

A comparative study of high-spin manganese and iron complexes

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Abstract. Different metal complexes of the general form $M(\text{OH})_n(\text{H}_2\text{O})_{6-n}$ have been studied for manganese and iron. Oxidation states considered for manganese are Mn(III), Mn(IV) and Mn(V) and for iron Fe(II), Fe(III) and Fe(IV). Oxygen containing ligands are used throughout with varying numbers of hydroxyl and water ligands. Some metal-oxo and some charged complexes were also studied. Large Jahn-Teller distortions were found for the Mn(III) and Fe(IV) complexes. Consequences of these distortions are that water ligands have to be placed along the weak JT-axis and that five-coordination by a loss of one of these water ligands is quite competitive with six-coordination in particular for manganese. For Fe(II) and Fe(III) lower coordinations than six are preferred due to the presence of two repulsive e_g electrons. For the metal-oxo complexes five-coordination is also preferred due to the strong trans effect from the oxo ligand. All complexes studied have high-spin ground states. An interesting effect is that the spin is much more delocalized on the ligands for the iron complexes than for the manganese complexes. This effect, which is chemically important for certain iron enzymes, is rationalized by the large number of 3d electrons on iron. For manganese with only five 3d electrons no spin delocalization is needed to obtain the proper high-spin states.

Key words: Oxygen ligands – Jahn-Teller effects – Trans effects – Spin-delocalization – Metal complexes

1 Introduction

Manganese and iron enzymes are common in biochemical systems. The most well known of the manganese enzymes is the tetranuclear system present in Photosystem II, which is active in the oxygen evolving step [1]. In a sequence of five steps, O_2 is produced from water after

hydrogen atoms have been abstracted by tyrosyl radicals [2–4]. Important iron containing enzymes are, for example, ribonucleotide reductase (RNR) and methane monooxygenase (MMO) [5, 6]. In these systems O_2 is activated by iron dimer complexes leading to a hydrogen abstraction from tyrosine in the RNR case and to formation of methanol from methane in the MMO case. Interestingly, the reactions catalysed by the manganese and the iron-containing enzymes are in some respect the reverse of each other. The main purpose of the present study is to gain insight into the different behaviour of this type of manganese and iron complexes. As a first step, monomer complexes are studied with simple ligands representative of those present in the enzymes. These simple ligands are chosen as water and hydroxyl groups and in a few cases also oxo groups, which lead to the characteristic high-spin ground states. The present study is built on two recent studies on the respective enzyme reactions. In the first of these, hydrogen abstraction from water coordinated to manganese was studied using both monomer and dimer manganese models [7]. In the second one, the mechanism of activation of methane was studied using an iron dimer model of MMO [8].

Transition metal complexes are rightly considered as some of the most difficult systems to model accurately by quantum chemical methods [9]. First row transition metal complexes are particularly difficult to handle for several reasons. From a standard quantum chemical ab initio viewpoint, there can be a very strong coupling between near degeneracy effects and large dynamical correlation effects for these transition metal complexes. From a density functional theory (DFT) viewpoint, one difficulty is the strong coupling between correlation effects and exchange effects, at least for cases with unfilled d -shells. One of the first persons to point out these difficulties was Jan Almlöf, to whom this issue of the journal is dedicated. In a set of careful studies, mainly on ferrocene [10–12] and iron pentacarbonyl [13], he showed, at a time when calculations on this size of systems was extremely difficult, that electron correlation is of fundamental importance for these systems and also that very large basis sets are required even for a

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qualitatively correct description of structures. The direct SCF technique [14], invented and developed by Jan Almlöf, was used extensively in these studies. The rapid development of quantum chemical methods in recent years has to a large extent overcome these difficulties [15, 16], mainly by the introduction of a few carefully chosen empirical parameters. The development of DFT has been particularly successful in this respect and in the present study this type of method is used throughout. The B3LYP method developed by Becke is used since this method has been shown by benchmark calculations to be the most accurate one [16, 17].

One of the most important questions raised in the present study concerns the number of ligands directly coordinated to the metal atoms. Conventionally, the manganese and iron atoms in these complexes are considered as octahedrally coordinated. However, in the present biochemical environment the situation is quite different from the one where these complexes have been directly studied before by experimental techniques. The dielectric constant of a protein is not very high ($\epsilon \approx 4$), much smaller than the one in water ($\epsilon \approx 80$), for example. One consequence of this is that information on metal complexes cannot be directly transferred to the biochemical situation from studies of isolated charged ions in crystals or solution as normally done previously, since this type of charged ions is normally not present in biochemical systems. The danger of doing this will be illustrated below on, for example, $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$, which is shown to have a quite different coordination mode from $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ even though the oxidation states are the same. This is therefore a situation where information based on accurate quantum chemical studies of relevant model systems should be most useful for providing information that is otherwise hard to obtain.

2 Computational details

The calculations were performed in two steps. First, an optimization of the geometry was performed using the B3LYP method and double zeta basis sets. In the second step the energy was evaluated, also at the B3LYP level, in the optimized geometry using large basis sets with several polarization functions. All calculations were performed using the GAUSSIAN-94 program [18].

The B3LYP functional used in the present calculations can be written as [19],

$$E^{\text{B3LYP}} = (1 - A) * F_x^{\text{Slater}} + A * F_x^{\text{HF}} + B * F_x^{\text{Becke}} + C * F_c^{\text{LYP}} + (1 - C)F_c^{\text{VWN}}$$

where F_x^{Slater} is the Slater exchange, F_x^{HF} is the Hartree-Fock exchange, F_x^{Becke} is the gradient part of the exchange functional of Becke [16], F_c^{LYP} is the correlation functional of Lee et al. [20] and F_c^{VWN} is the correlation functional of Vosko et al. [21]. A, B and C are the coefficients determined by Becke [16] using a fit to experimental heats of formation. However, it should be noted that Becke did not use F_c^{VWN} and F_c^{LYP} in the expression above when the coefficients were determined,

but used the correlation functionals of Perdew and Wang instead [22].

