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## Shedding light on active species in Fe, Ni and Cu catalysis

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*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

2013

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Draksharapu, A. (2013). *Shedding light on active species in Fe, Ni and Cu catalysis: photochemical, spectroscopic and electrochemical studies*. s.n.

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# **Shedding Light on Active Species in Fe, Ni and Cu Catalysis**

Photochemical, Spectroscopic and Electrochemical Studies

Apparao Draksharapu



university of  
 groningen

faculty of mathematics  
and natural sciences

This work described in this thesis was carried out at the Stratingh Institute for Chemistry, University of Groningen, The Netherlands.

This work was financially supported by: University of Groningen.

Printed by: Ipskamp Drukkers B. V., Enschede, The Netherlands.

Cover design by: Jeffrey Bos

ISBN: 978-90-367-6622-7 (printed version)

ISBN: 978-90-367-6621-0 (electronic version)

**RIJKSUNIVERSITEIT GRONINGEN**

**Shedding Light on Active Species in Fe, Ni and Cu Catalysis**

Photochemical, Spectroscopic and Electrochemical Studies

**Proefschrift**

ter verkrijging van het doctoraat in de  
Wiskunde en Natuurwetenschappen  
aan de Rijksuniversiteit Groningen  
op gezag van de  
Rector Magnificus, dr. E. Sterken,  
in het openbaar te verdedigen op  
vrijdag 13 december 2013  
om 9.00 uur

door

**Apparao Draksharapu**

geboren op 3 april 1987

te Madugula, India

Promotores :

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Dedicated to

Kanaka & Ganga Raju Draksharapu

“Arise, awake, and stop not till the goal is reached”

--- Swami Vivekananda

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# Prologue

This thesis ‘*Shedding light on active intermediates in Fe, Ni and Cu catalysis: Photochemical, spectroscopic and electrochemical studies*’ is mostly concerned with the trapping and spectroscopic characterisation of potentially active species formed from first row transition metal complexes in catalysis under catalytically relevant conditions. Electrochemistry and in particular Raman and resonance Raman spectroscopies are employed extensively to understand the properties of several iron and nickel oxygen based intermediates and the interaction of copper complexes with DNA. The goal is to understand how speciation can relate to catalytic activity.

UV/Vis absorption and Raman spectroscopies are key in the characterisation of active intermediates involved in iron and manganese based oxidation catalysis. In the first part of **Introduction** a survey of the use of Raman as a tool for fingerprinting in the characterisation of iron based intermediates such as  $\text{Fe}^{\text{III}}\text{-OOH(R)}$ ,  $\text{Fe}^{\text{III}}\text{-OO}$ ,  $\text{Fe}^{\text{III}}\text{=O}$ ,  $\text{Fe}^{\text{IV}}\text{=O}$ ,  $\text{Fe}^{\text{V}}\text{=O}$ ,  $\text{Fe}^{\text{III}}\text{-O-O-Fe}^{\text{III}}$  and to a lesser extent to  $\text{Ru}^{\text{IV}}\text{=O}$ ,  $\text{Mn}^{\text{III}}\text{=O}$ ,  $\text{Mn}^{\text{IV}}\text{=O}$ ,  $\text{Mn}^{\text{V}}\text{=O}$  and  $\text{Mn}^{\text{V}}\equiv\text{O}$  species. The fundamental differences between the complementary techniques of IR and Raman spectroscopy are addressed. The use of labelling experiments to assign Raman bands to modes with certainty is discussed also. Finally, the advantages and opportunities presented by the resonance Raman effect is discussed using a few examples. In the second part of **Introduction**, the electrochemistry of known  $\text{Fe}^{\text{IV}}\text{=O}$  complexes in water and in acetonitrile is discussed. The discrepancies between data from different sources are analysed critically to set the stage for the electrochemical and photochemical studies described in chapters 4 and 5. In the third part of **Introduction**, biochemical halogenation reactions are reviewed. The mechanisms proposed for halogenases and haloperoxidases are compared and contrasted.

In **chapter 2**, multiple spectroscopic and electrochemical techniques are applied to the speciation of the  $\text{Fe}^{\text{II}}(\text{N4Py})$  family of complexes in aqueous solutions of relevance to DNA cleavage studies. UV/Vis absorption and  $^1\text{H}$  NMR spectroscopy indicated that, in their aquated forms, *e.g.*,  $[(\text{N4Py})\text{Fe}^{\text{II}}(\text{OH})]^+$ , the complexes were present in solution as an equilibrated mixture of low and high spin states and showed a pH dependence on the coordination mode of the N4Py ligand. The equilibria established between two distinct complexes differing in the coordination number of the N4Py ligand and an equilibrium between singlet and quintet spin states in aqueous solution was proposed to be at the origin of the effectiveness of

## Prologue

$\text{Fe}^{\text{II}}(\text{N4Py})$  in cleaving DNA in water with  $^3\text{O}_2$  as terminal oxidant through the transient population of a triplet state.

In **chapter 3**, the remarkable photochemical enhancement of the rate of oxidation of iron(II) polypyridyl complexes by oxygen through outer sphere electron transfer is described. The data obtained represents a breakthrough in our understanding of the involvement of photochemistry in the activity of iron(II) polypyridyl complexes in the cleavage of DNA and in a more general sense in the perturbation of ground state spin equilibria in solution.

