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Theory of Hyperfine Interaction in Five-Liganded Divalent and Trivalent Manganese Porphyrin Systems

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Abstract: As part of a program for studying the electronic structures and associated properties of heme and hemoglobin systems with the iron atom replaced by other atoms, such as manganese and cobalt, we have studied in the present work two high-spin manganese porphyrin systems, divalent H_2O-manganese porphyrin ($S = \frac{5}{2}$) and trivalent Cl-manganese porphyrin ($S = 2$). The charge and spin distributions over these molecules have significant overall similarities with the corresponding heme systems involving iron as central atom, indicating in particular that the metal atom is close to neutrality and a substantial part of the unpaired spin population, about 30%, is drained away toward the neighboring atoms, the major part of this unpaired spin population appearing on the nitrogen atoms of ligand pyrrole rings and the fifth ligand. The hyperfine interaction tensors for the ^{55}Mn and ^{14}N nuclei have been analyzed using the calculated electronic wave functions and spin distributions for the two molecules. The results for ^{55}Mn in the divalent system, which is the only case for which experimental data are available, are in good agreement with experiment for the isotropic component of the hyperfine tensor and the component parallel to the plane of the porphyrin, the experimental value for the perpendicular component being somewhat (about 25%) higher than theory. Suggestions are made for bridging this difference between theory and experiment. It is hoped that experimental data on the ^{14}N hyperfine interaction in the divalent system and ^{55}Mn and ^{14}N hyperfine interactions in the trivalent compound will be available in the near future to allow comparison between theory and experiment, and further test the small but significant differences in charge and spin distributions found in these porphyrin systems when iron is replaced by manganese.

I. Introduction

The study of the electronic structures of manganese porphyrin compounds by themselves or attached to proteins is important both because of the relationship of these compounds to the corresponding iron compounds as well as for the understanding of the origin of their properties, among them

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magnetic and hyperfine properties, some of which are available[1,2] at the present time from magnetic resonance measurements and others likely to be available in the near future by the same and related techniques such as electron-nuclear double resonance (ENDOR).[3] Thus, it has been found[4] that on the one hand the affinity of oxygen for the manganese porphyrin compound with pyridine as sixth ligand is larger than with iron as central atom, while on the other[5] pure manganese hemoglobin appears to exhibit no cooperativity or reversibility for oxygen binding. One of the models proposed[6] for this lack of cooperativity is that the oxygen molecule replaces the histidine ligand and binds as a ligand itself, forming a five-liganded system. It would be valuable to understand the validity of this model as well as the relatively stronger affinity of oxygen in manganese porphyrins[4] from an electronic point of view.

With this aim in mind, we have been interested in the electronic structures of manganese porphyrin and manganese globins, with special emphasis on using them to understand the origin of their magnetic and hyperfine properties. Of particular interest is the influence of the bonding to the protein on the electron distribution on the manganese atom and the porphyrin ring. Experimentally observed properties like the hyperfine constants and zero-field splitting parameters are available in this respect for manganese protoporphyrin[1] and manganese tetraphenylporphyrin with a pyridine ligand[2] which can be used to test the correctness of the calculated electron distribution in the two systems and also to analyze the change in the electron distribution on manganese atom and the porphyrin ring when an aromatic fifth ligand is added analogous to the situation corresponding to the ligand imidazole in manganese globin.

In the present work we shall concentrate on manganese protoporphyrin systems without an aromatic fifth ligand. Our aim will be to study the charge and unpaired spin population distributions in both divalent and trivalent manganese systems. Both the variation in these distributions between the divalent and trivalent systems as well as the comparison with the corresponding ferric heme system[7] will be discussed both by looking at the charge and spin distributions themselves as well as with the hyperfine properties one obtains from them, such as the metal ion nuclear and ^{14}N hyperfine interaction constants. Comparison will be made with available experimental data on ^{55}Mn hyperfine interaction in the divalent manganese protoporphyrin system.[1]

In section II, the geometry of the molecular systems under study will be described and a brief description of the procedures used for calculating the electronic wave functions and hyperfine constants will be presented. Section III will present the results for both the charge and spin distributions and hyperfine constants and discussion. Section IV will present the main conclusions from the present investigations and necessary future experimental and theoretical investigations on manganese porphyrin systems suggested by the results of the present work and their comparison with experiment.

II. Description of Geometry and Procedure

No X-ray data are available for divalent manganese porphyrin compounds. For the trivalent compounds, however, X-ray data are available[8] for the Cl-Mn^{III} tetraphenylporphyrin (TPP) which show that the manganese atom is about 0.27 Å above the porphyrin plane. The coordinates of the trivalent model compound Cl-Mn^{III} porphyrin that we have used in our work are chosen to closely approximate X-ray data,[8] some of the typical distances being indicated in Figure 1. The side chains of the pyrroles are, as in our earlier work on heme and heme-protein systems,[7,9] replaced by hydrogen atoms for keeping the computational time reasonable. This approximation is not expected to influence the spin distributions in the central parts of the molecule, namely, on the manganese atom and its ligand nitrogen atoms on the pyrrole rings which are of immediate interest to us for the study of the ^{55}Mn and ^{14}N hyperfine interactions.

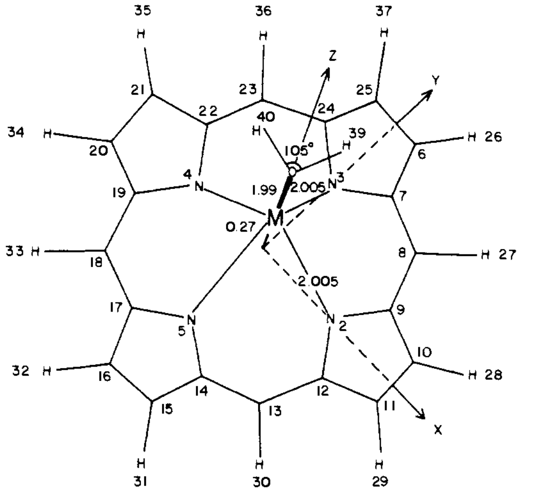

Figure 1. Arrangement of atoms in H_2O-manganese(II) porphyrin used in the present work. The plane of the H_2O molecule is assumed to contain the bisector of the angle between ON_2 and ON_3 which represents the X and Y axes. For the trivalent compound, Cl-manganese(III) porphyrin, the H_2O molecule is replaced by a chlorine atom on the Z axis, a distance of 2.36 Å away from the Mn atom.

