Role of solvent-ligand exchange in the reaction of iron(II) polypyridyl complexes with H_2O_2

Sandeep K. Padamati, D. Unjaroen, A. Draksharapu and W. R. Browne

Stratingh Institute for Chemistry, Faculty of Mathematics and Natural Sciences, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands.

Iron polypyridyl complexes have been shown to be potent catalysts for epoxidation and *cis*-dihydroxylation of alkenes as well as oxidation of alkyl C-H bonds to alcohols and ketones using H_2O_2.[1] Iron complexes with Tetradentate nitrogen ligands such as TPA and BPMEN have been used in the stereoselective epoxidation using H_2O_2.[2] The N3Py ligands, such as Bn-N3Py (figure 1) have been used for epoxidation also and have shown a strong dependence on solvent in their reactivity.[3] The complex $[Fe^{II}(BnN3Py)(CH_3CN)_2](ClO_4)_2$ (**1**) provided *cis*-diol products in acetonitrile and *trans*-diols in acetone for the same substrate. Complex **1** has two labile CH_3CN ligands, one of which is easily displaced by water. In this presentation, we will discuss ligand exchange and its effect on electrochemical and spectroscopic properties and its role in allowing these complexes to react with H_2O_2.

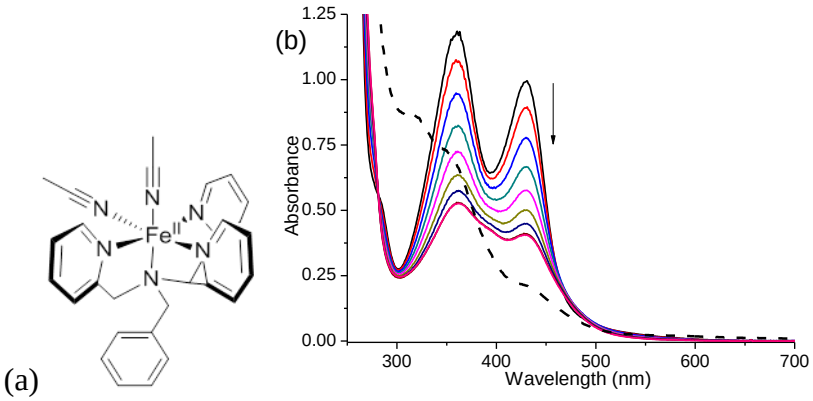

Fig 1: (a) Complex **1** ($[Fe^{II}(BnN3Py)(CH_3CN)_2](ClO_4)_2$ and (b) Changes observed in the UV/Vis absorption spectrum of **1**(0.5 mM) in acetonitrile upon addition of up to 10 vol% water (solid lines) and after addition of 1 eq of H_2O_2 (dashed)

References

1.Roelfes, G.; Lubben, M.; Chen, K.; Ho, R. Y. N.; Meetsma, A.; Genseberger, S.; Hermant, R. M. ;Hage, R.; Mandal, S. K.; Young, V. G., Jr.; Zang, Y.; Kooijman, H.; Spek, A. L.; Que, L., Jr.; Feringa, B. L., *Inorg. Chem.* **1999**, *38*, 1929-1936. l. Prat, A. Company, V. Postils, X. Ribas, L. Que Jr., J. M. Luis, M. Costas, Chem. Eur. J. **2013**, *19*, 6724–6738.

2. Chen, K.; Costas, M.; Kim, J.; Tipton, A. K.; Que, L., Jr., *J. Am. Chem. Soc*., **2002**, *124*, 3026-3035.

3. A. Draksharapu.; Q. Li.; H. Logtenberg.; T. A. van den Berg.; A. Meetsma.; J. S. Killeen.; B. L. Feringa.; R. Hage.; G. Roelfes.; W. R. Browne., *Inorg. Chem*., **2012**,*51*, 900-913.