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

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Chapter 9

Shedding light on active intermediates in Fe, Ni and Cu catalysis: future perspective

In this chapter the studies described in this thesis are placed in perspective and consideration to impact and future directions is given.

Chapter 9

9.1 Biomimetics

At the start of my PhD, as a beginner in oxidation chemistry, I wondered about the real meaning of the word '*biomimetic*'. Later I realised that it is the study of functional, and as much as possible structural, models for biological systems that mimic their catalytic properties in the laboratory flask. A number of biomimetic systems are alluded to in this thesis. For example, the complex $[(N4Py)Fe^{IV}(O)]^{2+}$ can be considered as a mimic for TauD[1] and CytC3[2] as discussed in chapter 5. Fe^{IV}=O species generated in the laboratory are mostly low spin (S = 1) in character. In sharp contrast, nature uses high spin (S = 2) complexes to achieve selectivity and reactivity in chemical reactions. Borovic, Que and Bakac and co-workers have reported a number of synthetic high spin Fe^{IV}=O complexes.[3] However, the reactivity of those complexes is less, rather than greater, compared even to known low spin Fe^{IV}=O species.[4] Of course, in obtaining high spin complexes, the bulky ligands and hydrogen bonding interactions used, can hinder the approach of a substrate towards the Fe^{IV}=O moiety. These challenges should be considered in new biomimetic systems, however, the synthesis of a new ligand and complexes may not necessarily be the only approach.

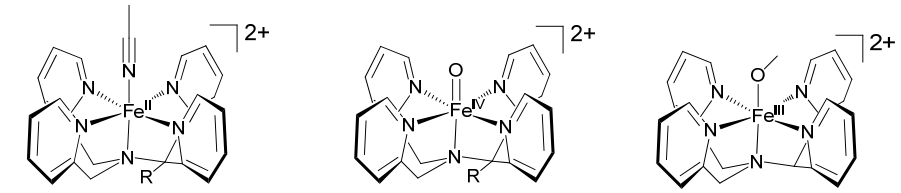


Figure 1 Structures of iron complexes discussed in the text.

It is claimed often that knowledge of biomimetic systems is of direct relevance to biological systems. I prefer to be cautious here. Except in a few cases, so called active intermediates in oxidation chemistry are generated in non-aqueous media. In sharp contrast, nature has no choice but to use water as its solvent. In many cases formation of distinct intermediates are observed depending on the solvent used in reactions carried out in the laboratory. For these reasons, the spectroscopic properties of intermediates and their direct comparison and relevance for biological systems is challenging. I am of course well aware that the solubilities of complexes and substrates limit the use of water as a solvent in biomimetic studies. Given that many of the generated intermediates are not stable at room temperature, often low temperatures are needed to observe them. With water one cannot readily go much

below 0 °C. This is not the case with non-aqueous solvents, which provide a larger temperature window (the exact boundaries depending on the solvent) to stabilise intermediates generated in a reaction. Acetonitrile is probably one of the most popular solvents used to study oxygen activated species, however, Fe^{IV}=O complexes (*e.g.,* **3** and **4**) are in fact more stable in water than in any non-aqueous solvents as shown in this thesis. For example, attempts to recrystallize **4** (Fe^{IV}=O) from acetonitrile/ether at -20 °C overnight yielded red needles of **2** (reduction occurs before crystallization). However, crystallization of **4** from water at 5 °C was successful and blue micro crystals were obtained overnight albeit of limited quality for X-ray diffraction studies. If complexes and intermediate species are stable in water, then why not study their spectroscopic and redox properties in water as well? Here my point is not to negate the value of using non-aqueous solvents, but to consider water also a solvent that is of direct relevance to the biological systems that are being referred to.

9.2 Speciation analysis

Prior to studying the spectroscopic properties and reactivity of unstable 'activated' intermediates, it is, in my view, worthwhile to study the properties of the complexes from which those intermediates are generated in the first place. The aqueous chemistry of Fe^{II}(N4Py) and its analogues were explored in chapter 2. The chemistry of the complexes (*e.g.* Fe^{II}(N4Py)) changes dramatically between acetonitrile and water.[5] In some regards this chapter can be viewed as a routine speciation of a complex system of species and to some extent this may be true. Nevertheless, a multi-technique approach was needed to explore the ligand exchange and spin state equilibria of species formed in water. The knowledge gained in this study of the speciation of Fe^{II}(N4Py) and its related complexes in water and in acetonitrile served as a basis that stimulated the research described in the major part of this thesis.