For divalent manganese porphyrin system in aqueous solution, it is not completely certain whether there are one or two ligands, but the proposal has been made[10] in a review on manganese heme compounds that, based on demetalation data, there seems to be one H_2O molecule strongly bound and one rather weakly bound, indicating that it is a reasonable approximation to consider the manganese atom to be five liganded with one H_2O molecule. Since the divalent manganese porphyrin system is also high spin ($S = 5/2$) like the corresponding heme compounds with iron and the latter have the iron atom substantially above the porphyrin plane,[11] it is safe to assume that the manganese atom in the divalent manganese porphyrin compound will also lie significantly above the porphyrin plane. In view of this consideration and the fact that the trivalent manganese porphyrin compound also has high spin ($S = 2$) and has the manganese atom significantly above the porphyrin plane, we have chosen the position of the manganese atom in the divalent porphyrin system to be the same as in the trivalent compound. Also, in the absence of X-ray structural data in the divalent compound, the other atomic positions, besides the atoms in the H_2O ligand, have also been chosen to be the same as in the case of the trivalent manganese porphyrin system.[8] For the Mn-O distance we have made use of the corresponding distance in ionic divalent manganese compounds, while the OH distances and HOH bond angle are taken as in the free H_2O molecule. The plane of the H_2O molecule is chosen to contain the bisector of the angle between the Mn-N lines in the porphyrin system, an orientation that appears plausible from steric considerations. Since the orientation of the plane of the H_2O molecule was found in our work to have only slight influence on the spin distributions on the manganese and nitrogen atoms, the choice of the H_2O orientation is not very crucial.

The procedure used to obtain the electronic wave functions is the self-consistent charge extended Hückel (SCCEH) procedure[12,13] in which the molecular orbital wave functions are written as a linear combination of atomic orbitals (AO) χ_i:

$$\phi_\mu = \sum_i C_{\mu i} \chi_i \tag{1}$$

where the $C_{\mu i}$'s are LCAO coefficients and the summation over i is carried over all valence orbitals, which consisted of 3d, 4s,

Table I. Net Charges and Unpaired Spin Populations in Divalent and Trivalent Manganese Porphyrin Compounds[a]

	charges		unpaired spin populations	
atom	H_2O-$Mn^{II}P$	Cl-$Mn^{III}P$	H_2O-$Mn^{II}P$	Cl-$Mn^{III}P$
Mn_1	0.075	0.123	3.574	2.868
N_2	−0.206	−0.167	0.192	0.083
C_6	−0.050	−0.037	0.022	0.017
C_7	0.017	0.036	0.023	0.016
C_8	−0.028	−0.014	0.019	0.019
C_{11}	−0.050		0.021	
C_{12}	0.017		0.024	
C_{13}	−0.028		0.020	
H_{26}	0.058	0.066	0.000	0.000
H_{27}	0.081	0.091	0.001	0.001
H_{29}	0.058		0.000	
H_{30}	0.081		0.001	
R_{38}[b]	−0.280	0.066	0.207	0.426
R_{39}[c]	0.308		0.004	—

[a] Spaces left blank represent atoms equivalent to some of the atoms already listed in the table while a space marked with — indicates that there is no such atom in the molecule. [b] R_{38} represents the oxygen atom in H_2O-$Mn^{II}P$ and chlorine atom in Cl-$Mn^{III}P$. [c] R_{39} represents one of the hydrogen atoms in H_2O of H_2O-$Mn^{II}P$.

and 4p orbitals of manganese, 2s and 2p orbitals of carbon, nitrogen, and oxygen, 3s and 3p orbitals of chlorine, and 1s orbitals of hydrogen. The details of the SCCEH procedure are available in the literature[12,13] and in some of our earlier publications[7,14] on hyperfine and magnetic properties of heme compounds. The procedure requires a knowledge of the ionization energies for the neutral atoms and ions. The carbon, nitrogen, oxygen, hydrogen, and chlorine ionization energies used were the same as in the work of Zerner, Gouterman, and Kobayashi[13] and in our earlier work.[7,14] For manganese, the ionization energies for the neutral atom and positive ion were taken from the work of Zerner and Gouterman.[15]

Since we shall be discussing the charges and unpaired spin populations on the atoms, we give here the expressions for the net populations q^{α}_i and q^{β}_i in different spin states in the atomic orbitals i of the different atoms, based on the Mulliken approximation,[16] namely

$$q^{\alpha}_i = \sum_{\mu} \left[(C^{\alpha}_{\mu i})^2 + \sum_{j \neq i} C^{\alpha}_{\mu i} C^{\alpha}_{\mu j} S_{ij} \right] n^{\alpha}_{\mu} \qquad (2)$$

and a corresponding relation for q^{β}_i with C^{β}_{μ} and n^{β}_{μ} for the down spin state replacing respectively $C^{\alpha}_{\mu i}$ and n^{α}_{μ}, the coefficient for atomic orbital i in molecular orbital μ in spin state α and the occupancy 0, 1, or 2 for this molecular orbital, S_{ij} being the overlap integral for atomic orbitals χ_i and χ_j:

$$S_{ij} = \langle \chi_i | \chi_j \rangle \qquad (3)$$

The net electronic population q_i and net unpaired population ρ in atomic orbital i are given by $(q^{\alpha}_i + q^{\beta}_i)$ and $(q^{\alpha}_i - q^{\beta}_i)$, respectively. The net charge on an atom l is given by

$$q_l = \zeta_l - \sum_{i(l)} q_i \qquad (4)$$

where the summation over i refers to all atomic orbitals in atom l. The SCCEH procedure[7,12-14] involves self-consistency with respect to the charges q_l. The quantity ζ_l refers to the core[7,13,14] charge on atom l, that is, the nuclear charge minus the number of electrons on the atom considered to be valence electrons which take part in formation of molecular orbitals, manganese atom, for example, having an effective core charge of seven and nitrogen of five. We shall discuss the results for the charge and spin distributions over the molecules in the next section. But first we consider the procedure for the evaluation of the hyperfine constants of ^{55}Mn and ^{14}N nuclei which makes use of the calculated wave functions and the unpaired spin populations on the atoms.

