Coordination chemistry of manganese and iron with N,O-donor ligands: oxidation catalysis and magnetochemistry of clusters

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Citation

Godbole, M. D. (2006, January 12). *Coordination chemistry of manganese and iron with N,O-donor ligands: oxidation catalysis and magnetochemistry of clusters*. Retrieved from https://hdl.handle.net/1887/4333

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Summary, General Discussion and Outlook

6.1 Summary

The development of the coordination chemistry of manganese and iron is driven and stimulated by the variety of applications that these compounds impart, as described in Chapter 1. In the research described in this thesis, three different aspects of the manganese and iron complexes have been mainly considered and studied: Catalase mimics, Oxidation catalysts, and Molecular Magnets.

The ligand HMesalim, which has the same N, O backbone as the Hphox (Hphox =2-(2'-hydroxyphenyl)-oxazoline) ligand has been studied. It has an additional proton on the imine nitrogen and a labile, solvent exchangeable alkoxy group instead of the oxazoline ring. In chapter 2, the synthesis of three complexes, $[Mn_2(Etsalim)_4(HEtsalim)_2](ClO_4)_2$ (**1**), $[Mn(Mesalim)_2(OAc)(MeOH)]\bullet MeOH$ (**2**), and $[Mn(Mesalim)_2Cl]$ (**3**) in which HMesalim and HEtsalim are methyl and ethyl salicylimidate respectively, has been described. The complexes have been fully characterized by X-ray analyses, magnetic susceptibility, UV-Vis and IR spectroscopy, and their interaction with dihydrogen peroxide has been studied. The complexes catalyze the disproportionation of dihydrogen peroxide into water and dioxygen; they show very high catalase activity exhibiting saturation kinetics. The rate and turnover numbers of the catalyzed reaction increase dramatically when a few equivalents of base (NaOH) are added to the reaction mixture. The complexes in combination with a few equivalents of sodium hydroxide are among the few catalase model systems that show turnover numbers up to 3000 in dihydrogen peroxide disproportionation.

To understand the mechanism of disproportionation the reaction has been studied in relation to kinetics, ligand-field spectroscopy, EPR and ESI-MS. Like most other catalase mimics, the results of these studies did not provide a complete picture of the mechanism. Nevertheless, the ESI-MS analyses in deuterated solvents furnish useful piece of information about the nature of the active species formed on addition of 5 eq of NaOH. Although the exact nature of the active species participating during turnover could not be confirmed presently, the proton on the imine N is replaced by the sodium ion (from NaOH), and the alkoxy groups are observed to be in fast exchange with the alkoxy groups of the used solvent (alcohol). Application of deuterated ethanol was very useful in explaining the ESI-MS analyses of these solutions. By using of the deuterated ethanol, a peculiar fragmentation pattern resulted due to which the ESI-MS spectrum and could be unambiguously interpreted.

In chapter 3, the synthetic and catalytic studies on manganese complexes with ligands of the type HphoxCOOR (R = H, Me) have been described. The complexes have been synthesized and characterized using X-ray analyses, ESI-MS, ligand-field spectroscopy, electrochemistry and paramagnetic ^{1}H NMR. The ligands, both chirally pure and racemic, influence the structures of the complexes formed. A dynamic coordination chemistry became apparent when the X-ray structures of these complexes were compared to the solution chemistry imparted by the complexes. As a result of the MnL_2 formulation of the complexes formed and the single ester/carboxyl substituent on the oxazoline ring, the ^{1}H NMR spectra of the complexes have been clearly interpreted. Ligand exchange reactions occur in solution giving rise to *meso* complexes is confirmed by ESI-MS and deuteration studies. Although no major structural differences have been observed in solid state for the two complexes [Mn(*R*-phoxCOOMe)$_2$Br] and [Mn(*R*-phoxCOOMe)$_2$Br][Mn(*S*-phoxCOOMe)$_2$Br] the solution structures have been found to be distinctly different. ESI-MS studies have shown that the complex [Mn(*R*-phoxCOOMe)$_2$Br][Mn(*S*-phoxCOOMe)$_2$Br] exchanges the enantiomeric ligands in solution, and exists, in fact, as a *meso* complex in solution, wherein two ligands of opposite chirality are bound to one metal center in [Mn(*R*-phoxCOOMe)*(S*-phoxCOOMe)]$^+$. The ester substituents, although small, were found to the very powerful in modulating the reactivity of complexes in solution. Imidazole coordination was found to occur upon reaction with the metal complex that contains two ligands with the same chirality (*R* and *R*), [Mn(*R*-phoxCOOMe)$_2$Br]. As a result of formation of the complex cation of type [Mn(*R*-phoxCOOMe)(*S*-phoxCOOMe)]$^+$ in solution starting from the complex [Mn(*R*-phoxCOOMe)$_2$Br][Mn(*S*-phoxCOOMe)$_2$Br], the added N-Meim has been found not to coordinate to the metal ion in the complex, because both the axial sites are geometrically blocked by the ester group on each ligand.