The B3LYP energy calculations were made using the large 6-311+G(2d, 2p) basis sets in the Gaussian-94 program. This basis set has two sets of polarization functions on all atoms including two *f*-functions on the metal, and also diffuse functions, which are found to be important when interactions with oxygen containing systems like water are studied. All results below will refer to the use of this basis set unless otherwise specified. In the geometry optimizations a much smaller basis set, the LANL2DZ set of the Gaussian-94 program, was used. For the manganese and iron atoms this means that a non-relativistic ECP according to Hay and Wadt [23] was used. The valence basis set used in connection with this is essentially of double zeta quality including a diffuse 3*d* function. The rest of the atoms are described by standard double zeta basis sets.

Zero-point vibrational effects were calculated at the B3LYP level for most of the systems. To allow for an analytical evaluation of the Hessians, these calculations were performed with an all-electron basis of double zeta quality using the Wachters basis [24] for manganese and iron. The zero-point vibrational effects on the relative energies discussed below were found to be small, in most cases below 1 kcal/mol, and are included in the results reported. In a few cases the Hessians were not calculated, since the effects are very small and the calculations very time-consuming. The zero-point vibrational effects were in these cases estimated from similar systems.

3 Results and discussion

The present section on the results is divided into two subsections, one for the manganese and one for the iron complexes. Three different oxidation states are considered for manganese Mn(III), Mn(IV) and Mn(V), since these are all highly relevant in oxygen evolution in Photosystem II [7]. For iron mainly two oxidation states, Fe(III) and Fe(IV), are discussed since these are the most important ones for MMO and RNR [8]. To simplify comparisons, oxygen-containing ligands are used for all systems. Varying numbers of water, hydroxyl and oxo ligands are therefore used to obtain the desired oxidation states and bond types. For most complexes six ligands were used to allow for possible octahedral coordination. The six-coordinated octahedral coordination (see Fig. 1) is then compared with five-coordination where the sixth ligand is in the second coordination shell (Figs. 2, 3). For manganese, investigations were furthermore performed to study how the ligand in the second coordination shell wants to be hydrogen bonded, to one directly coordinated hydroxyl and one water ligand (see Fig. 2) or to two directly coordinated hydroxyl ligands (see Fig. 3). Owing to the choice of the present oxygen-containing ligands, the complexes studied all have high-spin ground states. For many of them the high-spin to low-spin excitation is also determined.

Before the detailed results of the calculations are discussed, some general features of the present systems will be described. In most cases the electronic structure

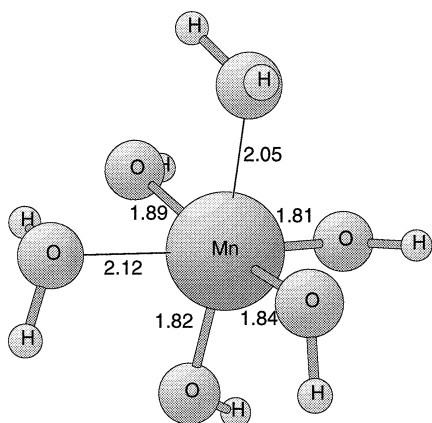


Fig. 1. Six-coordinated 4A Mn(IV)(OH)₄(H₂O)₂ complex with the two water ligands in a cis conformation. Distances in Å

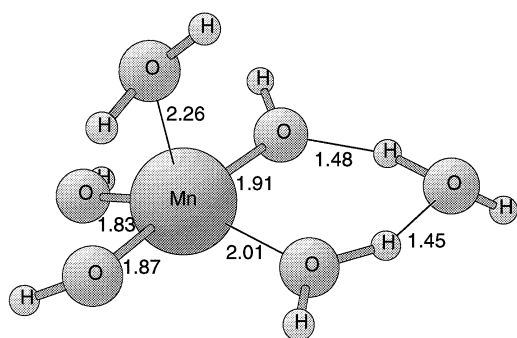


Fig. 2. (5+1)a coordinated structure of the 5A Mn(III)(OH)₃(H₂O)₃ complex, with the water ligand in the second shell hydrogen bonding to one hydroxyl and one water ligand. Distances in Å

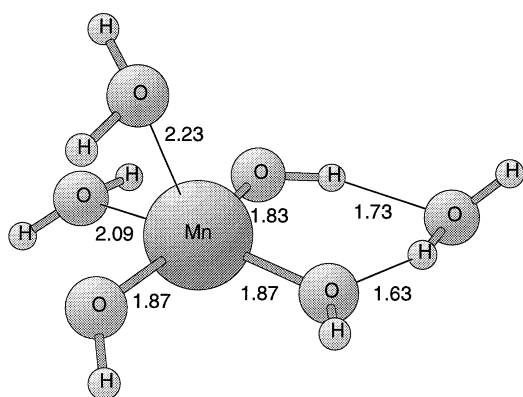


Fig. 3. (5+1)b coordinated structure of the 5A Mn(III)(OH)₃(H₂O)₃ complex, with the water ligand in the second shell hydrogen bonding to two hydroxyl ligands. Distances in Å

of the complexes can be characterized based on an octahedral field. This is true also in most cases where only five ligands are directly bound to the metal. In that case, one octahedral position can be regarded as unoccupied. In an octahedral field the d -levels are split into a lower energy, triply degenerate t_{2g} set and a higher energy, doubly degenerate e_g set. In the present case with ionic hydroxyl and oxo ligands and high-spin ground states, this means that the higher e_g level begins to be filled by

the fourth d -electron. The complexes with four d -electrons, which occurs for the Mn(III) and Fe(IV) oxidation states, are therefore expected to exhibit large Jahn-Teller (JT) distortions. As will be shown below, JT distortions play a fundamental role in these systems and are quite important for the different chemistry occurring in the MMO, RNR and PSII enzymes. The complexes with five d -electrons, on the other hand, which thus have two repulsive e_g electrons, are characterized by unstable octahedral configurations. For these complexes the tendency for five-coordination will thus be quite large. The characteristic feature of the oxo complexes is a strong trans effect, which will tend to make the position trans to the oxo bond unoccupied.