In **chapter 4**, the isolation and characterization of a new non-heme  $\text{Fe}^{\text{IV}}=\text{O}$  species was carried out both chemically and electrochemically in water. In this chapter the clean conversion of  $[(\text{MeN4Py})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})]^{2+}$  to the high valent species  $[(\text{MeN4Py})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$  via the complex  $[(\text{MeN4Py})\text{Fe}^{\text{III}}(\text{OH})]^{2+}$  at an applied potential 0.85 V vs. SCE in water is demonstrated and the redox potential of  $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{III}}$  couple compared and contrasted with those reported elsewhere.

In **chapter 5**, the photochemistry of  $\text{Fe}^{\text{IV}}=\text{O}$  complexes is explored for the first time in the solid state as well as in solution together with their reactivity in regard to the alkane hydroxylation and alkene epoxidation. In contrast to  $\text{Fe}(\text{II})$  complexes,  $\text{Fe}^{\text{IV}}=\text{O}$  complexes undergo photochemical reduction upon irradiation a 355 nm in acetonitrile. This process is faster in the presence of substrates such as ethyl benzene, benzyl alcohol, cyclooctene and indane etc. which undergo oxidation concomitantly. The enhanced reactivity of the  $\text{Fe}^{\text{IV}}=\text{O}$ , under irradiation, towards substrate oxidation is attributed to the population of an  $S = 2$  state.

In **chapter 6**, generation of a non-heme  $\text{Fe}^{\text{III}}\text{-OCl}$  species and its spectroscopic characterisation is reported. Addition of one or two equivalents of aqueous  $\text{NaOCl}$  to an aqueous solution of  $[(\text{MeN4Py})\text{Fe}^{\text{II}}(\text{Cl})]^+$  or  $[(\text{N4Py})\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})]^{2+}$  at room temperature generates the corresponding  $\text{Fe}^{\text{III}}\text{-OCl}$  adduct, assignment of these intermediates was carried out using UV/Vis absorption, (resonance)Raman and EPR spectroscopy and by Cryo ESI-MS. Raman characterisation of the  $\text{Fe}^{\text{III}}\text{-O}$  and  $\text{O-Cl}$  modes was aided by bromine ( $\text{Fe}^{\text{III}}\text{-O-Br}$ ) and with  $^{18}\text{O}$  labelling. Over time these intermediates convert to their  $\text{Fe}^{\text{IV}}=\text{O}$  analogues. In contrast to  $[(\text{TPFP})\text{Fe}^{\text{III}}(\text{OCl})_2]^-$  (which is stable at  $-60\text{ }^\circ\text{C}$  for 1 h in  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ ),  $[(\text{MeN4Py})\text{Fe}^{\text{III}}(\text{OCl})]^{2+}$  is stable in water at room temperature for at least 10

minutes. These intermediates can attack electron rich alkenes and give corresponding  $\alpha$ -hydroxy halides or diols.

In **chapter 7**, generation of non-porphyrinic Ni<sup>II</sup>-O<sup>•</sup> species and its spectroscopic characterisation is presented. Addition of 11 equivalents of aqueous NaOCl/Ca(OCl)<sub>2</sub> to acetonitrile solutions of [(<sup>H,Me</sup>PyTACN)Ni<sup>II</sup>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup> at room temperature generates a Ni<sup>II</sup>-O<sup>•</sup> species. Addition of acetic acid shows a positive effect on the extent of formation of the intermediate and its rate of formation. Characterisation of this intermediate was carried out with UV/Vis absorption, (resonance)Raman, NMR and EPR spectroscopies and by Cryo ESI-MS. The Ni<sup>II</sup>-O<sup>•</sup> species is proposed to activate the C-H bond and Ni<sup>II</sup>-OCl species to insert the halogen into the substrate.

[Cu<sup>II</sup>(L)(NO<sub>3</sub>)<sub>2</sub>] polypyridyl complexes catalyse enantioselective C-C bond forming reactions in water with DNA as the source of chirality. Among all, complex Cu<sup>II</sup>(dmbpy) shows the highest ee's and selectivity in DNA-based asymmetric catalysis, whereas the complex Cu<sup>II</sup>(terpy) yields the opposite enantiomer. In **chapter 8**, the interaction with salmon testes DNA of a series of [Cu<sup>II</sup>(L)(NO<sub>3</sub>)<sub>2</sub>] polypyridyl complexes in the absence of substrate was studied by various spectroscopic techniques. For the first time UV resonance Raman spectroscopy was employed to probe the interaction of Cu(II) complexes with DNA. In the presence of DNA, the complexes Cu<sup>II</sup>(dppz) and Cu<sup>II</sup>(dpq) which are intercalators show clear shifts in the Raman spectrum whereas the groove binders Cu<sup>II</sup>(bpy) and Cu<sup>II</sup>(dmbpy) do not. Overall the data suggest that the complexes Cu<sup>II</sup>(bpy) and Cu<sup>II</sup>(dmbpy) engage primarily through groove binding with DNA while Cu<sup>II</sup>(dppz) and Cu<sup>II</sup>(dpq) undergo intercalation. For complexes Cu<sup>II</sup>(phen) and Cu<sup>II</sup>(terpy) the data indicates that both groove binding and intercalation takes place, albeit primarily intercalation. These findings provide important insights into the complex structure of these DNA-based catalysts.