In earlier work on heme and hemoprotein systems, in particular in ref 7, hereafter referred to as I, we have discussed the derivation of expressions for the metal and nitrogen nuclei for the high-spin systems with spin $S = 5/2$. For the case of ^{55}Mn nuclei in the divalent manganese porphyrin system with $S = 5/2$ that we are studying here, we can take over the expressions for the ^{57}Fe nuclei in high-spin ferric heme systems.

Thus, the hyperfine terms in the spin Hamiltonian for all the nuclei in the system can be written in general as[17]

$$\mathcal{H}_{\text{spin}} = A_N \vec{I} \cdot \vec{S} + \vec{I} \cdot \vec{B}_N \cdot \vec{S} \qquad (5)$$

where A_N is the isotropic contribution and the tensor $\vec{B}_N$ represents the anisotropic contribution, the former arising[18] out of the electron-nuclear Fermi contact interaction between the electrons and the nuclear moment and the latter from the dipolar interaction. The isotropic term A_N is composed of contributions from three different mechanisms (direct, exchange core polarization, and exchange valence polarization effects):

$$A_N = A_{Nd} + A_{Nc} + A_{Nv} \qquad (6)$$

The direct term represents the contact contribution from the unpaired spin valence electron molecular orbital states, the main part of this effect, from past experience in I with ferric heme compounds, being expected to arise from the manganese 4s components of the unpaired spin molecular orbitals.

$$A_{Nd} = a_{^{55}Mn} \sum_{\mu} |\phi_{\mu}(M)|^2 \qquad (7)$$

where

$$a_{^{55}Mn} = \frac{8\pi}{6Sh} \gamma_e \gamma_{^{55}Mn} \hbar^2 a_0^{-3} \qquad (8)$$

S being the spin of the molecular system, $5/2$ for the divalent and 2 for the trivalent compound, and $|\phi_{\mu}(M)|^2$ represent the density from the molecular orbital ϕ_{μ} at the ^{55}Mn nucleus. The other two contributions A_{Nc} and A_{Nv} to the hyperfine constant in eq 6 result from the exchange interaction between the unpaired valence electrons and the electrons in respectively the paired core orbitals on the manganese atom and paired valence orbitals, which lead to differences in the wave functions for up and down spin states. The expressions for these contributions, as derived in earlier work,[7] are given by

$$A_{Nc} = \frac{q'_{3d}(\text{unpaired})}{q_{3d}(\text{unpaired})} a_{^{55}Mn} \times \sum_{j=1}^{3} \left[|\chi^{\alpha}_{Mnjs}(0)|^2 - |\chi^{\beta}_{Mnjs}(0)|^2 \right] \qquad (9)$$

$$A_{Nv} = \frac{q'_{3d}(\text{unpaired}) q'_{4s}(\text{paired})}{q_{3d}(\text{unpaired}) q_{4s}(\text{paired})} \times a_{^{55}Mn} \left[|\chi^{\alpha}_{Mn4s}(0)|^2 - |\chi^{\beta}_{Mn4s}(0)|^2 \right] \qquad (10)$$

In eq 9 and 10 q_i and q'_i refer respectively to the electron populations in the ith AO of the neutral isolated atom and in the atom in the molecule, with the latter often referred to as the "pseudoatom". The AO χ^{α}_{is} and χ^{β}_{is} in eq 9 and 10 refer to the wave functions of is electrons in the neutral atom with up and down spins, respectively, the difference between the two being obtained by either unrestricted Hartree-Fock procedure[19] or perturbation methods,[20,21] both of which take account of the difference in the exchange interaction between $is\alpha$ and $is\beta$ states with the unpaired 3d electrons in the atom.

For the dipolar term in the spin Hamiltonian, the tensor $\vec{B}$ at the ^{55}Mn nucleus, using the actual protoporphyrin ring, is expected to depart from axial symmetry because the protoporphyrin ring has side chains on the pyrroles which make the former depart from tetragonal character about the Z axis perpendicular to the ring and passing through its center. However, this departure from axial symmetry is expected to be small, because the side chains on the pyrrole rings are not expected to influence the symmetry at the ^{55}Mn nucleus significantly. In our model compound, we have replaced the side chains by hydrogen atoms, which removes this source of departure from axial symmetry. There can also be a slight departure from axial symmetry from the presence of the H_2O ligand in the divalent manganese compound. But this effect was found to be small in our work so that one can assume axial symmetry to be valid, with

$$B_{xx} = B_{yy} = \frac{-1}{2} B_{zz} \tag{11}$$

and use for $B_{zz} = 2B$ for the divalent manganese compound with $S = \frac{5}{2}$ the expression derived in I, namely

$$\begin{aligned} B = {} & \frac{3}{16\pi} a_{^{55}\mathrm{Mn}} \\ & \times \sum_{\substack{\mu \\ (\text{unpaired MO})}} \left[\frac{2}{7} \langle r^{-3} \rangle_{\mathrm{Mn3d}} (2C_{\mu 3\mathrm{d}_{z^2}}{}^2 + C_{\mu 3\mathrm{d}_{xz}}{}^2 \right. \\ & + C_{\mu 3\mathrm{d}_{yz}}{}^2 - 2C_{\mu 3\mathrm{d}_{x^2-y^2}}{}^2 - 2C_{\mu 3\mathrm{d}_{xy}}{}^2) \\ & + \frac{2}{5} \langle r^{-3} \rangle_{\mathrm{Mn4p}} (2C_{\mu 4\mathrm{p}_z}{}^2 - C_{\mu 4\mathrm{p}_x}{}^2 - C_{\mu 4\mathrm{p}_y}{}^2) \\ & \left. + \frac{4}{\sqrt{5}} \langle r^{-3} \rangle_{\mathrm{Mn4s,3d}} C_{\mu 3\mathrm{d}_{z^2}} C_{\mu 4\mathrm{s}} \right] \end{aligned} \tag{12}$$

where $\langle r^{-3} \rangle_{\mathrm{Mn3d}}$ and $\langle r^{-3} \rangle_{\mathrm{Mn4p}}$ represent the radial expectation values of r^{-3} over the Mn 3d and Mn 4p radial functions and $\langle r^{-3} \rangle_{\mathrm{Mn4s,3d}}$ represents a corresponding integral involving Mn 4s and Mn 3d functions. For the case of the trivalent system with $S = 2$, the term involving $C_{\mu 3\mathrm{d}_{x^2-y^2}}$ is absent. In addition to the direct contribution to B in eq 12 there can also be exchange core polarization contributions, but these effects are expected to be substantially smaller[22] than in the contact case and also relatively less important. The latter feature is expected because in the dipolar case the direct contribution is itself significant[7,9] for the metal nucleus while in the contact case the direct effect is very small.

