Inorg. Chem. **2007**, *46*, 1948−1950

Inorganic Chemistry
Communication

An Anomalous Spin-Polarization Mechanism in High-Spin Manganese(III) Porphyrin Complexes

Ru-Jen Cheng,* Shu-Hao Chang, and Kuo-Cheng Hung

*Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan 402,
Republic of China*

Received September 12, 2006

Confluence of NMR for paramagnetic molecules and the complementary density functional theory calculations reveals an anomalous spin-polarization mechanism that is maximized in high-spin d^4 complexes. It is critical to realize this mechanism to correctly rationalize the spin-density distribution around the porphyrin macrocycle.

NMR of paramagnetic complexes potentially can yield information about magnetic anisotropy, d-orbital occupation, unpaired spin-delocalization mechanisms, and perturbations of electronic structure.[1] For paramagnetic metalloporphyrins, because C atoms proximal to the central metal could have significant spin contributions through the bonding skeleton ^{13}C NMR spectra would be particularly informative.[2] However, correlations between ^{13}C NMR shift patterns and d-orbital occupation are not as straightforward as those for ^{1}H NMR spectra. It would take larger efforts to interpret ^{13}C NMR spectra. Thus, general application of this unique technique has long been inhibited.

Five-coordinate manganese tetraphenylporphyrin complexes Mn(TPP)X (X = Cl, Br, I) with $S = 2$[3] have been studied extensively by ^{1}H and ^{13}C NMR spectroscopy,[4,5] and parts of the data are collected in Table 1. The most distinct feature of these NMR data is the presence of both upfield and downfield pyrrole C signals that cannot be rationalized by any well-recognized spin-transfer mechanisms. Attempts to analyze the isotropic shifts by the Karplus−Fraenkel equation yielded totally different spin densities at α-C atoms in two different reports.[4,5] Other than the generally recognized high-spin $\mathrm{Mn^{III}}$ ground state ($d_{xy}^{1}d_{xz,yz}^{2}d_{z^2}^{1}$, $^{5}B_2$), the contribution of an intermediate- or high-spin $\mathrm{Mn^{II}}$ with porphyrin cation radical $\mathrm{Mn^{II}(TPP)^{\bullet +}X}$ has been proposed.[5,6] Density functional theory (DFT) calculations for this system with the gross spin populations have been reported. However, the patterns of NMR shifts have never been rationalized.[7a]

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts and [Isotropic Shifts][a] of Mn(TPP)X Complexes Taken in CD_2Cl_2 at 298 K

	X =		
	Cl	Br	I
C_α	393 [242.7]	398 [247.7]	408 [257.7]
C_β	−158 [−290]	−163 [−295]	−158 [−290]
C_{meso}	110 [−11.2]	95 [−26.2]	65 [−56.2]
C_q	204 [60.2]	210 [66.2]	217 [73.2]
β-H	−22.3 [−31.1]	−23.5 [−32.3]	-25.9 [−34.7]

[a] $\delta_{iso} = \delta_{obs} - \delta_{dia}$; diamagnetic shifts were taken from the reference complex Zn(TPP).

The complementary nature between theoretical calculations and NMR spectroscopy of paramagnetic molecules now makes possible the bonding analyses for iron(III) porphyrin complexes.[8,9] It is important to be able to dissect the total electron spin density at each atom into the corresponding π spin density and the Fermi contact spin density. Detailed analysis of the spin distribution on the macrocycle may disclose specific bonding interactions between iron and porphyrin. Most of all, a qualitative comparison between the calculated Fermi contact spin densities and the NMR data would help to identify the major contribution from different electronic states.[9] It is our goal in this research to explore the possible application of these techniques to evaluate the electronic structure and spin distribution of the Mn(TPP)X system.

DFT calculations have been carried out for the most probable electronic states with $S = 2$ under C_{4v} symmetry (Chart 1). The net spin populations, the corresponding π spin

---

* To whom correspondence should be addressed. E-mail: rjcheng@mail.nchu.edu.tw. Tel: 886-4-22871190. Fax: 886-4-22862547.

(1) La Mar, G. N. In *Spin Delocalization and Electronic Structure*; La Mar, G. N., Horrocks, J. W. D., Holm, R. H., Eds.; Academic Press: New York, 1973.

(2) Goff, H. M. In *Nuclear Magnetic Resonance of Iron Porphyrins*; Lever A. B. P., Gray, H. B., Eds.; Addison-Wesley Publishing Co.: Reading, MA, 1983.

(3) Behere, D. V. *Inorg. Chem.* **1980**, *19*, 992.

(4) Goff, H. M.; Hansen, A. P. *Inorg. Chem.* **1984**, *23*, 321.

