*Short Communication*

On the Proximal Effect of the Nitrogen Ligands on the Oxomanganese Porphyrin System

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It is well known that the reaction properties of many metalloenzymes are greatly influenced by the nature of the ligand *trans* to the catalytic site.[1] Manganese porphyrins in combination with an oxygen donor have been used to mimic the catalytic oxidation properties of e.g., the cytochrome P-450 and peroxidase enzymes.[1,2] Manganese(III) porphyrins, 1, have been shown to act as catalysts for e.g. alkene epoxidation, and it has been found that the reaction rate and stereoselectivity of 1 are increased by the presence


1
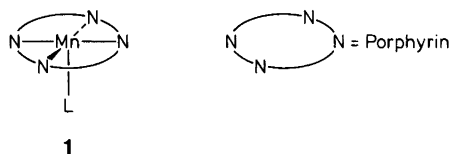
of pyridine or imidazole compared with chloride all of which presumably behave as axial ligands of the metalloporphyrin.[2,3] Although numerous investigations have been performed on the effect of pyridine, as well as other nitrogen bases, on the properties of the oxomanganese porphyrins,[2,3] there has, to our knowledge, not yet been given any explanation of the influence the axial nitrogen base ligand has on the oxomanganese moiety.

This communication offers an explanation on the influence of pyridine on both the geometrical and electronic structure of the oxomanganese porphyrins. For these purposes we have performed a number of *ab initio* calculations.[4] The calculations were performed with the Gaussian 86 program using an STO-3G* basis set, where the * denotes an extra set of five d-functions for manganese added to the ordinary STO-3G basis set.[4] Due to their diffuseness these additional d-functions provide flexibility to the manganese valence shell. During the optimization of the oxomanganese porphyrin system we simulated the porphyrin moiety using four NH_2^- fragments due to the extensive size of the complete system. The use of four NH_2^- fragments as a model for the porphyrin moiety has been found useful in other theoretical investigations where structural, as well as electronic, properties of metalloporphyrins are discussed.[5] The four NH_2^- fragments were kept fixed relative to

the manganese atom and only the Mn–O and Mn–Cl/N (pyridine) bond lengths were allowed to vary during the optimization. The optimized Mn–O and Mn–N (pyridine) bond lengths with the four NH_2^- fragments present were then used in the calculations where the complete porphyrin moiety is present.

Table 1 gives the optimized geometries and electronic data of interest for the present study of the oxomanganese porphyrin chloride and pyridine complexes, in which the four NH_2^- fragments are used as a model for the porphyrin moiety, 2 and 3, respectively. For the sake of completeness we also optimized the oxomanganese porphyrin cation with no ligand attached, 4. Table 1 also lists the results where the complete porphyrin moiety is present; 3a is with pyridine as the axial ligand and 4a is for the cationic system (see later). The optimized structures are shown in 2–4.

2   **3**

4
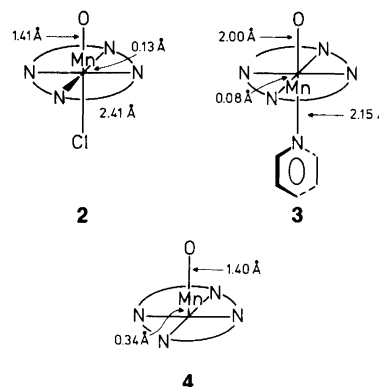
The Mn–O bond lengths in 2 and 4 were calculated to be 1.41 and 1.40 Å, respectively, indicating that the chloride ligand has no influence on the Mn–O bond length compared with the cationic system. The Mn–O bond length in 2 corresponds well to that obtained recently in a similar type of system.[6] The small difference between the Mn–O bond lengths in 2 and 4 is also the reason why we carried out the calculations on the cationic system, 4a rather than that with chloride present. The Mn–Cl bond length in 2 (2.54 Å) agrees well with the findings for chloro-α, β, γ, δ-tetraphenylporphinato(pyridine)manganese(III), 5.[7]

Table 1. Mn–O bond lengths and some electronic data for **2–4a**.

	2	**3**	**4**	**3a**	**4a**
Mn–O bond length/Å	1.41	2.08	1.40	2.08	1.40
Mn–O bond order	0.33	0.07	0.35	0.19	0.41
Mn–O π-bond order	0.32	0.00	0.32	0.04	0.27
Mn net charge	0.50	0.42	0.42	0.54	0.62
O net charge	−0.24	0.12	−0.18	−0.05	−0.35
N net charge (NH$_2$ or porphyrin)	−0.51	−0.57	−0.51	−0.22	−0.21
Charge (pyridine)		0.19		0.27	
Total charge	−2	−1	−1	+1	+1
No. of 2p electrons at O	4.3	3.9	4.3	4.1	4.5

Changing the axial ligand to pyridine (**3**) leads to some geometrical changes. The most conspicuous is the increase of the Mn–O bond length to 2.08 Å. At the same time, the manganese atom is shifted slightly to the other side of the porphyrin plane. The axial Mn–N (pyridine) bond length in **4** (2.15 Å) is about 0.3 Å shorter than the same bond in **5**. In its most stable configuration, the pyridine plane bisects the perpendicular NMnN angle; this is in accordance with the orientation of pyridine in **5**.[7]

The reason for the increase in the Mn–O bond length when pyridine is present as the ligand can be traced to orbital interaction between the LUMO of **4** with the HOMO of pyridine as shown in the Fig. 1 (only the contribution from the nitrogen of the HOMO in pyridine is shown).