Turning next to the hyperfine interaction of the ^{14}N nucleus, we can again have both contact and dipolar contributions. For the contact contribution, there can again be direct and exchange core polarization contributions.[7,23] In contrast to the case of the nucleus of the metal atom where the direct contribution is rather small and is completely dominated by the exchange core polarization contribution, in the case of the nitrogen nucleus in metal porphyrin compounds[7] the major contribution arises from the direct effect, since the unpaired spin molecular orbitals have substantial nitrogen atom 2s character. The direct contribution is given by an equation similar to eq 7, namely

$$A_{\mathrm{Nd}} = a_{^{14}\mathrm{N}} \sum_{\mu} |\phi_{\mu}(N)|^2 \tag{13}$$

where

$$a_{^{14}\mathrm{N}} = \frac{8\pi}{6Sh} \gamma_{\mathrm{e}} \gamma_{^{14}\mathrm{N}} \hbar^2 a_0{}^{-3} \tag{14}$$

S being again the spin of the molecule and $|\phi_{\mu}(N)|^2$ the density from the molecular orbital μ at the ^{14}N nucleus. The exchange polarization contribution, as discussed in I, is difficult to calculate because there is substantial 2s-2p orbital mixing in both the unpaired spin and paired spin molecular orbitals and so an atomic-type approximation as in eq 7 and 8 is not suitable. Therefore, as in I, we shall also omit the exchange polarization contribution in our present work, to make comparison with the theoretical results in the iron porphyrin systems[7] on the same footing and again derive information on the importance of the exchange polarization contribution from comparison of the present results with experimental data on ^{14}N hyperfine interaction when available.

Next, considering the dipolar contribution, again there is a marked contrast with the situation for the metal nucleus. Thus, while the symmetry at the metal nucleus is close to axial, at the nitrogen nuclei there is strong departure from axial symmetry. One therefore has to obtain[14] all the components of the tensor $\vec{\boldsymbol{B}}$ in the molecular axis system in Figure 1 and carry out a diagonalization process to obtain the principal components. In the molecular axis system, the components of $\vec{\boldsymbol{B}}$ are given as in I by eq 15, which is based on taking only the local contribution to $\vec{\boldsymbol{B}}$ from the nitrogen atom orbital components of the unpaired spin molecular orbitals. The nonlocal and distant contributions involving the influence of neighboring atom orbitals are rather small.

We shall present and discuss the results for the hyperfine interaction tensors at the ^{55}Mn and ^{14}N nuclei in the next section after a discussion of the charges and unpaired spin populations on the various atoms in the divalent and trivalent manganese porphyrin compounds that we have studied.

III. Results and Discussion

We start by discussing the charges and unpaired spin populations on the atoms in the two molecules which are presented in Table I. We have taken advantage of the symmetry of the molecular systems in listing the atoms in Table I, the charges and unpaired spin populations on the atoms not listed being obtainable from the listed ones by symmetry. In the case of the divalent system, which has twofold symmetry, a few more atoms beyond those for the trivalent system, namely, C_{11}, C_{12}, C_{13}, H_{29}, and H_{30}, were needed to completely specify the charges and unpaired spin populations on all the atoms in the molecule.

The overall features of the charge distribution over the two molecules are very similar to those of the five-liganded hemin derivatives that have been studied recently.[7] Thus, the manganese atom is very different in nature from ionic and in fact is almost neutral in both the compounds studied, indicative of strong bonding between the d orbitals of the manganese atom and the orbitals of the pyrrole and fifth ligands. The strong bonding, however, as in the case of hemin and its derivatives, still leads to a reasonably close spacing of the molecular orbitals involving the metal atom, so that a state with high spin having more exchange energy is preferred[13] over low spin. The charges on none of the atoms are highly positive or negative, the overall distribution being nearly neutral. The only significant charges are carried by the nitrogen atoms of the pyrrole rings and the oxygen and hydrogen atoms of the H_2O ligand in the divalent compound. Making a more detailed comparison with the five-liganded hemin derivatives,[7] the charge on the manganese atom is found to be somewhat smaller than on iron. This indicates a somewhat stronger bonding between the metal atom and the ligand in the former case, especially for the trivalent compound which has only four occupied d orbitals and would have a charge of +3 in the extreme ionic case so that a stronger

$$\vec{\boldsymbol{B}} = \frac{3}{8\pi} \langle r^{-3} \rangle_{\mathrm{N2p}} a_{^{14}\mathrm{N}} \sum_{\substack{\mu \\ (\text{unpaired MO})}} \begin{bmatrix} \frac{2}{5}(2C_{\mu x}{}^2 - C_{\mu y}{}^2 - C_{\mu z}{}^2) & \frac{6}{5}C_{\mu x}C_{\mu y} & \frac{6}{5}C_{\mu x}C_{\mu z} \\ \frac{6}{5}C_{\mu y}C_{\mu x} & \frac{2}{5}(2C_{\mu y}{}^2 - C_{\mu z}{}^2 - C_{\mu x}{}^2) & \frac{6}{5}C_{\mu y}C_{\mu z} \\ \frac{6}{5}C_{\mu z}C_{\mu x} & \frac{6}{5}C_{\mu z}C_{\mu y} & \frac{2}{5}(2C_{\mu z}{}^2 - C_{\mu x}{}^2 - C_{\mu y}{}^2) \end{bmatrix} \tag{15}$$