(5) Turner, P.; Gunter, M. J. *Inorg. Chem.* **1994**, *33*, 1406.

(6) Richert, S. A.; Tsang, P. K. S.; Sawyer, D. T. *Inorg. Chem.* **1988**, *27*, 1814.

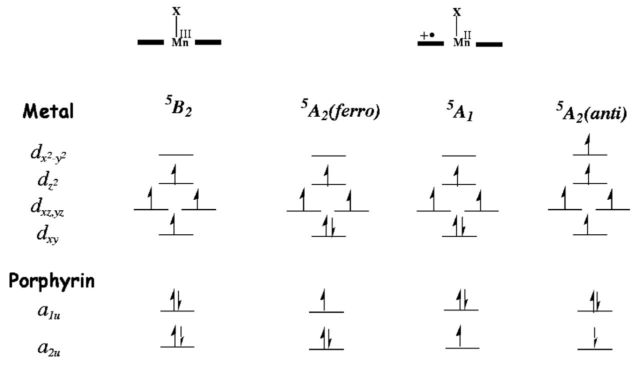
(7) (a) Ghosh, A.; Vangberg, T.; Gonzalez, E.; Taylor, P. *J. Porphyrins Phthalocyanines* **2001**, *5*, 345. (b) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1975**, *97*, 5103.

(8) Cheng, R.-J.; Chen, P.-Y.; Lovell, T.; Liu, T.; Noodleman, L.; Case, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 6774.

(9) Cheng, R.-J.; Wang, Y.-K.; Chen, P.-Y.; Han, Y.-P.; Chang, C.-C. *Chem. Commun.* **2005**, 1312.

10.1021/ic0617238 CCC: $37.00

Chart 1. Possible Electronic Structures of Mn(TPP)X with $S = 2$



populations, and the Fermi contact spin populations on each symmetry-distinct atom type for Mn(TPP)Cl with four different electronic structures from spin-unrestricted ADF calculations are summarized in Table 2. As we would expect, the $^5A_1$ state with an a_{2u}-type α-spin makes *meso*-C highly positively populated but α-C highly negatively populated, which is in contrast to the isotropic shifts observed. Also, the experimental isotropic shift of −11 ppm of *meso*-C is not consistent with the very large negative spin populations of $^5A_2$(anti) and $^5A_2$(ferro), which, in fact, might be closer to the small positive spin population of the $^5B_2$ state. Ultimately, $^5B_2$ is the only state with a positive Fermi contact spin density at α-C and a negative Fermi contact spin density at β-C, which is coherent with the observed isotropic shifts. Generally, electronic structures of $Mn^{II}P^{\bullet+}X$ will end up with too large spin populations on both α- and *meso*-C atoms. Therefore, correlations of the experimental isotropic shifts with the calculated Fermi contact spin densities suggest $^5B_2$ as the leading contributor to the ground state of Mn(TPP)-Cl.

Although we cannot preclude the contribution of another electronic structure, inclusion of other electronic structures with porphyrin cation radical character to induce a significant downfield shift of α-C and an upfield shift of β-C is evidently not necessary. The self-consistent-field (SCF) energies shown in Table 2 also suggest $^5B_2$ as the most stable ground state, consistent with a previous report.[7] However, $^5A_2$(anti), instead of the electronic state $^5A_2$(ferro) proposed by Turner et al., seems to be the first excited state that might make a significant contribution to the ground state. The $^5A_2$(anti) state with high-spin Mn^{II} and a porphyrin a_{2u} cation radical is favored by both its half-filled d^5 electronic manifold and a_{2u} oxidation for the TPP system. However, contribution of the $^5A_2$(anti) state will make β-C and β-H significantly downfield shifted, which contradicts the experimental data. Correlations between the spin populations for Mn(TPP)X (X = Cl, Br, I) complexes of the $^5B_2$ state (Table 2) and the NMR data (Table 1) further support our ground-state assignment. Nevertheless, the unexpected spin populations on the macrocycle for $^5B_2$ high-spin Mn^{III} must be pursued further, as discussed below.

There are two major spin-transfer mechanisms within paramagnetic transition-metal complexes. One is spin delocalization through σ- or π-bonding interactions between the metal and the ligand. The other is spin polarization induced by the electron correlation between half-filled and filled molecular orbitals. Generally, the direct spin delocalization from metal to ligand causes a positive spin density and a downfield shift of the nuclei. Negative spin density corresponding to an upfield shift can only be induced from neighboring atoms through indirect spin polarization. Mostly, the direct spin delocalization instead of the indirect spin-polarization mechanism will dominate the spin population on the ligand.