Epoxidation reactions of various alkenes with H_2O_2 as the oxidant reveal that the complexes give turnover numbers in the range of 10-35 in 5 h, the epoxide being the major product. The catalytic activity depends on the additives used, and a base effect is observed.

However, while complex [Mn(*R*-phoxCOOMe)$_2$Br][Mn(*S*-phoxCOOMe)$_2$Br] shows significantly higher catalytic epoxidation activity than [Mn(*R*-phoxCOOMe)$_2$Br], present studies signify that imidazole binding is not necessary for good activity, which is in contrast with proposals in literature.[1-3] The latter fact unambiguously shows that imidazole binding is not a prerequisite for higher turnover numbers, which is different from the Mn-Schiff base catalysts. In fact the results in this thesis support the increasingly popular hypothesis that 'basicity is sufficient property for catalytic activity' which seems to apply not only to bases as carboxylate, or carbonate salts,[4, 5] but also to substituted imidazoles. Comparison of the reactivity of the manganese complexes of HphoxCOOMe and Hphox*i*pr ligands with the original [Mn(phox)$_3$] catalyst in catalytic epoxidation studies shows that both the electron-donating as well as electron-withdrawing substituents at C4 of the oxazoline ring decrease the catalytic activity of the manganese complexes. Despite the low activity, the complexes have been found to be very useful to contribute to the intricate coordination chemistry of the Mn(phox-R) system.

In chapter 4 the synthesis and catalytic studies on iron complexes with the ligands HphoxCOOH and Hphox*i*pr (*i*pr = isopropyl) has been described. The complexes have been characterized by X-ray analyses, ESI-MS, and ligand field spectroscopy. The complexes have been studied for their catalytic activity in catalytic oxidations of alkanes. The complex (NEt$_3$)$_2$[Fe(phoxCOO)$_2$](ClO$_4$) displays modest activity in catalytic alkane oxidations while the complex [Fe(phox*i*Pr)$_3$] is inactive. The iron complex of the ligand HphoxCOOH is the first structural model of iron complex of a siderophore analog.

In Chapter 5, the synthesis and magnetic properties of three novel manganese and iron clusters has been described. Manganese and iron complexes of the ligand HMesalim were found to give a rich structural chemistry. Starting from the mononuclear complex [Mn(Mesalim)$_2$(OAc)(MeOH)]•MeOH, the hexanuclear complex [Mn$_6$O$_4$(OMe)$_2$(OAc)$_4$(Mesalim)$_4$], as well as the octanuclear complex [Mn$_8$O$_2$(OH)$_2$(OMe)$_{12}$(OAc)$_2$(Mesalim)$_4$], could be obtained by recrystallization, depending upon the reaction conditions and solvents used. Similarly, starting from the purple-colored mononuclear complex [Fe(Mesalim)$_2$Cl] the orange-colored decanuclear iron(III) cluster [Fe$_{10}$O$_4$(OMe)$_{14}$Cl$_2$(Mesalim)$_6$] has been obtained upon recrystallization. The complex [Mn$_6$O$_4$(OMe)$_2$(OAc)$_4$(Mesalim)$_4$] has a novel face-sharing double-cubane [Mn$_6$O$_6$] core, unique in transition metal chemistry. The compounds [Mn$_8$O$_2$(OH)$_2$(OMe)$_{12}$(OAc)$_2$(Mesalim)$_4$] and [Fe$_{10}$O$_4$(OMe)$_{14}$Cl$_2$(Mesalim)$_6$] are composed of [M$_3$O$_4$] partial cubanes. All complexes belong to a class of oxo-bridged cubic close-packed (ccp) molecular clusters resembling the metal oxide/hydroxide ores. The complex $[Mn_8O_2(OH)_2(OMe)_{12}(OAc)_2(Mesalim)_4]$ is the first octanuclear manganese(III) cluster that exhibits ferromagnetic interactions within the cluster as first evidenced from DC magnetic susceptibility studies in the range of 1.8 – 300 K. The frequency dependence of the AC susceptibility of the novel octanuclear cluster $[Mn_8O_2(OH)_2(OMe)_{12}(OAc)_2(Mesalim)_4]$ was measured at different temperatures down to 1.83 K under zero applied dc field. The complex presents SMM behavior as indicated by an out-of-phase signal in the AC magnetic susceptibility studies. An Arrhenius plot gave relatively large experimental activation energy of 36.0 K. The magnetic properties of the clusters $[Mn_6O_4(OMe)_2(OAc)_4(Mesalim)_4]$ and $[Fe_{10}O_4(OMe)_{14}Cl_2(Mesalim)_6]$ are dominated by antiferromagnetic interactions leading to zero-spin ground states.