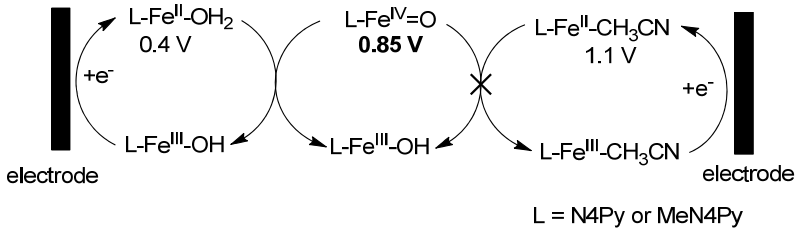
The power of such speciation analysis is illustrated with an example taken from the literature. My intention in this is not to criticise the authors work but to exemplify the benefit that can be drawn from such studies. Recently, Nam and coworkers[6] reported the photochemical generation of $[(N4Py)Fe^{IV}(O)]^{2+}$ using $[Ru(bpy)_3]^{2+}$ as a photo-oxidant and $[Co^{III}(NH_3)_5Cl]^{2+}$ as terminal oxidant. The authors described the studies where the initial form of the complex in solution is a $Fe^{II}(OH_2)$ species (*i.e.* in scheme 2 in reference 6). Such a species is unlikely to be present in solution, however, when acetonitrile is present (chapter 2). The initial complex that should be

considered in the system is an Fe^{II}-CH_3CN species, which requires 1.1 V *vs.* SCE to be oxidized to an Fe^{III}-CH_3CN species. Of course ligand exchange with H_2O will followed this redox event. This is essential to understanding the system since if a $Fe^{II}(OH_2)$ species were present then weaker oxidants would serve just as well. In this case the use of the strong oxidant $[Ru^{II}(bpy)_3]^{2+*}$ (E_{ox} = 1.18 V *vs.* SCE) meant that the observations were not in disagreement with the scheme they drew to describe the system but this is beside the point.

9.3 Redox chemistry of Fe^{II} and Fe^{IV}=O complexes

Knowledge of the redox properties of complexes is highly desirable for a better understanding of the catalytic properties of metal complexes. Determination of Fe^{III}/Fe^{II} redox potentials of Fe^{II}(N4Py) complexes is straightforward due to electrochemical reversibility and fast rates of heterogeneous electron transfer. For example, complex **2** shows reversible redox chemistry at 1.1 V *vs.* SCE in acetonitrile ascribed to the $Fe^{III}/Fe^{II}(CH_3CN)$ redox couple, but in water a reversible redox wave (of course depending on pH) was observed at ca. 0.4 V *vs.* SCE ascribed to the Fe^{III}/Fe^{II}(OH) redox couple. However, determination of Fe^{IV}/Fe^{III} redox potential by cyclic voltammetry is rather difficult due to the sluggish rates of heterogeneous electron transfer encountered for this redox couple. Recording cyclic voltammograms on isolated Fe^{IV}=O complexes will not help and in fact has led to confusion in the literature. The approach taken by Nam and Fukuzumi in using one electron donors such as ferrocene and its derivatives, however, neglects the fact that electrochemically irreversible processes are involved in the case of Fe^{IV}(O)/Fe^{III}(OH)/Fe^{II}(OH) redox processes due to ligand exchange with CH_3CN.[7] Spectropotentiometric titrations of Fe(II) complexes in acetonitrile followed by UV/Vis absorption spectroscopy has already shown its potential, however, in determining the Fe^{IV}/Fe^{III} redox couple, simply due to the fact that the absorption spectrum can be obtained at any time after application of a potential so even slow electron transfer is not a real issue.[8] As discussed in chapter 4, the incorrect assignment of the redox potential of the Fe^{IV}/Fe^{III} couple is due to the higher oxidation potential required to oxidise the $Fe^{II}(CH_3CN)$ to $Fe^{III}(CH_3CN)$ in the first place in acetonitrile. Whereas in water this is absent due to the lower potential needed to oxidise the Fe^{II}(OH) species. The comproportionation reaction between Fe^{II}-OH and Fe^{IV}=O, to generate Fe^{III}-OH is shown in scheme 1. In water the Fe^{IV}=O species (0.85 V *vs.* SCE) can easily oxidise Fe^{II}-OH (0.4 V *vs.* SCE). However, the analogous reaction does not occur between $Fe^{II}(CH_3CN)$ and Fe^{IV}(O). In this case Fe^{IV}=O is not a powerful enough oxidant to oxidize $Fe^{II}(CH_3CN)$ (1.1 V