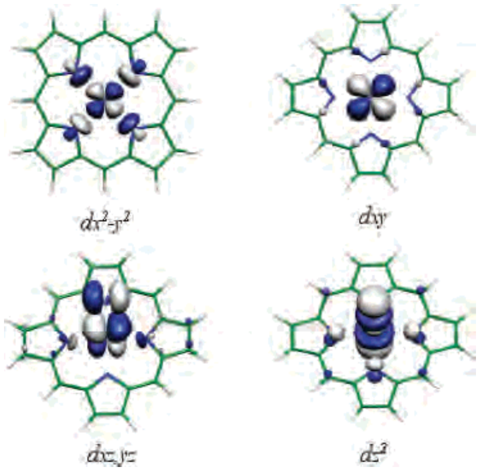


Figure 1. Molecular orbitals based on spin-restricted calculation depicting bonding interactions between metal d orbitals and the porphyrin macrocycle.

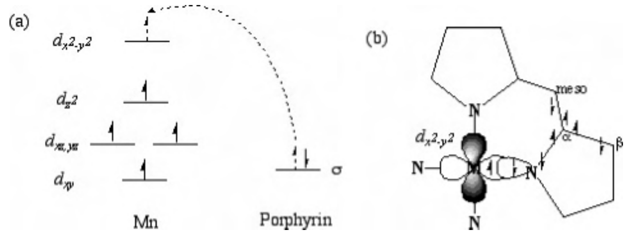


Figure 2. Anomalous spin-polarization mechanism in $Mn^{III}PX$ through P → Mn σ donation.

Molecular orbitals involving the five d orbitals of high-spin MnPCl complex resulting from the spin-restricted ADF calculation displayed by MOLEKEL[10,11] are shown in Figure 1. Accordingly, the $d_{x^2-y^2}$ orbital interacts strongly with a porphyrin σ-type molecular orbital with nodal planes passing through *meso*-C atoms. While the metal d_π orbitals ($d_{xz,yz}$) interact mainly with the out-of-plane π-type molecular orbitals $e_g(\pi)$, the d_{xy} orbital shows weak in-plane π bonding with the porphyrin macrocycle. Similar to the corresponding five-coordinate high-spin FePCl complex, the bonding interaction between d_{z^2} and a_{2u} orbitals is clearly visible but smaller for MnPCl, with orbital contributions of 62.2% d_{z^2} and 10.0% a_{2u}. With the $d_{x^2-y^2}$ orbital empty for the high-spin Mn^{III} complex, an unpaired electron density can be transferred through the other four bonding interactions. However, $d_\pi-e_g$ and $d_{z^2}-a_{2u}$ interactions will put positive π spin densities at β- and *meso*-C atoms, respectively, and make them shift downfield. There must be some unusual spin-

---

(10) Flukiger, P. F.; Luthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL*; Swiss Center for Scientific Computing: Manno, Switzerland, 2000−2002.
(11) Portmann, S.; Luthi, H. P. *Chimia* **2000**, *54*, 766.

Table 2. Net Spin Populations, the Corresponding π Spin Populations (in Parentheses), and the Fermi Contact Spin Populations (in Brackets) on Each Symmetry-Distinct Atom Type[a] for Mn(TPP)X from Unrestricted DFT Calculations

Mn(TPP)Cl	$^5B_2$	$^5A_2$(ferro)	$^5A_1$	$^5A_2$(anti)
Mn	3.7805 (1.7509) [0.75465]	2.6321 (1.6430) [0.58228]	2.7150 (1.7011) [0.60859]	4.1767 [1.7905] [0.81159]
N	−0.0530 (−0.0022) [−0.04107]	−0.0877 (−0.0334) [−0.04017]	0.0494 (0.0750) [−0.01108]	−0.0488 (−0.0636) [0.08989]
C_α	0.0089 (0.0082) [0.00226]	0.1716 (0.1429) [0.02225]	−0.0166 (−0.0004) [−0.01118]	0.0299 (0.0177) [0.01404]
C_β	0.0073 (0.0080) [-0.00044]	0.0403 (0.0434) [0.00069]	0.0126 (0.0156) [0.00019]	0.0102 (0.0076) [0.00510]
C_{meso}	0.0029 (0.0037) [0.00021]	−0.0428 (−0.0180) [−0.01161]	0.02248 (0.1902) [0.03127]	−0.0830 (−0.0683) [−0.01230]
C_q	−0.0001 (0.0001) [0.00026]	0.0021 (0.0004) [0.00059]	−0.0149 (−0.0021) [−0.00730]	0.0042 (0.0009) [0.00282]
β-H	−0.0006 [−0.00009]	−0.0051 [−0.00097]	−0.0007 [−0.00031]	0.0004 [0.00019]
SCF energy	−534.0776 eV	−531.9226 eV	−532.1239 eV	−533.3236 eV