6.2 General Discussion

Due to environmental reasons, the development of manganese and iron-based oxidation catalysts for industrial applications is regarded with immense interest. The ideal oxidant for catalytic oxidations would be dioxygen, which would perform oxidations in an efficient way just like nature carries out most oxidations. However, for practical applications, the oxidant of choice for catalytic oxidations is dihydrogen peroxide, because it is relatively cheap, environmentally friendly, and readily available, gives water as the only by-product and does not need an external reductant (as is often necessary with the use of O_2 as an oxidant). However, the main drawback of the combination of a Mn or Fe catalyst and dihydrogen peroxide is that these complexes also usually display a “catalase” like reaction with dihydrogen peroxide. In addition, the combination of Fe with H_2O_2 generates also $OH^{\bullet}$ radicals (Fenton chemistry); leading to lower selectivity and also lower substrate conversion. Thus, the dihydrogen peroxide added to the catalytic solution is partly decomposed to dioxygen and water, and hence, the total efficiency of the oxidant in oxidizing a substrate (alkane, alkene etc.) may be strongly reduced.

The catalase reaction and catalytic oxidations are very closely related reactions. Both reactions need a metal catalyst, and consume dihydrogen peroxide. Both reactions are promoted by addition of a basic additive.[5, 6] Thus, the mechanisms of both reactions are very similar, at least up to a certain point during the reaction. However, the conditions driving selective epoxidation reactions over the catalase reaction are not completely resolved.

To search for conditions to suppress the catalase reaction and increase the dihydrogen peroxide efficiency is a topic dealt with in several ways. The two most important strategies include: (1) Use of syringe pump for controlled addition of the dihydrogen peroxide solution, by which the oxidant is added very slowly (for about six hours), and (2) addition of a few equivalents of a carboxylic acid as an additive to the reaction mixture. Addition of an acid has been reported to successfully suppress the catalase reaction; several examples have been reported in literature where their use in catalytic oxidations has been found to be advantageous.[2, 7-9] However, addition of an acid may also suppress the catalytic oxidation reactions as described in chapter 3. The use of acetic acid in excess amount to that of the catalyst has been suggested to promote peracetic acid formation on reaction with dihydrogen peroxide, thereby, inhibiting the catalase reaction.[7, 10] The crucial point is to understand the structural factors governing efficiency of epoxidation reaction over the catalase reaction, and to identify the structural and electronic factors differentiating the two reactions.

The work described in chapter 2 shows that the catalase activity increases in the manganese-Mesalim complexes on use of NaOH as well as N-Meim. Dinuclear manganese complexes bridged by μ-oxide or hydroxide ions have been reported to be the main active species during catalysis.[6, 11-14] In addition, it has been reported previously that the principal factors governing catalase activity are (1) the availability of an intramolecular base sufficiently basic to deprotonate H_2O_2 and (2) unobstructed substrate binding to the bridging site between the Mn ions as the deprotonated, end-on (μ-η_2) hydroperoxy anion.[6] The crystal structures reported in chapters 2 and 5 of the Mn-Me/Etsalim complexes, show that di/poly-nuclear complexes are readily formed with the HMesalim or HEtsalim ligand. The presence of the proton on the imine nitrogen possibly could also help in the formation of dinuclear oxo- or hydroxo-bridged species by hydrogen bonding interactions with the added substrate or hydroxide molecules. As a result, the manganese-Mesalim complexes described in this thesis are among the most efficient manganese catalase mimics reported so far in literature.