The present ligands are conventionally regarded as giving rise to a weak ligand field, which is experimentally identified by the high-spin ground states. The fact that hydroxyl ligands give rise to a weak ligand field is not immediately obvious. The M—OH bonds are quite covalent, as seen by their geometries with strongly bent M—O—H angles. Strongly ionic bonds would have had linear M—O—H geometries. It is clear that the covalency in the M—OH bond is much larger than the one in M—CO, for example, even though carbonyl is considered as a strongly covalent ligand giving rise to a strong ligand field. The reason the carbonyl ligands will tend to lower the spin is clearly the presence of π -covalency. For the hydroxyl groups there is only strong covalency in the M—OH σ bond, but this bond is still sufficiently ionic to lead to a basically ionic description of the electronic structure. The π -covalency for the hydroxyl group should be very small, which is thus the main explanation for the high-spin ground states of these complexes. The fact that there is no covalency in the M—OH₂ bond is more obvious and the water ligands will therefore not tend to lower the spin either.

3.1 Manganese complexes

In Tables 1 and 2 all the manganese complexes studied are listed. In Table 1 the metal spin and $3d$ populations are given together with the relative energies for complexes with the same composition, using the truly six-coordinated complexes as reference when possible. The total charges obtained from the Mulliken population analysis are not given, since these charges are quite arbitrary and depend strongly on the basis sets used. In particular the metal spins, but also the $3d$ populations are less basis set dependent. As an example, the manganese spin and $3d$ population for the first complex in Table 1 is 3.87 and 5.27, respectively, obtained using the medium size double zeta quality basis set. The large basis set with diffuse functions and two sets of polarization functions give 3.91 and 4.90, respectively. The metal spin is thus very similar for the two basis sets, 3.87 and 3.91. The $3d$ populations are in general somewhat smaller for the large basis set, but still quite similar to the smaller basis set. In Table 2 the metal-oxygen distances for the different types of ligands are given for all complexes. In Table 3, finally some oxo and oxyl complexes are compared.

Table 1. Metal spin, $3d$ population and relative energies for some manganese monomer complexes with different oxidation states and coordination. The $(5+1)$ -coordinated complexes have one water ligand in the second coordination shell, see Figs. 2 and 3. Negative relative energies mean higher stabilities

Complex	State	Oxidation state	Coord.	Spin (Mn)	$3d(\text{Mn})$	Relative energy
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_3$	^5A	III	(5+1)a	3.87	5.27	-6.3
			(5+1)b	3.86	5.28	-0.6
			6	3.88	5.31	0.0
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2$	^5A	III	5	3.86	5.31	-
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^6A	III	(5+1)a	3.76	5.31	+0.4
			(5+1)b	3.80	5.32	0.0
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_2\text{O}$	^6A	III	5	3.75	5.33	-
$\text{Mn}(\text{OH})_4(\text{H}_2\text{O})_2$	^4A	IV	(5+1)a	2.97	5.24	+1.0
			(5+1)b	2.96	5.27	+4.1
			6(trans)	2.81	5.35	+8.7
			6(cis)	2.93	5.31	0.0
$\text{Mn}(\text{OH})_4(\text{H}_2\text{O})$	^4A	IV	5	2.92	5.28	-
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$	^5A	IV	(5+1)a	2.73	5.31	+3.6
			(5+1)b	2.60	5.34	+10.3
			6	2.69	5.39	0.0
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})\text{O}$	^5A	IV	5	2.66	5.34	-
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^4A	IV	(5+1)a	2.68	5.38	-1.7
			(5+1)b	2.95	5.39	-2.0
			6	2.62	5.48	0.0
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_2\text{O}$	^4A	IV	5	2.76	5.40	-
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$	^3A	IV	(5+1)a	2.28	5.33	+11.6
			(5+1)b	1.93	-	0.0
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})\text{O}$	^3A	V	5	1.91	5.37	-

Table 2. Metal-oxygen bond distances (\AA) for some manganese monomer complexes with different oxidation states and coordination. The $(5+1)$ -coordinated complexes have one water ligand in the second coordination shell; see Figs. 2 and 3