vs. SCE). This is strong evidence that the Fe^{IV}=O redox potential is in between 0.4 and 1.1 V *vs.* SCE.



Scheme 1 Reaction between Fe^{II} and Fe^{IV}=O complexes in water and in acetonitrile.

These electrochemical studies have direct implications for discussions in the literature. First of all the redox potential of the Fe^{IV}/Fe^{III} couple is 0.85 V *vs.* SCE in water. The presence of acetonitrile, *e.g.,* for solubility, and the failure to take into account mediated electron transfer is at the root of the misassignment of the redox potential of the Fe^{IV}/Fe^{III} couple. In future studies, in cases where Fe^{IV}=O species are stable in water, I would recommend studying their redox properties in water as well and to take into account time scales for electron transfer.

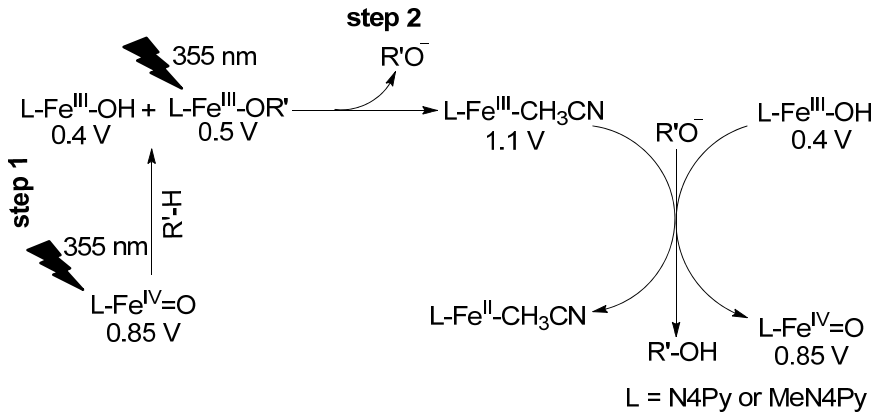
9.4 Photochemistry of iron complexes

It can hardly be over emphasized that the photochemical properties of iron complexes are overshadowed by its group partner 'ruthenium'. Li *et al* reported that the first step in the cleavage of DNA by **1** with oxygen ($^3O_2$) is enhanced under irradiation,[9] suggesting that Fe^{II}(N4Py) complexes are photochemically active. The photochemistry of a series of Fe(II) (**1** and **2**), Fe^{IV}=O (**3** and **4**) and Fe^{III}-OMe (**5**) complexes were explored in chapters 3 and 5. Complexes **1** and **2** undergo photoinduced oxidation under irradiation in various solvents such as water, methanol and dichloromethane with dioxygen as terminal oxidant. The photochemistry of Fe(II) complexes is of direct relevance to the photochemical enhancement of DNA cleavage by **1** observed by Li *et al*.[9] It has been proposed that the interconversion between the singlet and higher spin states occurring in aqueous solution involves an intermediate triplet state, form which electron transfer to $^3O_2$ occurs readily. Excitation of N4Py based Fe^{II}-OH complexes is believed to increase the population of complexes in the triplet state and, hence, increased activity.

One challenge here for the future is that the characterisation of the primary and secondary photoproducts of **2** in methanol. It is likely that Fe^{III}-OR (R = alkyl) complexes are also photochemically active as well. Exploring the photochemistry of

Fe^{III}-OR complexes is highly desirable with regard to understand the rebound mechanism discussed below.