The main difference in the ligands HMesalim and $HphoxCOOCH_3$ is the labile imine proton which is present in HMesalim and is absent in $HphoxCOOCH_3$. The manganese complexes of HMesalim do not yield any conversion of styrene, whereas the manganese complexes of HphoxCOOMe are able to epoxidize styrene to styrene oxide. Thus, all the dihydrogen peroxide added to the solutions of manganese complexes of HMesalim, is quantitatively converted to water and dioxygen without getting incorporated in the oxide product. The imine proton in HMesalim probably helps hydrogen bonding interactions with the dihydrogen peroxide molecule.

The [Mn(R-phox)n] complexes developed in Leiden, show good activity in the epoxidation of styrene, with turnovers up to 200.[1] A substituted phox ligand containing an electron-withdrawing nitro-group was found to show activity for a long time resulting in even higher turnover numbers.[1] The prolonged activity has been associated with the higher stability of the catalyst due to the electron-withdrawing nitro group. Therefore, substituent effects on the oxazoline backbone has been a topic of consideration in the present study. Recently, Ito *et al*. reported a carboxylate-substituted Mn(salen) catalyst, which resulted up to 9,200 turnovers and 99% ee in the epoxidation of 2, 2-dimethylchromene derivatives.[15] Therefore, the ligands Hphox-COOR (R = H, CH_3) containing electron-withdrawing carboxylate or ester groups have been synthesized in the present work and their manganese and iron complexes have been studied in catalytic epoxidations. However, these complexes show lower activity than the original [Mn(phox)$_3$] catalysts for reasons described in chapter 3.

The studies described in this thesis provide an important insight in the understanding of the mechanism of manganese catalyzed epoxidations. Nitrogen-containing bases have been used for long time in catalytic epoxidations by metal complexes as additives and were considered to coordinate to the metal center during catalysis thereby reducing the high Lewis acidity of the metal.[3, 16] However, other bases such as carboxylate salts[5] and sodium hydrogen carbonate[4] have also been used efficiently in metal-catalyzed epoxidations. The exact role of these additives to coordinate to the metal ion or simply maintain the optimum pH has been a matter of crucial issue. The results described in this thesis provide confirming evidence for the proposal, that the main role of the additive is mainly to maintain the pH during catalysis, and it is not necessary for the additive to coordinate to the metal center for effective catalysis to occur. In addition, an interesting point to note here is that the coordination of the nitrogen-containing base has been controlled, not even by changing a functional group on the ligand but simply by varying the chirality on the ligands used. These results demonstrate how delicate the factors responsible for increasing catalytic epoxidation activity are. As the catalysis takes place in solution it is of utmost importance that the solution chemistry is well understood. It must be emphasized in this respect that ESI-MS studies coupled with deuteration of solvent and the ligand, as well as ^{1}H NMR spectroscopy have successfully been established to be very effective in understanding the coordination chemistry of the complexes in solution.

The catalytic activity of the Fe-phoxR complexes in the oxidation of alkanes described in chapter 4, is also interesting. In contrast to the Mn-analogs, the iron complex of the HphoxCOOH ligand has been found to show better activity than that of the HphoxCOOMe ligand.

Another interesting topic of potential future prospects has been described in chapter 5. The accidental discovery of the manganese and iron clusters of the HMesalim ligand, wherein the octanuclear manganese complex has been shown to be an SMM, is an important additional finding in this work. Although the ligand does not exhibit any bridging mode in these complexes, the small size and feasibility to easily coordinate with metal salts, forming complexes with varying geometries, makes it a useful ligand for further exploration of coordination chemistry.

6.3 Future Outlook

6.3.1 Development of More Stable and Active Manganese Epoxidation Catalysts

Mechanistic studies on manganese-catalyzed epoxidations has been the central topic of research described in this thesis.

As dinuclear manganese complexes containing μ-oxo/hydroxo bridges are active catalysts in catalase reactions,[6, 11-14] ligands that would hinder the formation these bridged manganese complexes should be the ligands of choice for catalytic epoxidations, to favor epoxidations over the catalase reaction.

Additionally, manganese complexes of the ligands containing pyridine-amine groups, such as *R*,*R*'-mcp (*R*,*R*'-mcp = *N*,*N*'-dimethyl-*N*,*N*'-bis(2-pyridylmethyl)-1*R*,2*R*-diaminocyclohexane) have been reported to show good activity in catalytic epoxidations.[10] Thus, replacing the phenol ring in the phox ligand with a more oxidatively stable group such as pyridine and replacement of the oxazoline ring with a 1,3 oxazolidine ring could be useful in increasing the activity of the complexes. Although an oxazoline C=N is generally considered to be more stable than the salen imine group, the oxazoline ring still poses limitations to the oxidative stability of an imine C=N. In order to develop more stable epoxidation catalyst, it might be important to replace the imine C=N completely with an amine or an amide. Pure amide-based ligands can are known to yield a completely inactive catalyst.[17] Recently, manganese complexes of mixed amide/imine functionalities have been reported to give moderate activity and selectivity in the epoxidations of methylstyrenes (TON up to 25 and ee 30-60 %).[18] The same approach could be developed further for synthesis of new mixed amine/amide/imine ligands for improving the present manganese epoxidation catalysts.