Complex	State	Ox. state	Coord.	Mn—OH ₂	Mn—OH	Mn—O
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_3$	^5A	III	(5+1)a	2.01,2.26,3.48	1.83,1.87,1.91	-
			(5+1)b	2.09,2.23,3.50	1.83,1.87,1.87	-
			6	2.07,2.26,2.43	1.86,1.88,1.90	-
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2$	^5A	III	5	2.07,2.24	1.83,1.85,1.89	-
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^6A	III	(5+1)a	1.99,2.27,3.44	1.85,1.90	1.85
			(5+1)b	2.02,2.30,3.43	1.82,1.87	1.91
$\text{Mn}(\text{OH})_4(\text{H}_2\text{O})_2$	^4A	IV	(5+1)a	1.98,3.46	1.80,1.80,1.81,1.90	-
			(5+1)b	2.07,3.45	1.78,1.81,1.82,1.85	-
			6(trans)	2.00,2.01	1.84,1.84,1.87,1.87	-
			6(cis)	2.05,2.12	1.81,1.82,1.84,1.89	-
$\text{Mn}(\text{OH})_4(\text{H}_2\text{O})$	^4A	IV	5	2.03	1.80,1.80,1.82,1.83	-
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$	^5A	IV	(5+1)a	1.98,3.45	1.80,1.83,1.88	1.76
			(5+1)b	2.02,3.41	1.82,1.84,1.84	1.73
			6	2.06,2.08	1.83,1.85,1.85	1.77
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})\text{O}$	^5A	IV	5	2.02	1.79,1.82,1.85	1.76
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^4A	IV	(5+1)a	2.04,2.07,3.34	1.82,1.87	1.65
			(5+1)b	2.10,2.13,3.41	1.80,1.90	1.63
			6	2.08,2.16,2.19	1.82,1.87	1.66
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_2\text{O}$	^4A	IV	5	2.13,2.14	1.81,1.82	1.64
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$	^3A	V	(5+1)a	1.96,3.41	1.78,1.81,1.91	1.62
			(5+1)b	2.03,3.38	1.74,1.78,1.86	1.60
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})\text{O}$	^3A	V	5	2.10	1.78,1.78,1.81	1.60

Table 3. Spin densities and relative energies for the oxo-complexes. The $(5+1)$ -coordinated complexes have one water ligand in the second coordination shell; see Figs. 2 and 3. Negative relative energies mean higher stabilities

Complex	State	Oxidation state	Coord.	Spin(Mn)	Spin(Oxo)	Relative energy
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^6A	III	(5+1)a	3.76	0.98	+21.3
	^4A	IV	(5+1)a	2.68	0.32	0.0
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^6A	III	(5+1)b	3.80	1.02	+21.1
	^4A	IV	(5+1)b	2.95	-0.04	0.0
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_3\text{O}$	^4A	IV	6	2.62	0.37	-
$\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_2\text{O}$	^6A	III	5	3.75	1.00	+19.0
	^4A	IV	5	2.76	0.20	0.0
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$	^5A	IV	(5+1)a	2.73	0.90	+8.4
	^3A	V	(5+1)a	2.28	-0.36	0.0
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})_2\text{O}$	^5A	IV	(5+1)b	2.60	0.85	+27.8
	^3A	V	(5+1)b	1.93	0.13	0.0
$\text{Mn}(\text{OH})_3(\text{H}_2\text{O})\text{O}$	^5A	IV	5	2.66	0.92	+24.4
	^3A	V	5	1.91	0.08	0.0

One of the first things to notice in Table 1 is the constancy of the $3d$ populations. In all complexes, irrespective of metal oxidation state, manganese has close to five $3d$ electrons, varying between 5.24 and 5.48 using the medium-sized basis set as listed in the table. As mentioned above, the large basis set with diffuse and polarization functions give somewhat smaller d -populations, but still close to five $3d$ electrons on the manganese atom in all the complexes. This shows that the manganese atom in the complexes keeps the same number of $3d$ electrons as in its ground atomic state, ${}^6S(3d^5s^2)$. It should be noted here that for manganese a completely ionic and a completely covalent picture of the bonding between the metal and the ligands gives the same total spin for the complex. This is different to iron, as will be discussed below.

For each oxidation state of manganese and total spin state of the complex, there are in most cases four different complexes included in the list of complexes studied: one is truly six-coordinated (Fig. 1), two are $(5+1)$ -coordinated (Figs. 2, 3), having one of the water ligands bound in the second coordination shell and the fourth complex has only five ligands (Fig. 4), and is included mainly to show the similarities in electronic and geometric properties to the complexes with six ligands. As can be seen in Table 1, the oxidation state of the manganese atom can be directly read from its spin density, and corresponds to the oxidation state expected based on the types of ligands and the total spin of the complex. Thus, the Mn(III) complexes have spin densities on the manganese atom in the range 3.75–3.88 electrons, indicating a very slight delocalization of the spin density. Similarly, the Mn(IV) complexes have manganese spin densities of 2.6–3.0 electrons and the Mn(V) complexes about 2 electrons.

There are two groups of complexes listed in Tables 1 and 2 in which manganese has oxidation state III, the 5A Mn(OH)₃(H₂O)₃ complexes and the 6A Mn(OH)₂(H₂O)₃O oxyl complexes. In the ionic picture, the Mn(III) complexes have four $3d$ electrons left and, as mentioned above in an octahedral field these complexes are Jahn-Teller unstable. Therefore, owing to the single high energy e_g electron the axial ligands are repelled, and in some cases one of them is lost, which can be considered as an extreme case of Jahn-Teller distortion.

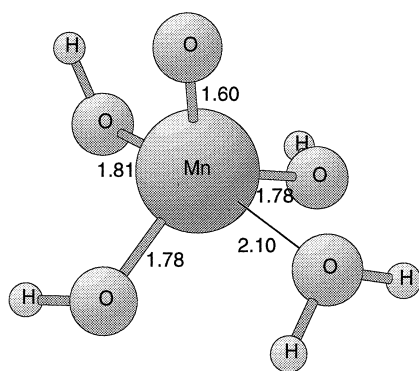


Fig. 4. Five-coordinated structure of the 3A Mn(V)(OH)₃(H₂O)O oxo complex. Distances in Å

Looking at the energetics for the 5A Mn(III)(OH)₃(H₂O)₃ complexes in Table 1 it can be seen that the complexes with $(5+1)$ coordination, i.e. with one empty position on the JT axis, are more stable than the six-coordinated complex that it was actually possible to converge to in this case. For this six-coordinate 5A Mn(III)(OH)₃(H₂O)₃ complex the bond distance to one of the water ligands is as long as 2.43 Å (see Table 2). One of the $(5+1)$ complexes is as much as 6.3 kcal/mol more stable than the six-coordinated structure. For the 6A Mn(OH)₂(H₂O)₃O complexes it was not (yet) possible to converge to a six-coordinate structure. Starting from that kind of structure one of the water ligands fell off in the optimization procedure leading to one of the $(5+1)$ structures, indicating an unstable character of the six-coordination also for this complex.

