaction between these metal centres. Experimental and computational studies collectively imply that the installation of internal electrostatic fields exerted by M^{2+} ions in 1_2M complexes alters the electronic structure of Fe^{III}.

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[1] Leonard, N. G.; Dhaoui, R.; Chantarojsiri, T.; Yang, J. Y. *ACS Catal.* **2021,** *11*, 10923-10932.

[2] Weberg, A. B.; Murphy, R. P.; Tomson, N. C. *Chem. Sci.* **2022,** *13*, 5432-5446.