Complexes **1** and **2** are not photochemically active in acetonitrile reflecting their higher oxidation potentials and firmly low spin nature. In sharp contrast, complexes **3** and **4** undergo reduction under photo irradiation (UV and vis light). On the one hand this is a problem as it is often struggle to obtain resonance Raman spectra of such photochemically unstable compounds, but, on the other hand I took advantage of this photochemical instability of the Fe^{IV}=O complexes (**3** and **4**) to explore their photocatalytic properties.



Scheme 2 Steps involved in the photochemical reaction of Fe^{IV}=O complexes in acetonitrile.

There are two steps involved in the photochemical process. The first step is the conversion of the Fe^{IV}=O species to an Fe(III) species followed by a second photochemical step in which the Fe(III) species formed is reduced to an Fe^{II}-CH_3CN species (scheme 2). The formulation of the Fe(III) intermediate was obtained from the knowledge of the photochemical properties of the Fe(II) complexes (**1** and **2**, chapter 3). As mentioned above, complexes **1** and **2** undergo photoinduced oxidation under irradiation in various solvents with dioxygen as terminal oxidant. Interestingly, in methanol, the primary photoproduct (Fe^{III}-OMe) is also photochemically active albeit at that time this was not understood fully. Moreover, Fe^{III}-OMe (**5**) undergoes photochemical reduction in acetonitrile under photo irradiation. By contrast, the Fe^{III}-OH complex in acetonitrile is photochemically much less active. Hence, the primary photoproduct in the reduction of Fe^{IV}=O is not an Fe^{III}-OH species, but instead an Fe^{III}-OR (R = alkyl) species. These data indicate that C-H hydroxylation goes via a rebound mechanism and is to the best of my knowledge, the only example of direct spectroscopic

evidence for the rebound mechanism. In the second photochemical step the Fe^{III}-OR species may convert to an Fe^{III}-CH_3CN. The Fe^{III}-CH_3CN species is a powerful enough oxidant to convert Fe^{III}-OH/OR to Fe^{IV}=O and forming Fe^{II}-CH_3CN also. The enhanced reactivity of the Fe^{IV}=O species, under irradiation, towards substrate oxidation is attributed to the transient population of an S = 2 state. If this is the case, then photochemistry is an alternative way to populate the S = 2 state and to obtain better reactivities. It remains to be seen whether this is a general feature of low spin Fe^{IV}=O complexes.

9.5 Haloperoxidases

Nature uses haloperoxidases to achieve halogenation of substrates in a highly specific and selective manner. Within this class of enzymes, vanadium bromo peroxidase is perhaps the most eminent example due to its applications in the biosynthesis of a number of halogenated natural products. It has been proposed that with this class of enzymes a M-OCl adduct is responsible for halogenation, however, direct spectroscopic evidence for heme-Fe^{III}-OCl species was provided only very recently by Hiroshi *et al*.[10] More examples of haloperoxidase mimics and their spectroscopic characterisation would be of considerable benefit to improve the understanding of their biological function. To the best of my knowledge these species have not been reported in any of the non-heme and non-porphyrinic systems. The formation and spectroscopic characterisation of a non-heme Fe^{III}-OCl species is reported in chapter 6.

Addition of aqueous NaOCl to acidic aqueous solution of **1** or **2** at room temperature generates the Fe^{III}-OCl species, which was characterised by ESI-MS and by Raman spectroscopy. In chapter 6, substitution of chlorine with bromine (heavy isotope) and ^{16}O with ^{18}O, was employed to assign the resonance Raman spectrum of the Fe^{III}-OCl species. The catalytic activity of Fe^{III}-OCl intermediate was, however, only explored in a preliminary manner, but does show promise for applications. Preliminary catalytic studies with styrene sulfonate as substrate confirm the formation of a halohydrin. In this case the substrates scope for catalysis is limited due to solubility in aqueous media. In addition, considerable background reactions are observed under the reaction conditions also. More substrates could be employed if the same species (Fe^{III}-OCl) could be generated in non-aqueous medium (*e.g.,* acetonitrile). Another aspect that I would like to emphasize is the effect of acid on the generation and stability of Fe^{III}-OCl species. Surprisingly, it is difficult to identify the Fe^{III}-OCl species in the absence of acid at room temperature.