Turning to the structures of the Mn(III) complexes a few interesting points can be noted. First, after the expulsion of one of the water ligands, the complexes remain rather closely in an octahedral type of structure, with one empty position; no other types of distortions seem to occur (see Figs. 2, 3). Secondly, both the ligands along the JT axis are always water ligands. This can be explained by the covalent character of the metal-hydroxyl bonds, making it much more costly to elongate these Mn—O bonds than the water Mn—O bonds. Third, the remaining water ligand along the JT axis (i.e. in most cases trans to the empty position) has a longer bond distance to manganese than all other water ligands. Summarizing the results in Table 2, the remaining water ligand on the JT axis in all complexes has a bond distance of 2.23–2.30 Å, while most other water ligands in the manganese complexes of different oxidation states have bond distances in the range 2.0–2.1 Å.

There are three groups of complexes listed in Tables 1 and 2 in which manganese has oxidation state IV: the 4A Mn(OH)₄(H₂O)₂ complexes, the 5A Mn(OH)₃(H₂O)₂O oxyl complexes and the 4A Mn(OH)₂(H₂O)₃O oxo complexes. In an ionic picture the Mn(IV) complexes are d^3 complexes, which in octahedral symmetry give rise to a t_{2g}^3 high-spin configuration and there are thus no e_g electrons present. For these systems the six-coordinated structure turns out to be the lowest in energy, by 1.0–4.1 kcal/mol for the 4A Mn(OH)₄(H₂O)₂ hydroxyl complexes and by 3.6–10.3 kcal/mol for the 5A Mn(OH)₃(H₂O)₂O oxyl complexes, (see Table 1). For the five-coordinated complexes the ligand trans to the empty position is always a hydroxyl for the 4A hydroxyl complexes and an oxyl group for the 5A oxyl complexes. Thus, the larger relative stability of six-coordination for the Mn(IV)(OH)₃(H₂O)₂O oxyl complexes (3.6–10.3 kcal/mol) as compared to the Mn(IV)(OH)₄(H₂O)₂ hydroxyl complexes (1.0–4.1 kcal/mol) shows that six-coordination is more stable with an oxyl ligand trans to one of the water ligands than with hydroxyl ligands trans to all water ligands. This result can also be expressed such that a water ligand binds stronger to manganese trans to an oxyl group than trans to a hydroxyl group, which is also confirmed by a comparison between the complexes with only five ligands to the six-coordinated complexes. This latter result seems to be in contradiction to the result that upon five-coordination, the oxyl com-

plexes loses the water ligand trans to the oxyl group rather than the one trans to a hydroxyl group. Apparently, when there are both oxyl and hydroxyl ligands in the same complex as in the $\text{Mn(IV)(OH)}_3(\text{H}_2\text{O})_2\text{O}$ oxyl complexes, the binding of the hydroxyl ligand is somewhat different than when there are only hydroxyl ligands, as in the $\text{Mn(IV)(OH)}_4(\text{H}_2\text{O})_2$ hydroxyl complexes. Another indication of such differences can be found in the spin densities. As can be seen in Table 1, the spin density on manganese in the ^4A hydroxyl complexes is 2.92–2.97 electrons, thus very close to the expected three electrons. In the ^5A oxyl complexes the spin density on manganese is only 2.60–2.73 electrons, and one of the hydroxyl ligands in these complexes obtains a spin density of 0.2–0.4 electrons. From the geometric parameters given in Table 2 it can be seen that the Mn–O bond distance of the oxyl ligand, 1.73–1.77 Å, is somewhat shorter than for the hydroxyl ligands, 1.8–1.9 Å. Furthermore, the five-coordinated Mn(IV) complexes are somewhat more distorted from an octahedral type structure than are the corresponding five-coordinated Mn(III) complexes, as discussed above. Finally, for the six-coordinated ^4A Mn(OH)₄(H₂O)₂ complex a cis and a trans conformation of the two water ligands was investigated. As can be seen in Table 1 the cis conformation (Fig. 1) is 8.7 kcal/mol more stable than the trans conformation. This is different to the iron case, as will be discussed below.

There are two groups of oxo complexes studied, the ^4A Mn(IV)(OH)₂(H₂O)₃O complexes and the ^3A Mn(V)(OH)₃(H₂O)₂O complexes. For one of these groups, the ^4A Mn(IV)(OH)₂(H₂O)₃O systems, oxo complexes were obtained in all coordination cases, as can be seen on the spin densities in Table 1, where manganese has spin densities between 2.62 and 2.95, indicating an oxidation state of IV. For these complexes five-coordination is more stable than six-coordination by 1.7–2.0 kcal/mol. The empty position in the five-coordinated complexes is always trans to the double bonded oxo group, and the complexes are strongly distorted towards a trigonal bipyramid (see Fig. 4). As can be seen in Table 2 the Mn–oxo distance is about the same for all coordination cases, 1.63–1.66 Å, indicating an Mn–O double bond. In Table 3 it can be seen that the excitation to the corresponding ^6A oxyl complex is quite high, and rather constant for the different coordination cases, 21.3 kcal/mol for the (5+1)a coordination, 21.1 kcal/

mol for the (5+1)b coordination and 19.0 kcal/mol for the five-coordination. For the six-coordinated case the Jahn-Teller unstable oxyl complex was not possible to converge to, as mentioned above.