Table II. Contributions to the ^{55}Mn Hyperfine Constants in Divalent and Trivalent Manganese Porphyrin Compounds[a,b]

	A_{Nd}	A_{Nc}	A_{Np}	A_N	B_{zz}
H_2O-Mn^{II}P	8.4	−258.8	28.5	−221.9	−4.3
Cl-Mn^{III}P	8.5	−259.3	34.9	−215.9	11.0

[a] The contributions to the hyperfine constants are stated in megahertz. [b] The contributions of A_{Nd}, A_{Nc}, and A_{Np} to the isotropic hyperfine constant A_N are obtained from eq 7, 9, and 10. The dipolar constant B_{zz} is obtained using eq 12.

bonding per electron is required to have a weaker charge than the iron atom in the hemin derivatives. The smaller positive charge on the metal atom in the case of manganese compounds is in keeping with the smaller overall charges on the atoms in the rest of the molecule, as indicated, for example, by the negative charge[7] on the chlorine ligand in hemin and the slight positive charge (Table I) in the case of the trivalent manganese compound.

Turning next to the unpaired spin distributions on the atoms in the two molecules listed in Table I, the influence of the strong bonding between the metal atom and its ligands is also reflected, as in the hemin derivatives, by the substantial reductions of the unpaired spin populations on the manganese atom from the values 5 and 4 that would have been found in the divalent and trivalent compounds, respectively, if there was only a weak coupling with the ligands, with the manganese atom being effectively in Mn^{2+} and Mn^{3+} ionic states. A more detailed comparison between the unpaired spin populations in the manganese porphyrin systems in Table I and the hemin derivatives[7] indicates that there is somewhat less delocalization of the unpaired spin population in the divalent manganese compound as compared to the high-spin ferric systems corresponding to the hemin derivatives, the unpaired spin population on manganese being about 70% of the total population of five, about 10% larger than in the hemin system. This feature, when contrasted with the slightly stronger overall bonding for the divalent manganese compound indicated by the charge on the manganese atom, suggests that there is a relatively larger d population in the paired molecular orbitals, a feature that was seen to hold from an examination of the sizes of the atomic orbital coefficients in the paired molecular orbitals in the manganese and iron compounds.[7] The unpaired spin population on the manganese atom in the trivalent compound is seen from Table I to be significantly smaller than for the divalent compound, which is not unexpected because the spin of the trivalent compound is smaller, namely, $S = 2$, corresponding to four molecular orbitals with single unpaired spin electrons, in contrast to five for the divalent compound. However, the fractional unpaired populations per single spin, obtained by dividing these populations by 4 and 5, respectively, are seen to be comparable in the trivalent and divalent compounds.

Turning next to the unpaired spin populations on the ligand atoms, the delocalization of unpaired spin population away from the manganese atom is manifested by the appearance of significant unpaired spin populations (Table I) on the rest of the atoms. The major parts of the drainage, 1.43 and 1.23, in the unpaired spin populations out of the manganese atom are seen to appear on the ligand nitrogen atoms of the four pyrrole rings and the oxygen and chlorine ligands in the divalent and trivalent compounds, respectively. There are also small but finite unpaired spin populations on the meso carbon atoms and the carbon atoms of the pyrrole rings, the unpaired spin populations on the former having important influence on the meso proton hyperfine constants as in the case of the five-liganded hemin derivatives.[17]

We consider next a more detailed comparison of the spin distributions over the ligand nitrogens and the other atoms in the molecules (besides the metal atom) in Table I, between the divalent and trivalent compounds among themselves, and with those on the five-liganded high-spin hemin derivatives.[7] Thus, for the divalent manganese compound, the spin populations on the nitrogen atoms of the pyrrole rings are seen to range from about 10 to 20% lower than the corresponding populations in various high-spin five-liganded hemin derivatives studied in I. Similar relative decreases with respect to the hemin derivatives are also observed for the spin populations on the rest of the atoms in the divalent manganese compound. These relative decreases are all a consequence of the small increase in localization of unpaired spin population on the metal atom in the divalent manganese compound with respect to that on iron in hemin derivatives, pointed out earlier in this section.

The difference in the unpaired spin populations on the nitrogen atoms between the divalent and trivalent manganese compounds is seen from Table I to be more dramatic. Thus the unpaired spin populations on the nitrogen atoms in the trivalent compound are only about 40% of those in the divalent compound. Allowing for the differences in spins and hence in the numbers of unpaired spin electrons in the divalent and trivalent compounds, 5 and 4, respectively, the unpaired spin population on each nitrogen atom per unit spin in the trivalent manganese compound is still about 50% of that in the divalent compound. This sizable difference can be understood by noticing that, in the trivalent manganese compound with spin $S = 2$, there are only four unpaired spin electrons in the d_{z^2}-, d_{xy}-, d_{yz}-, and d_{zx}-like molecular orbitals, the $d_{x^2-y^2}$-like molecular orbital being empty, in contrast to the divalent compound with $S = 5/2$ where the $d_{x^2-y^2}$-like molecular orbital is also occupied by one electron with its spin unpaired. Since the $d_{x^2-y^2}$ orbital on the metal atom has lobes pointing directly at the four nitrogen atoms, this molecular orbital is expected to involve significant nitrogen atom orbital components. Therefore, when this molecular orbital is empty, it is not surprising to find reduced unpaired spin populations on the nitrogen atoms. It is interesting in this respect that the unpaired spin population on the chlorine atom at the fifth ligand site in the trivalent manganese compound is not substantially different from that on the chlorine in hemin.[7] The unpaired spin population on the fifth ligand is determined by the d_{z^2}-, d_{xz}-, and d_{yz}-like molecular orbitals and these of course contain unpaired spin populations in both the trivalent manganese compound and hemin (and divalent manganese porphyrin) with spin $S = 5/2$.