It appears from the Fig. 1 that the LUMO of **4**, which is Mn–O antibonding, interacts with the π-system of pyridine

leading to the bonding and antibonding combinations. This interaction results in a donation of electron density from the pyridine to the Mn–O antibonding orbital, thus leading to the increase in bond length between manganese and oxygen. The donation of electron density from pyridine to the Mn–O antibonding orbital is evident from the total charge of pyridine in **3** and **3a** in Table 1 where it appears that 0.19 and 0.27 electrons are donated, respectively. Analysis of the atomic charge distribution shows that the porphyrin moiety accepts electron density from the pyridine ligand and the oxygen.

The ground states of all five species **2**, **3**, **3a**, **4** and **4a**, are closed-shell singlets ($^1A_1$). We have found that the atomic net charges on oxygen in **2** and **4** are similar, i.e. the influence of the chloride ligand is small. The atomic net charge on oxygen in **3**, however, differs completely from those in **2** and **4** (Table 1). Replacement of chloride by
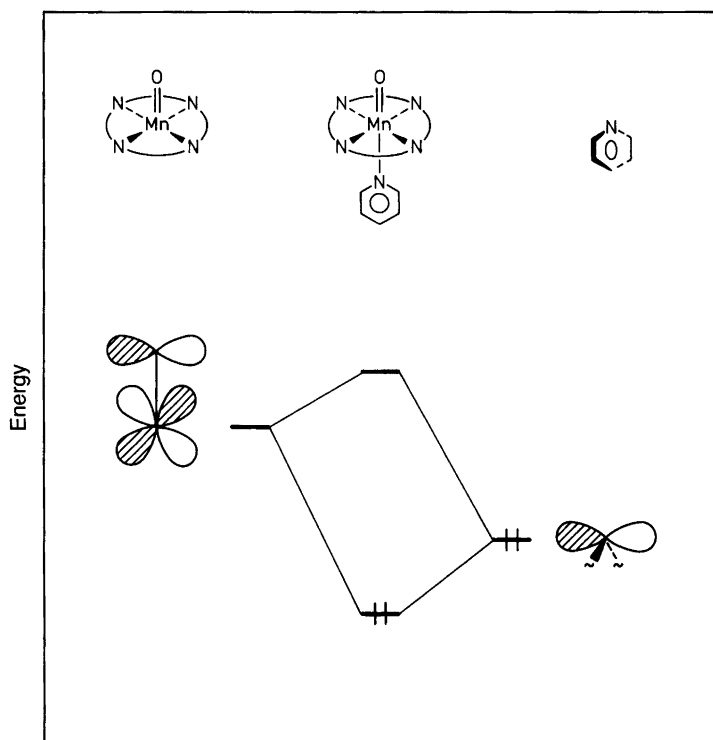

Fig. 1. The interaction of the LUMO of **4** (**4a**), to the left, with the HOMO of pyridine (only shown for the contribution from nitrogen), to the right.

pyridine thus changes the nature of the oxygen atom in the oxomanganese porphyrin from nucleophilic-like (in **2** and **4**) to electrophilic-like (in **3**)! The same trends are observed for the systems where the complete porphyrin moiety is present, **3a** and **4a** (Table 1). The introduction of pyridine as the axial ligand also changes the electronic distribution at the oxygen. In **2** and **4** the Mulliken population of the $2p$ level on oxygen is 1.4 in all three orbitals, whereas in **3** the population of p_x drops to zero; this is compensated for by an increase in p_y and p_z to about 2. The overall Mulliken population of the oxygen $2p$-level is reduced by approximately 0.4 electrons when pyridine is introduced as a ligand (Table 1) for both the model and the complete systems. The Mn–O π-bond order of the oxomanganese system is also affected by the nature of the axial ligand: pyridine substantially reduces the bond order (Table 1). The oxygen in the porphyrin systems where pyridine is present (**3** and **3a**) is obviously very weakly bound to the rest of the manganese porphyrin compared with **2**, **4** and **4a**.

The present results provide us with some information about the influence of the axial pyridine ligand on some of the properties of the oxomanganese porphyrin. An axial pyridine ligand in the oxomanganese porphyrin leads to three important electronic changes of the oxomanganese function compared with the cation or with the system in which chloride is present as the axial ligand: (i) the oxygen becomes less negatively charged, (ii) the oxygen becomes a better acceptor of π-electron density and (iii) the oxomanganese bond is weakened. The observed donation of electron density into the oxomanganese antibonding orbital leading to a weaker bond is in accordance with results obtained very recently by Raman excitation studies of cytochrome P-450.[8] The results presented here offer an explanation for the increased reaction rates in manganese(III) porphyrin catalyzed epoxidations when pyridine is present. To account for the change in stereospecificity, calculations of the transition states for the different approaches of an alkene to the oxomanganese porphyrin are necessary and in progress.

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