For the ^3A Mn(V)(OH)₃(H₂O)₂O complexes the situation is different. For the six-coordinated case convergence was obtained but it turned out to be a low-spin coupling of an Mn(IV) oxyl structure. The spin was found to be 2.83 on the manganese, indicating Mn(IV), and –0.85 on the oxygen ligand, and the excitation energy to the high-spin (^5A) Mn(IV) oxyl complex was calculated to be only 3.6 kcal/mol. Also the Mn–O distance of 1.73 Å obtained for the ^3A Mn(OH)₃(H₂O)₂O complex shows that there is no double bond present. Many attempts were made to find a six-coordinated Mn(V) oxo species but without success. The five-coordinated complexes, on the other hand, have short Mn–O distances of 1.60–1.62 Å (Table 2), spin densities close to 2 electrons (Table 1) and fairly high excitation energies to the corresponding high-spin (^5A) oxyl complexes, 27.8 kcal/mol for the (5+1)b coordination and 24.4 kcal/mol for the five-coordination (Table 3). However, for the (5+1)a coordination a rather low excitation energy of 8.4 kcal/mol is obtained but this is for a solution that is not a completely true oxo species. The spin densities on manganese and the oxo ligand, 2.28 and –0.36 respectively, indicate an intermediate wave function between Mn(IV) and Mn(V). Finally, it should be noted here that for the five-coordinated Mn(OH)₃(H₂O)₂O complex a singlet state was also studied and was found to be 14.6 kcal/mol higher in energy than the ground state.

3.2 Iron complexes

The metal spin, 3d populations and relative energies for the iron complexes investigated are given in Table 4 and the bond distances in Table 5. One of the first and major points to be noted in Table 4 in comparison to the manganese results in the previous subsection is that the spin is less localized on the metal for the iron complexes. This is particularly clear for the Fe(III) and Fe(IV) complexes. For the Fe(II) complexes the spins are 3.75, 3.81 and 3.84 out of a total spin population of 4.0 for these ^5A states. For the Fe(III) and Fe(IV) complexes essentially an entire unit of spin is delocalized on the

Table 4. Metal spin, 3d population and relative energies for some iron monomer complexes with different oxidation states and coordination. The five-coordinated complexes have one ligand in the second coordination shell. Negative relative energies mean higher stabilities

Complex	State	Oxidation state	Coord.	Spin(Fe)	3d(Fe)	Relative energy
$\text{Fe(OH)}_2(\text{H}_2\text{O})_4$	^5A	II	4	3.75	6.31	–
$\text{Fe(H}_2\text{O)}_6^{3+}$	^5A	II	5	3.81	6.26	+ 8.1
			6	3.84	6.26	0.0
$\text{Fe(OH)}_3(\text{H}_2\text{O})_3$	^6A	III	5	4.02	6.09	–8.0
			6	4.08	6.10	0.0
$\text{Fe(H}_2\text{O)}_6^{3+}$	^6A	III	5	4.21	5.93	+ 10.1
			6	4.25	5.94	0.0
$\text{Fe(OH)}_4(\text{H}_2\text{O})_2$	^5A	IV	5	3.20	6.27	+ 1.1
			6	3.26	6.28	0.0
$\text{Fe(OH)}_2(\text{H}_2\text{O})_3\text{O}$	^5A	IV	5	2.97	6.35	–12.6
			6	2.96	6.39	0.0

Table 5. Metal-oxygen bond distances (Å) for some iron monomer complexes with different oxidation states and coordination. The five-coordinated complexes have one ligand in the second coordination shell. Values in parentheses indicate the number of equal bond distances

Complex	State	Oxidation state	Coord.	Fe—OH ₂	Fe—OH	Fe—O
Fe(OH) ₂ (H ₂ O) ₄	⁵ A	II	4	2.03,2.05	1.97(2)	—
Fe(H ₂ O) ₆ ²⁺	⁵ A	II	5	2.08,2.10(2),2.11,2.12	—	—
			6	2.14(4),2.17(2)	—	—
Fe(OH) ₃ (H ₂ O) ₃	⁶ A	III	5	2.06,2.30	1.83(2),2.04,2.04	—
			6	2.18,2.19,2.22	1.87,1.89,2.03	—
Fe(H ₂ O) ₆ ³⁺	⁶ A	III	5	1.95,1.97,2.01,2.04(2)	—	—
			6	2.05(6)	—	—
Fe(OH) ₄ (H ₂ O) ₂	⁵ A	IV	5	2.14	1.77,1.81,1.82,1.89	—
			6	2.24,2.25	1.82,1.83,1.84,1.85	—
Fe(OH) ₂ (H ₂ O) ₃ O	⁵ A	IV	5	2.00,2.16	1.83,1.90	1.65
			6	2.09,2.25,2.29	1.84,1.91	1.67

ligands. For the Fe(III) complexes the spins are 3.81, 3.84, 4.02 and 4.08 out of a total of 5.0 for these ⁶A complexes. For the Fe(IV) complexes the situation is similar with iron spins of 3.20, 3.26, 2.97 and 2.96 out of a total of 4.0 for these ⁵A complexes. The iron spin populations are furthermore essentially independent of the coordination number of the iron atoms. A consequence of the spin delocalization for these iron complexes is that the ligands will be more reactive in general than in the case of the manganese complexes. For example, the bridging μ -oxo groups of the iron dimer complexes present in RNR and MMO will have strong radical character and will therefore be active in abstracting hydrogen atoms from surrounding molecules like tyrosine for RNR and methane for MMO. The corresponding μ -oxo bridges in the Mn₄ complex in PSII have almost no radical character and will therefore not be as active in abstracting hydrogen atoms from surrounding molecules. The spin delocalization on the iron complexes is therefore a key feature responsible for the particular chemistry that these complexes are involved in.