The various features of the unpaired spin distribution just discussed are reflected in the hyperfine interactions for the ^{55}Mn and ^{14}N nuclei which have been studied using eq 6–15, the calculated wave functions for the two molecules, and the unpaired spin populations on the atoms listed in Table I. The contributions A_{Nd}, A_{Nc}, A_{Nv}, and B_{zz} to the ^{55}Mn hyperfine interaction in both the divalent and trivalent manganese compounds are listed in Table II. As mentioned earlier, the structures of the two compounds, even in the case of the divalent compound with the H_2O ligand, lead to nearly axially symmetric spin distributions around the metal atom. This is manifested, for instance, by the near-equality of the unpaired spin populations on corresponding members of the sets of atoms (C_6, C_7, C_8) and (C_{11}, C_{12}, C_{13}) in the divalent manganese porphyrin compound (Table I). These were in principle expected to be different because of the departure from tetragonal symmetry produced by the H_2O ligand. The near-axial symmetry of the spin distribution is also seen in the components of the dipolar interaction tensor $\vec{B}$ where B_{xx} and B_{yy} are found to differ from $-B_{zz}/2$ by less than 5% in both molecules, which is less than 0.1% of the dominant contribution A_{Nc}. This is the reason for tabulating only the B_{zz} component in Table II. While A_{Nc}, the exchange core polarization contribution, is the dominant one for the isotropic hyperfine constant, the exchange valence polarization and direct contributions, A_{Nv} and

Table III. Hyperfine Interaction Constants for ^{14}N Nuclei in Divalent and Trivalent Manganese Porphyrins[a]

molecule	A_{Nd}[b]	A_{xx}	A_{yy}	A_{zz}[c]	$A_{x'x'}$	$A_{y'y'}$	$A_{z'z'}$[d]
H_2O-$Mn^{II}P$	5.889	9.139	3.795	4.757	4.709	2.616	9.161
Cl-$Mn^{III}P$	1.287	2.026	0.302	1.534	0.302	2.041	1.519

[a] The contributions to the hyperfine constants are stated in megahertz. [b] A_{Nd} represents the isotropic contribution to the hyperfine constants. [c] A_{xx}, A_{yy}, and A_{zz} represent the components of the net hyperfine tensor with respect to the axis in Figure 1. [d] $A_{x'x'}$, $A_{y'y'}$, and $A_{z'z'}$ represent the principal components of the net hyperfine tensor.

A_{Nd}, are seen to be nonnegligible from Table II and have to be included in making comparison with experiment. In view of the axial symmetry of the $\bar{B}$ tensor for ^{55}Mn, we can obtain the components of the hyperfine interaction constant tensor parallel and perpendicular to the normal to the porphyrin plane by the relations

$$A_{\parallel} = A_N + B_{zz} = A_N + 2B \qquad (16)$$

$$A_{\perp} = A_N + B_{xx} = A_N - B \qquad (17)$$

The value of the isotropic hyperfine constant A_N is seen from Table II to be −221.9 MHz, which is equivalent to −0.007 40 cm^{-1} in units of wavenumbers and to a field at the ^{55}Mn nucleus of −525.5 kOe. Using eq 16, the value of $A_{\perp}$ = −219.7 MHz, −0.007 32 cm^{-1}, and −520.2 kOe in other units. This value is in excellent agreement with the magnitude of 0.0073 cm^{-1} (sign not measured) for $A_{\perp}$ found experimentally.[1] The value of $A_{\parallel}$ from our results in Table II using eq 17 comes out as −226.2 MHz, −0.007 54 cm^{-1}, and −535.6 kOe in other units. This value is not in as good agreement with the experimental magnitude[1] of 0.011 cm^{-1} as was the case for $A_{\perp}$. Before discussing possible ways of resolving this difference between theory and experiment in the case of $A_{\parallel}$, one should note that the experimental magnitude of the isotropic part A of the hyperfine constant given by $[(A_{\parallel})_{expt} + 2(A_{\perp})_{expt}]/3$, namely, 0.0086 cm^{-1}, is in better agreement with our theoretical value of −0.0074 cm^{-1}, although the agreement is not as close as in the case of $A_{\perp}$.

The reasonably satisfactory agreement between theory and experiment[1] for the isotropic component A_N of the hyperfine interaction indicates that the main reason for the difference between theory and experiment for $A_{\parallel}$ could be associated with the size of the dipolar interaction constant B, which may have been underestimated with respect to experiment. A possible reason for this is the fact that our assumption of a single H_2O ligand[6] may not be a good model for the environment of the manganese porphyrin in frozen aqueous solution. An inspection of the dipolar component B_{zz} in the trivalent compound indicates that in this system B_{zz} is twice as large in magnitude as that in the divalent system. This is of course expected since the trivalent system has only four d-like orbitals occupied, with the $d_{x^2-y^2}$-like orbital missing, which leads to a stronger departure from effective spherical symmetry of the immediate environment of the ^{55}Mn nucleus as compared to the divalent system. But the relatively small difference in the absolute magnitudes of B_{zz} in the divalent and trivalent compounds also indicates that only a change in the d character of the unpaired molecular orbitals in the divalent system may not be sufficient to resolve the apparent remaining difference between the theoretical and experimental A and some additional admixture of 4p character, especially for the d_{z^2}-like molecular orbital, may be necessary, the p orbital having a larger value of $1/r^3$ than the d orbital. It would be interesting to investigate if indeed the presence of a sixth H_2O ligand, perhaps at a longer distance from the manganese atom than the fifth ligand, can provide the required admixture of $4p_z$ character to the d_{z^2}-type orbital. Further, a reexamination of the experimental situation with respect to $A_{\parallel}$ would be helpful. Thus, for the analogous five-liganded compound Mn^{II}(TPP)py in toluene, the hyperfine tensor is found[2] to be rather isotropic and have a magnitude[24] of 0.0069 cm^{-1}. Further the zero-field splitting tensor terms, which are also sensitive to the departure in the spin distributions from spherical symmetry, are found experimentally[1,2] to be quite close in magnitude for manganese(II) protoporphyrin in aqueous solution and Mn^{II}(TPP)py in toluene. In view of this situation, a remeasurement of the anisotropy of the hyperfine tensor in the frozen aqueous manganese(II) protoporphyrin system, perhaps by the electron-nuclear double resonance (ENDOR) technique,[3] would be helpful. It should, however, be emphasized that, apart from this difference between theory and experiment for the anisotropy of the hyperfine tensor, which is actually a relatively small fraction of the isotropic component of the hyperfine interaction constant and of the individual values of $A_{\parallel}$ and $A_{\perp}$, the agreement between theory and experiment is rather satisfactory, indicating that the results in Table I provide a reasonably good description of the unpaired spin-population distribution in the vicinity of the manganese atom. In particular, the result for the spin population on manganese atom in Table I, indicating the drainage of about 30% of the unpaired spin population (five) in the divalent compound away from the manganese atom to the ligand atoms, is verified experimentally. In the absence of this drainage, the theoretical values of the isotropic component A_N and the component $A_{\perp}$ could be about 40% larger than in Table II and the good agreement with experiment for these quantities would no longer hold.