The effect of acid on the system is not clear at present and this is something to be explored in the future.

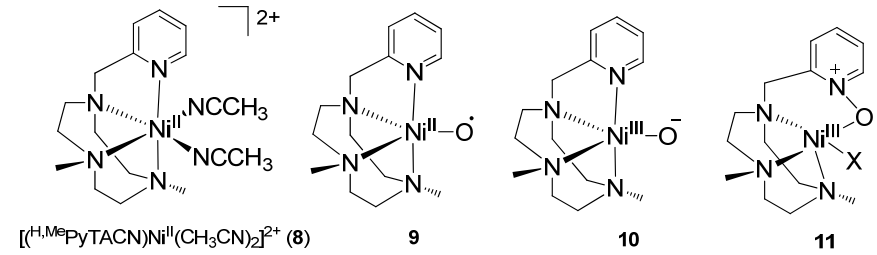


Figure 2 Structures of Ni(II) complex and possible intermediates discussed in the text. The exact nature of 'X' is still unclear.

The existence of metal oxo complexes beyond d^5 ions is unlikely due to the 'oxo wall' (Fe-Ru-Os), *i.e.* metals to the right of the wall will not support a terminal oxo group in tetragonal environments.[11,12] For example, the recent claims of the existence of Pt^{IV}=O (d^6) were retracted after quite a heated debate.[13] In chapter 7, I was tempted to assign an intermediate as a terminal Ni^{III}=O species by analogy to iron systems. Addition of aqueous NaOCl to acetonitrile solutions of **8** generates an orange intermediate. From ESI-MS analysis the intermediate Ni^{II}-OCl was determined. To support this assignment Raman studies were carried out on the system. In the Raman spectrum of the orange solution only one oxygen-18 sensitive mode was observed at 724 cm^{-1}. And the band is not halogen sensitive. So the species can't be assigned to the Ni^{II}-OCl species obtained by ESI-MS. Due to its oxygen sensitive and halogen insensitive nature, its vibrational frequency (724 cm^{-1}, in the range of Fe^{III}-O and Mn^{III}-O bands) and Ni(III) EPR signal I was tempted to assign this intermediate as a Ni^{III}=O species. However, consideration of the oxo wall persuaded me to assign the species as a Ni^{II}-$O^{\cdot}$ species (**9**), which has Ni(III) character. These species are proposed to be active intermediates in Ni(II)/oxidant catalysed reactions and to the best of my knowledge this is first direct spectroscopic evidence for their existence in a reaction. Regardless, other possible structures such as Ni^{III}-O^{-} (**10**), N-oxides (**11**) and multi-nuclear complexes cannot be excluded at present (Figure 2). Complexes **9** and **10** are drawn as Lewis structures which is in my view misleading. Unfortunately, evidence for a Ni^{II}-$O^{\cdot}$ was only obtained by Raman spectroscopy and evidence for Ni^{II}-OCl was only obtained by ESI-MS. Further support from other spectroscopic techniques is perhaps necessary to be conclusive. However, these intermediates are able to insert halogen into substrates and hence can be regarded as functional models for haloperoxidases.

9.6 DNA-based asymmetric catalysis

In the latter part of my PhD research attention shifted to quite a different catalytic system, *i.e.* copper(II) catalysed reactions involving DNA. Speciation analysis was the first step taken in studying DNA based asymmetric catalysis (chapter 8). The challenges addressed are (1) how are the catalytically active complexes bound to DNA, (2) do the catalysts interactions with DNA change, and if so in what way, when bound to the substrate, and (3) how does DNA affect catalysis. To address these challenges the binding mode of the kinetically competent complexes to DNA needs to be established. The interaction with DNA of a series of Cu(II) polypyridyl complexes in the absence of substrate was studied by a range of techniques, and the data means that now the stage to state that the complexes that induce the highest *ee* in DNA-based asymmetric catalysis are primarily groove binders has been reached. However, things may change in the presence of substrate (*e.g.,* aza-chalcone). Notably, complex **7** generates the opposite enantiomer in DNA-based asymmetric catalysis compared to Cu(II) complexes with bidentate ligands (*e.g.,* dmbpy and phen, Figure 3). This observation indicates that the coordination geometry of the substrate to the copper ultimately determines enantiopreference.[14] Of course, to understand the catalysis itself, the substrate should be introduced into the system.