The origin of the different spin delocalisation for the manganese and iron complexes is related to the optimal number of 3d electrons in these complexes. When the optimal spin state is deduced it is possible to use either an ionic or a covalent description of the bonding. For manganese the situation is simple and the same optimal spin state will be reached in both descriptions. The 3d population in the manganese complexes is close to five (see Table 1), which is the same as the 3d population in the isolated Mn atom. In a covalent description, the bonding Mn state will be an octet with the occupation 3d⁵4s¹4p¹. Each hydroxyl group will then form a covalent bond with a singly occupied orbital on Mn. This will lead to a ⁵A state for Mn(III) and a ⁴A state for Mn(IV), in line with the results in Table 1. With an ionic picture the result will be the same. In this case each hydroxyl group will take a single electron from Mn and the same spin state is obtained. However, the total 3d population of five for the manganese complexes is only consistent with a description where the 3d bonds are covalent. In a totally ionic picture Mn(III) would have four and Mn(IV) only three 3d electrons. For iron the situation is much more complicated, since the 3d population is close to six (see Table 4). It can be noted that also the Fe atom

has six 3d electrons, and in the respect of being similar to the isolated atoms the manganese and iron complexes thus behave the same way. However, with six 3d electrons one of the 3d orbitals is a closed shell orbital and this 3d orbital will stay doubly occupied in an entirely covalent description of the bonding. Therefore, the optimal spin state will be low-spin for the iron complexes if the Fe—OH bonds are considered as entirely covalent. The only way a high-spin state would be obtained in a covalent description of the iron complexes would be if the bonding state was a nonet 3d⁶4s¹4p² state, but this state does not have six 3d electrons. In an entirely ionic description, where the hydroxyl groups take an electron each from iron, an optimal high-spin state is reached. Since the correct ground state is high-spin, the ionic description is a better one in this respect. However, the resulting 3d population is not consistent with the ionic description. Rather than six 3d electrons, the Fe(III)-complexes should have five 3d electrons and the Fe(IV)-complexes should have only four 3d electrons. In order to keep six 3d electrons and still obtain a high-spin state it is clear that the unpaired spin therefore needs to be spread out among the ligands to some extent for the iron complexes, while this is not necessary for the manganese complexes. At this stage it can be argued that the 3d population could be an artifact of the Mulliken population analysis. Even though this to some extent is a valid argument, the fact that the optimal 3d population is the same as for the isolated atoms is probably a real representation of the high energetic cost to change the 3d population of metal atoms significantly. Also, and even more importantly, the consequence of the above arguments related to the 3d population, that the unpaired spin is more delocalized in iron complexes than in manganese complexes, is a real effect which has also been noted in experimental EPR studies [25]. In summary, a correct description of the bonding in these complexes is probably a mixture of covalent and ionic bonding. For manganese it is possible with this description to rationalize reasonably well both the 3d population and the high-spin ground state, while for iron a spin delocalization on the ligands is required. This result is in line with experimental EPR measurements and also in line with the higher reactivity of the ligands observed for iron complexes.

A few general comments can first be made on the geometries of the iron complexes. First, the low oxidation state Fe(II) complexes have two repulsive e_g electrons and the neutral $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4$ complex is therefore rather unstable in an octahedral six-coordinated arrangement of the ligands. In fact, the complex converged to a four-coordinated structure even though the starting point for the geometry optimization was six-coordinated. As seen in Table 5, the situation is quite different for the charged Fe(II) complex, which is actually more stable as six-coordinated than as five-coordinated by as much as 8.1 kcal/mol. This illustrates the danger of solely classifying these complexes by their oxidation states. As already emphasized, the neutral complexes should be better models than the charged ones for the low-dielectric situation in proteins. If we consider the Fe(III) complexes, which also have two repulsive e_g electrons, the situation is quite similar. In the case of the neutral $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$ the five coordinated complex is preferred over the six-coordinated one by 8.0 kcal/mol, while in the case of the charged complex six-coordination is preferred by 10.1 kcal/mol. In the charged complex, the large positive charge on the metal is apparently able to compensate for the repulsion to the e_g electrons by a strong electrostatic attraction.

The most interesting complexes are perhaps the Fe(IV) complexes, which have been shown to be of key importance in the hydrogen abstraction chemistry of MMO and RNR. With one e_g electron these complexes exhibit typical JT distortions. Just as for the case of the Mn(III) complexes, water ligands are optimally placed along the weak JT axis. This means that for the $\text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2$ complex, the trans orientation of the water ligands is strongly preferred to a cis orientation by 32.5 kcal/mol. Since the corresponding manganese complex $\text{Mn}(\text{OH})_4(\text{H}_2\text{O})_2$ only has three $3d$ electrons in an ionic description, it is not JT unstable and instead prefers a cis orientation by 8.7 kcal/mol, as described above. Due to the presence of only one repulsive e_g electron for Fe(IV) compared to two for Fe(II) and Fe(III), six-coordination for the neutral $\text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2$ is quite competitive with five-coordination as seen in the table and is actually preferred by 1.1 kcal/mol. The corresponding charged Fe(IV) complex with four positive charges did not keep together during the geometry optimization but released a positively charged water ligand. The neutral Fe(IV) oxo complex finally prefers five-coordination by 12.6 kcal/mol, not so much owing to the JT distortion but because of the large trans effect of the iron-oxo bond.