We consider next the results for the ^{55}Mn in the trivalent manganese compound. The major features of the theoretical results in Table III are very similar to those in the divalent compound, the isotropic contributions being of comparable magnitudes. This is to be expected because the spin Hamiltonian $A\bar{\mathbf{I}}{\cdot}\bar{\mathbf{S}}$ involves the total spin linearly, so that A is proportional to the hyperfine field per unpaired spin electron and, for instance, for A_{Nc}, the comparable magnitudes in the divalent and trivalent compounds are expected from the occurrence of the ratio q'_{3d}(unpaired)$/q_{3d}$(unpaired) (eq 9). For A_{Nd} and A_{Nv} one has a dependence on the 4s orbital characters of the molecular orbitals, the unpaired and paired ones, respectively, for A_{Nd} and A_{Nv}. The close similarity of A_{Nd} in the divalent and trivalent compounds indicates comparable 4s hybridizations with 3d in the two cases for the unpaired orbitals. The results for A_{Nv} indicate a slightly larger 4s hybridization for the paired orbitals in the trivalent compound.

The dipolar contribution in the trivalent compound is different from that of the divalent compound, both in magnitude, the trivalent compound result being more than twice as large, and in sign. The difference is again not unexpected in view of the greater anisotropy from spherical symmetry arising from the fact that the $d_{x^2-y^2}$-like molecular orbital is empty in the trivalent compound. The predicted difference between $A_{\parallel}$ and $A_{\perp}$ using eq 16 and 17 is now about 8%. It will be very useful to have experimental data on ^{55}Mn hyperfine interaction in the trivalent compound not only to study this anisotropy associated with $A_{\parallel}$ and $A_{\perp}$ but also to check the prediction of comparable isotropic hyperfine constants A_N in the divalent and trivalent manganese compounds. This will enable a verification of the features of the spin distribution on the manganese atom, namely, the significant drainage of unpaired spin population from the manganese atom in the trivalent compound, comparable to that in the divalent compound, and also the anisotropy of the spin distribution as manifested by the difference between $A_\parallel$ and $A_\perp$.

We consider next the hyperfine tensors for the ^{14}N nuclei on the porphyrin ring in the two molecular systems. As discussed in section II dealing with the procedure, the dipolar hyperfine tensor at the nitrogen nuclei is not expected to be axially symmetric. We have therefore obtained the nine components B_{ij} in the XYZ coordinate system in Figure 1 and also the three components in the principal axis system as listed respectively in eq 18 and 19 for the divalent compound and eq 20 and 21 for the trivalent system. The tensors are listed for one of the four pyrrole nitrogen atoms, namely, the atom N$_2$ in Figure 1.

$$\vec{B} = \begin{bmatrix} 3.2248 & 0.0065 & 0.4624 \\ 0.0065 & -2.0930 & 0.0050 \\ 0.4624 & 0.0050 & -1.1318 \end{bmatrix} \tag{18}$$

for divalent Mn-porphyrin system in MHz in the coordinate system in Figure 1 and

$$\vec{B} = \begin{bmatrix} -1.1803 & 0 & 0 \\ 0 & -2.0930 & 0 \\ 0 & 0 & 3.2733 \end{bmatrix} \tag{19}$$

in the principal axis system with the principal axes X', Y', and Z' defined in the order of increasing magnitudes for the principal components. For the trivalent Mn–porphyrin system

$$\vec{B} = \begin{bmatrix} 0.7387 & -0.0001 & -0.0890 \\ -0.0001 & -0.9855 & -0.0001 \\ -0.0890 & -0.0001 & 0.2468 \end{bmatrix} \tag{20}$$

and

$$\vec{B} = \begin{bmatrix} -0.9855 & 0 & 0 \\ 0 & 0.7538 & 0 \\ 0 & 0 & 0.2317 \end{bmatrix} \tag{21}$$

in the principal axis system.

In view of the near equivalence of the four nitrogen atoms in the porphyrin plane, the dipolar hyperfine tensors at the other three nitrogen atoms can be obtained quite well by fourfold rotation about the axis through the manganese atom perpendicular to the porphyrin plane. We have also listed in Table III the isotropic contributions A_{N} to the ^{14}N hyperfine constants in the two compounds, the values of A_{zz}, A_{xx}, and A_{yy} in reference to the coordinate system in Figure 1, using eq 18–21, and the values of $A_{x'x'}$ and $A_{z'z'}$ in the principal axis system obtained by combining A_{N} with the components $B_{x'x'}$, $B_{y'y'}$, and $B_{z'z'}$ in the principal axis system. The values of $A_{x'x'}$, $A_{y'y'}$, and $A_{z'z'}$ could be obtained from EPR and ENDOR measurements on single crystals while A_{xx}, A_{yy}, and A_{zz} could be related to hyperfine patterns obtained from resonance measurements associated with the frequencies corresponding to the components $g_\parallel$ and $g_\perp$ of the g tensor (which is expected to have symmetry close to axial in view of the near-axial symmetry around the manganese atom in both compounds).

It is hoped that data on the ^{14}N hyperfine frequencies will be available in the future to compare with the predictions in Table III both in terms of actual values of the hyperfine frequencies as well as the major relative features of these frequencies in the two systems. One of these features is the substantially larger value of the ^{14}N hyperfine frequency for the divalent compound, a result that is a consequence of the empty character of the $d_{x^2-y^2}$ orbital in the trivalent compound which, as explained earlier in this section in discussing the unpaired spin population distributions, leads to the substantially weaker spin density at the nitrogen atom in this compound relative to the divalent one where the $d_{x^2-y^2}$ has an unpaired spin electron. A second feature is the somewhat larger fractional departure from isotropy in the trivalent compound as compared to the divalent, as represented by $(A_{z'z'} - A_{x'x'})/A_{z'z'}$. Finally, when the ^{14}N hyperfine constants are measured, it will be interesting to check the nature of the absolute agreement between experimental results and theory. This will allow one to draw conclusions, as in the case of the hemin derivatives,[7] regrading the relative importance of $A_{\mathrm{N_c}}$ due to the exchange core-polarization effect that has not been included in our results for the isotropic hyperfine constants A_{N} for the ^{14}N nuclei.