Increasing the denticity of the ligands could be beneficial for two reasons: (1) to decrease the dynamics of the solution structure, so that the catalyst structure in the solid state does not too much differ from the one in solution, and (2) the polydenticity could increase the stability of the catalyst towards oxidative degradation of the metal complex catalyst. The ligand HMesalim reacts easily with several modifiable functional groups. The ligand thus offers a good starting point for synthesis of a variety of novel and new polydentate ligands that could be useful in development of new Mn, Fe oxidation catalysts.

In cases of complexes where the catalase activity is dominant when using dihydrogen peroxide, peracetic acid may be used as an alternative oxidant; for achieving higher conversion and selectivity. Use of additives, such as nitrogeneous bases, carboxylate salts or acids is often used for increasing and optimizing the activity and selectivity in catalytic epoxidations by Mn, Fe complexes.

The exact nature of the catalytically active species in catalytic epoxidations still remains to be elusive. Detailed kinetic studies are necessary for the better understanding and future development of the efficient manganese epoxidation catalysts. Thorough kinetic studies would reveal several aspects of these reactions, such as rate constants and order of the reaction, pH and solvent dependency, and the exact active species responsible for catalytic activity. Furthermore, a broader range of substrates should be studied to investigate and correlate the selectivity and activity correctly to the structures of the catalysts. Combinatorial techniques could be useful in this respect to study the catalytic epoxidations with different ligands, varying the additives, substrates at different concentrations, thus increasing the efficiency in all the screening studies. From the combined catalytic, mechanistic and kinetic studies of metal complexes using systematically varied structures of the ligands, certainly more powerful epoxidation catalysts are likely to be discovered soon.

6.3.2 Development of New Varieties of Magnetic Clusters

SMMs (single molecule magnets) are highly promising materials for their applications in information-storage devices as they would, in principle, require very small space to store vast amount of data. The main goal in the field of synthetic molecular magnets is to develop new SMMs with high blocking temperatures that would allow their use in practical applications in memory storage devices, and to understand the magnetic interaction in these molecules. The low blocking temperatures (less than 5 K) is the real issue in the industrial applications of SMM. In spite of its potential applications, no SMM has been patented for real industrial application yet. For achieving higher blocking temperatures, increasing the number of coupled spins and keeping the interactions between the individual spins strong is the best way forward.

Some interesting results from the research described in chapter 5 have potential for the future. HMesalim-based ligands are excellent starting ligands for the further development of new varieties of metal clusters. The ligand is easily modifiable in order to control the geometries and nuclearities of the complexes formed.

For this reason, the role of bridging ligands is of paramount importance. So far, μ, μ_3, μ_4 and even μ_6 bridging O^{2-} groups have been found to be very efficient for promoting strong coupling between transition metal ions. CN^- is also an interesting bridging ligand; it allows easier control in the cluster self-assembly reactions over the oxides and it is more predictable in terms of the nature of spin coupling between the metal centers.[19-22] the requirement for obtaining SMM behavior is an easy axis (Ising) type magnetic anisotropy. Metal ions, such as iron(III), manganese(III), cobalt(II) are interesting for this reason, although the bulk anisotropy of the cluster will actually depend on the geometry of the whole structure. Therefore, even if it is certainly a good approach to exploit transition-metal ions which have non-degenerate ground states, serendipity still plays an important role in the development of SMMs.[23-28]

Synthesis of metal complexes with lower nuclearities could help in the correct determination of the magnetic parameters for the clusters. It is difficult to control the nuclearities and geometries in manganese-carboxylate clusters similar to the ones described in this thesis (chapter 5). However, a more detailed study by systematically changing the functional groups on the HMesalim ligand could help in rationalizing the conditions for the formation definite geometries and their magnetic interactions. Substituting the alkoxy group on the HMesalim ligand with a hydroxy group, for instance would open new possibilities for bridging modes, which would be useful to obtain novel metal clusters without a carboxylate bridge, which in turn would be useful in achieving more control over the geometries of the complexes formed.

6.4 References

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