Adiabatic high-spin to low-spin excitation energies were calculated for most of the iron complexes discussed above. For the neutral Fe(II) complex $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4$, the optimal low-spin ^3A state was found to be five-coordinated and the excitation energy to this state from the ground state is 24.5 kcal/mol. The low-spin ^4A state of $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$ is found to be six-coordinated and the excitation energy 13.2 kcal/mol. Finally, the ^3A state of $\text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2$ is found to be six-coordinated with an excitation energy of 11.8 kcal/mol. This low-spin state is found to have a cis-orientation of the water ligands in contrast to the high-spin state where these ligands are

trans. It is interesting to note that when the water ligands are cis-oriented the low-spin state is actually lower in energy than the high-spin state by 20.7 kcal/mol. This is a good illustration of the large JT effects present in these systems, which strongly destabilize the cis-oriented high-spin state. In fact, the high-spin state with cis-orientation is so destabilized that the hydroxyl group along the JT axis obtains a large amount of radical character due to the elongated Fe—O distance. This partly breaks the covalency in the bonding, which is the origin of the preference for low-spin coupling.

In order to test how sensitive the above findings are on the precise choice of ligands a few other ligands were tried. With water ligands the preference for six-coordination over five-coordination in the high-spin state of $\text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2$ is 1.1 kcal/mol, as seen in Table 4 and discussed above. When ammonia is used instead of water this preference goes up very slightly to 2.1 kcal/mol. With another nitrogen bound ligand imine (NHCH_2), which has a C—N double bond, the preference is very similar with 1.9 kcal/mol. It is therefore probable that the present findings with water ligands are quite general for lone-pair bound ligands.

A result of some general interest can be found by summing the bond distances for the ligands directly bound to the metal in the complexes in Table 5. For the five-coordinated complexes 10.51 Å is obtained for Fe(II), 10.06 and 10.01 Å for Fe(III) and 9.43 and 9.54 Å for Fe(IV). The sum of the bond distances thus goes down for the higher oxidation states in a characteristic manner, which can be used to experimentally assign oxidation states from measured bond distances. For the six-coordinated complexes the sums are 12.90 Å for Fe(II), 12.38 and 12.30 Å for Fe(III) and 11.83 and 12.05 Å for Fe(IV).

In order to test the sensitivity of the present geometries to the basis set choice a few optimizations were done using a much larger basis set. For iron an all-electron basis including diffuse $4s$, $4p$ and $3d$ functions were used [24] and for oxygen the 6-311+G($1d$) basis was used. The hydrogen basis set was kept as in the small basis. For the six-coordinated high-spin ^5A state of $\text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2$ with the water ligands in a trans orientation, the Fe—O bond distances for the hydroxyl groups shortened by only 0.01–0.02 Å. For the Fe—O distances of the water ligands along the JT axis, the effect is instead an increase by 0.04 Å. Similar effects were found when the water ligands were put in a cis orientation. The total energy change owing to these geometry changes was only 2.2 kcal/mol for the trans complex. Very small changes on relative energies were therefore found. For example, the cis to trans energy difference changes by only 0.1 kcal/mol owing to these geometry changes.

4 Conclusions

One of the most surprising findings in the present study is that for many of the neutral manganese and iron complexes, five-coordination is preferred to the more conventional octahedral six-coordination. There are

somewhat different explanations for this effect for the different types of complexes. For the Fe(II) and Fe(III) complexes there are two repulsive e_g electrons which make the octahedral six-coordination unstable. For the Mn(III) and Fe(IV) complexes there is a large Jahn-Teller destabilization which leads to an easy loss of a water ligand along the weak JT axis. For the metal-oxo complexes finally, the trans effect of the metal-oxo bond is so strong that the trans position tends to be empty. It should be noted that for the charged $\text{Fe}(\text{H}_2\text{O})_6^{n+}$ complexes the normal six-coordination is strongly preferred.

It might be argued that the origin of the destabilization of six-coordination for the Jahn-Teller Mn(III) and Fe(IV) complexes is basically the same as the one for the destabilization noted for the non-JT Fe(II) and Fe(III) complexes, where the effect is simply due to the presence of repulsive e_g electrons. Although this argument is partly correct there is a very good reason to classify the distortions in Mn(III) and Fe(IV) as JT distortions, and this is that the type of distortion is very characteristic and can explain a number of surprising features. A good example of this was recently demonstrated for the Fe(IV) bis- μ -oxo dimer complex in MMO [8]. In this case the presence of a bridging carboxylate forces the weak JT axis on the iron centres to be located in the Fe-O₂-Fe plane. This explains the surprising features that the iron centres prefer five-coordination and also that the iron-oxo bond trans to the empty position is much longer, since it is along the JT axis, than the other iron-oxo bond. The presence of the long and weak iron-oxo bond explains why this oxo group obtains radical character and therefore becomes active in the hydrogen abstraction chemistry. For the same reason, the absence of bridging carboxylate groups in the Mn(III) dimers in PSII explains why the weak JT axis in this case is perpendicular to the Mn-O₂-Mn plane and why the manganese-oxo bond distances are therefore essentially the same in this case.

The present study has shown that the neutral $\text{M}(\text{OH})_n(\text{H}_2\text{O})_{6-n}$ complexes have a number of surprising features not expected based on previous knowledge from charged complexes in crystals and solutions. The preference for lower coordination than six for many of the complexes is probably the most striking of these features. Since the biochemical situation in a protein is characterized by a low dielectric constant, neutral complexes should be favoured and one must therefore be careful in directly extrapolating results for charged complexes to metallo-enzymes.

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