IV. Conclusion

Our investigations on the charge and spin distributions in divalent manganese porphyrin with H$_2$O as a fifth ligand and trivalent manganese porphyrin with chlorine as a fifth ligand have both shown that the overall features of these distributions are very similar to those in high-spin five-liganded and six-liganded heme systems.[7,9] One major feature of these distributions is that the metal atom is close to neutrality rather than with a charge +2 or +3 as one would expect if there were weak interaction between the metal atom and the porphyrin and the fifth ligand and one had virtually a Mn^{2+} or Mn^{3+} ion in the two systems. Secondly, of the net unpaired spin populations of 5 and 4 associated with spins $S = 5/2$ and 2 for the divalent and trivalent compounds, only about 70% of this population is located on the manganese atom, the rest being drained out to the ligand atoms, with major shares going to the four nitrogen atoms of the pyrrole groups and the fifth ligand atom or molecular group. Both these features are supportive of strong bonding between the metal atom and its ligands. The contributions of the spin distribution to the ^{55}Mn and ^{14}N hyperfine interactions are studied, including both the contact and dipolar interactions. Experimental data are available[1] for comparison only for ^{55}Mn nucleus in the divalent compound. The agreement between theory and experiment is found to be satisfactory for the isotropic component A_{N} of the hyperfine tensor and very good for $A_\perp$, the component of the net hyperfine interaction tensor parallel to the porphyrin plane. There is some difference for the anisotropy $A_\parallel - A_\perp$, the theoretical result indicating significantly less anisotropy than experiment. Possible additional theoretical and experimental investigations to resolve this difference have been suggested. However, the good agreement between A_{N} and $A_\perp$ and experiment does lend support to the picture of the unpaired spin distribution obtained from the theoretical investigations in this work on the divalent compound. It would be helpful to have experimental data on the ^{14}N hyperfine interaction in this compound to have a further test of the calculated spin distribution. Also, theoretical investigation of the zero-field splitting parameters D and E which are experimentally available[1] for this molecule would also provide an additional test of the calculated wave functions and associated spin distributions. Experimental data are also needed for the ^{55}Mn and ^{14}N hyperfine interactions in the trivalent compound to compare with the theoretical predictions in the present work.

Additionally, we plan to carry out in the future, as part of our continuing investigations on manganese porphyrin and manganese globin systems, the study of the electronic charge and unpaired spin population distributions in manganese porphyrin with imidazole and pyridine ligands to draw inferences regarding the influence of binding of manganese porphyrin to the protein chain in manganese globin. It will be interesting in particular to make comparison between theoretical results and experimental hyperfine data[2] in Mn$^{\mathrm{II}}$(TPP)py which indicate that the ^{55}Mn hyperfine tensor in that system is rather isotropic.

Finally, as regards the difference in oxygen affinity[4,5] between manganese porphyrin compounds and manganese globin and the corresponding heme systems, actual calculations of the electron distributions and energy levels of the oxygen-liganded systems will be needed to understand these differences in affinity from a theoretical point of view. However, the comparison between the charge and spin distributions between the five-liganded divalent manganese compound studied here and the distributions on the five-liganded heme systems[7] shows that there are small and significant differences between the two types of systems. Among these differences are the greater tendency toward neutrality of the manganese compound and about 5% larger unpaired spin population on the metal atom in the manganese compound. These small but significant differences suggest that the electronic interaction between the manganese porphyrin and oxygen molecule as compared to that between the heme group in heme systems and oxygen can be appreciably different enough to explain the differences in oxygen affinity.

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Synthesis of Perfluoroalkyl Trifluoromethanesulfonates from Perfluoroalkyl Halides. Substitutive Electrophilic Dehalogenation with Chlorine(I) and Bromine(I) Trifluoromethanesulfonates

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Abstract: The reactions of chlorine(I) and bromine(I) trifluoromethanesulfonates with a variety of perfluoroalkyl halides are reported. The reactions form Br_2, Cl_2, or BrCl and the corresponding trifluoromethanesulfonate derivatives of the alkyls in good yields. Twelve new esters are reported and characterized. An $S_{E}i$-type mechanism for the reactions is proposed with complete retention of configuration by the alkyl on substitution.

Introduction

The utility of electropositive halogen compounds in synthesis is rapidly being recognized.[3,4] In particular, the simple concept that a formal positive halogen atom in a general compound $M^{\delta-}$-$X^{\delta+}$ can react with a negatively polarized atom in $N^{\delta+}$-$Y^{\delta-}$ to give MN and XY has resulted in many interesting syntheses. In order to have a formal positive halogen, it is necessary that the halogen be bonded to an element more electronegative than itself, as in ClF, where chlorine is the formal positive halogen. In addition, if the halogen is contained in a polyatomic molecule, it must be bonded to an element of comparable or greater electronegativity and the rest of the molecule must have a group electronegativity greater than that of the halogen. This requirement is ideally met in fluorinated compounds such as $(CF_3)_2NCl$, SF_5OCl, CF_3OCl, FSO_2OCl, $(FSO_2)_2NCl$, etc.

One of the most interesting reactions of the above type and the first utilization of a fluorinated compound in this way was the low-temperature reaction of $BrOSO_2F$ with $CFCl_3$ as shown in the equation[5]

$$BrOSO_2F + CFCl_3 \rightarrow CFCl_2\,OSO_2F + BrCl$$

This reaction can be termed substitutive electrophilic dehalogenation. A similar transformation employing FSO_3^- or $FSO_3\cdot$ is not possible under the same conditions. While the detailed mechanism of this reaction is unknown, it probably involves the initial interaction FSO_2O-$Br^{\delta+}$—$Cl^{\delta-}$-$CFCl_2$.

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