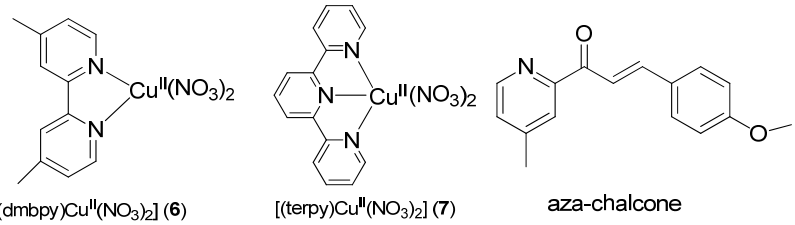


Figure 3 Structures of Cu(II) complexes and aza-chalcone discussed in the text.

Preliminary studies, not discussed in this thesis, indicate the important role resonance Raman will play in unravelling a reasonable mechanism. Aza-chalcone shows an absorption band at 350 nm and hence can be monitored by resonance Raman at λ_{exc} 355 nm. The DNA-Cu-aza complex absorbs at 448 nm,[15] and hence resonance Raman at λ_{exc} 473 nm is useful. Resonance enhancement of Raman signals of the Cu(II) bounded aza-chalcone makes it possible to study its coordination to Cu-L complexes. Under catalytically relevant conditions Resonance Raman spectroscopy at λ_{exc} 355 nm reveals that the intensity of the band of aza-chalcone at *ca.* 1600 cm^{-1} decreases roughly 75% in the presence of DNA. These preliminary results demonstrate that the aza-chalcone itself interacts with DNA. UV/Vis absorption and resonance Raman spectra are shown in Figure 4. Addition of **6** to aza-chalcone does not lead to new absorption bands. However,

addition of **6** to the DNA-azachalcone mixture results in an absorption band at 448 nm appearing in the UV/Vis absorption spectrum and strong bands are observed by Raman spectroscopy at λ_{exc} 473 nm. These preliminary data indicate that complex **6** drags the aza-chalcone out from DNA, but keeps it in proximity to DNA for catalysis. This might be the key to understanding DNA-based asymmetric catalysis and in particular rate enhancement through local concentration of substrate and catalysts. Of course more studies are needed to draw firm conclusions on DNA-based asymmetric catalysis.

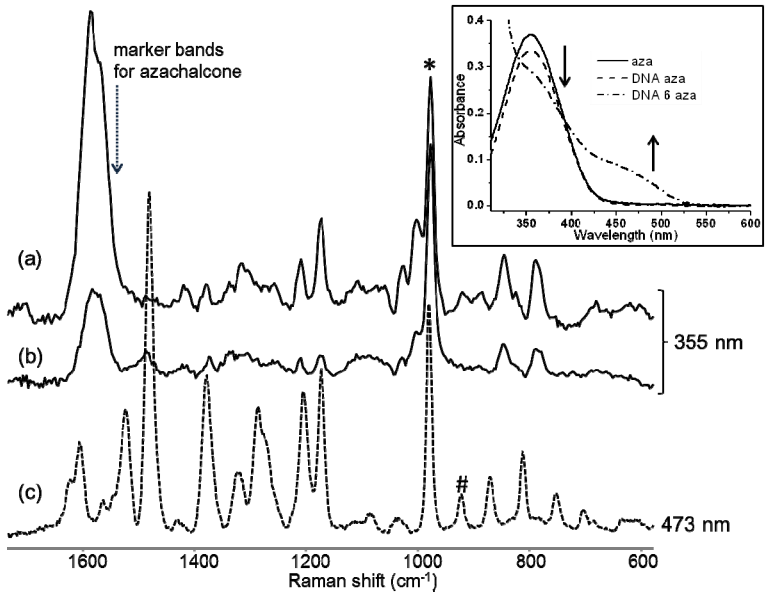


Figure 4 Raman and resonance Raman spectra of (a) aza-chalcone and (b) st-DNA + aza-chalcone at λ_{exc} 355 nm and (c) st-DNA + **6** + aza-chalcone at λ_{exc} 473 nm. Conditions: aza-chalcone (20 μM), **6** (0.3 mM), st-DNA (1.33 mg/mL) in 20 mM MOPS buffer at pH 6.5. * Sulfate and # acetonitrile modes. Inset: Corresponding UV/Vis absorption spectra.

9.7 Concluding remarks

In Chart 1, I summarised how one research chapter stimulated research work described in other chapters in this thesis. Speciation analysis described in chapter 2 played a key role in understanding other systems investigated in this thesis. Especially, knowledge of the electrochemistry of Fe(II) complexes in water and in acetonitrile built a strong basis to explore the redox properties of Fe^{IV}=O complexes discussed in chapter 4. The photochemistry of Fe(II) complexes in various solvents (chapter 3) stimulated the study of the photochemistry of Fe^{IV}=O and Fe^{III}-OMe complexes (chapter 5). Haloperoxidase mimics, *i.e.,* Fe^{III}-OCl (chapter 6) and

Ni^{II}-OCl (chapter 7) mutually stimulated exploration of their chemistry and catalytic properties. As it stands, chapter 8 is unfinished business and does not provide conclusions regarding DNA-based asymmetric catalysis in itself but the studies discussed in this thesis provide already the basis for understanding the complex picture of catalysis and substrate-catalyst interactions.

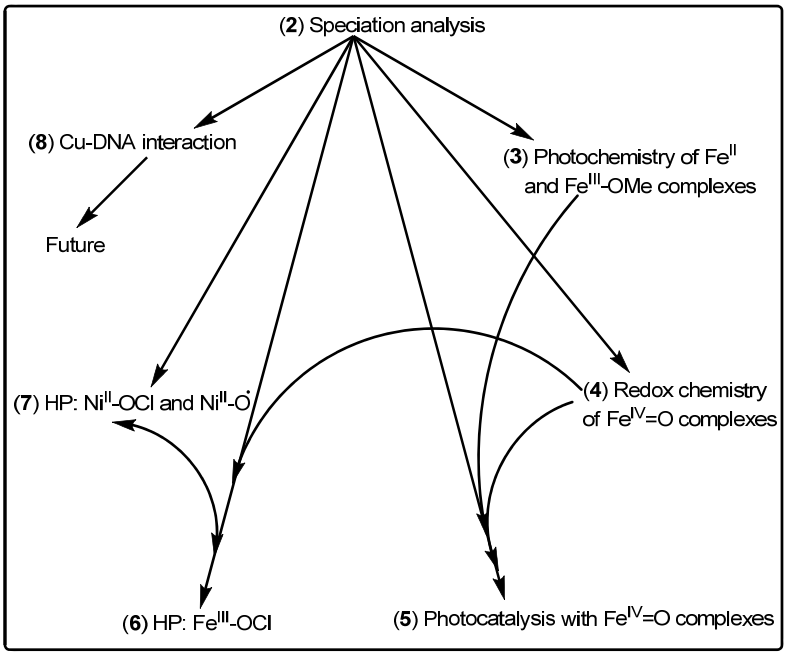


Chart 1 Thesis chapters and their relation to one another. 'HP' is haloperoxidases.

In this thesis spectroscopic characterisation of several new intermediates such as Fe^{III}-OCl, Ni^{II}-OCl and Ni^{II}-$O^{\bullet}$ is described. However, the effect of acid on the generation of these intermediates was not explored in detail and should be part of future.

Another aspect which is still unexplained is the effect of the methyl group in N4Py. Iron complexes of MeN4Py are more stable in water and are also more stable under lower pH conditions compared to their corresponding N4Py complexes. This remarkable stability under acidic conditions makes it possible to study the generation of Fe^{III}-OCl species.

In conclusion, the extension of these studies to other iron and nickel systems is of importance to establish the generality of the observations described in this thesis and indeed one recent study has done in the case of the iron bispidine complexes already.[16]

9.8 References

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