$^5B_2$	Mn(TPP)Cl	Mn(TPP)Br	Mn(TPP)I
Mn	3.7805 (1.7509) [0.75465]	3.7698 (1.7467) [0.76934]	3.7113 (1.8146) [0.78456]
N	−0.0530 (−0.0022) [−0.04107]	−0.0529 (−0.0019) [-0.04176]	−0.0513 (−0.0011) [−0.04317]
C_α	0.0089 (0.0082) [0.00226]	0.0089 (0.0081) [0.00220]	0.0091 (0.0082) [0.00220]
C_β	0.0073 (0.0080) [−0.00044]	0.0075 (0.0083) [−0.00039]	0.0085 (0.0090) [−0.00033]
C_{meso}	0.0029 (0.0037) [0.00021]	0.0026 (0.0034) [0.00008]	0.0016 (0.0026) [−0.00026]
C_q	−0.0001 (0.0001) [0.00026]	−0.0001 (0.0001) [0.00028]	−0.0001 (0.0002) [0.00034]
β-H	−0.0006 [−0.00009]	−0.0005 [−0.00010]	−0.0007 [−0.00012]

[a] Atom types as defined in Figure 2b.

Table 3. Mulliken Closed-Shell (Open-Shell) Populations for the Manganese d Orbitals in the Mn(TPP)Cl Complex with Different Spin States from Unrestricted DFT Calculations

Mn(TPP)Cl	$d_{x^2-y^2}$	d_{z^2}	$d_{xz,yz}$	d_{xy}
$d_{xy}^1 d_{xz,yz}^2 d_{z^2}^1 d_{x^2-y^2}^0$, $S = 2$	0.5712 (0.1641)	0.4220 (0.7306)	0.2308 (0.8410)	0.0000 (0.9573)
$d_{xy}^2 d_{xz,yz}^2 d_{z^2}^0 d_{x^2-y^2}^0$, $S = 1$	0.5516 (0.0788)	0.5682 (0.1773)	0.2574 (0.8483)	1.9396 (0.0122)

polarization mechanisms to compensate for these positive spin densities and bring these C atoms upfield as observed.

It is informative to notice the large negative net spin population on pyrrole N atoms for the $^5B_2$ state. Both $d_\pi-e_g$ and $d_{z^2}-a_{2u}$ bonding interactions will make the pyrrole N atoms positively populated with π spin densities. The only possibility to make the pyrrole N atoms negative is through P → Mn σ donor interaction from the porphyrin N lone pairs to the empty $d_{x^2-y^2}$ orbital. Electron correlation favors the transfer of α spin from the ligand to the metal, thereby leaving a net β-spin density in the N donor orbital, as shown in Figure 2a. Spin polarization along the bonding skeleton can further rationalize all of the unexpected spin populations on the porphyrin macrocycle (Figure 2b). These types of spin polarization mechanisms were first described by Levy and Orgel.[12] However, with four unpaired electrons and vacant $d_{x^2-y^2}$ orbital in high-spin Mn^{III} complexes, the effect of electron correlation will be maximized. This can be demonstrated with an open-shell population of 0.1641 in the $d_{x^2-y^2}$ orbital, which is the excess of the α spin donated from the N lone pairs. As the number of total unpaired electrons decreases to two ($S = 1$), the open-shell population in the $d_{x^2-y^2}$ orbital decreases to 0.0788 (Table 3). Therefore, for d^4 high-spin transition-metal complexes, this influence might overrule other direct spin-delocalization pathways and result in an extreme spin-polarization mechanism. Whether a similar influence will be effective on other systems with three or two unpaired electrons and a vacant $d_{x^2-y^2}$ orbital will depend on the efficiency of other coexisting spin-delocalization mechanisms.

In summary, both spin distributions based on theoretical calculations and the NMR data from experiments strongly support the assignment of the high-spin Mn^{III} electronic structure to the Mn(TPP)X (X = Cl, Br, I) complexes. The combined results from the unusual spin distribution and the bonding analysis reveal an anomalous spin-polarization mechanism unique to the high-spin Mn^{III} system with four unpaired electrons. The DFT-based calculation appears to be very promising for handling spin polarization without significant spin contamination for complicated open-shell systems. Although there have been many theoretical studies of paramagnetic metalloporphyrins, not all useful information has been extracted from the available data. To the best of our knowledge, this extreme spin-polarization mechanism has been demonstrated for the first time. Also, it is critical to realize this mechanism to correctly rationalize the spin-density distribution around the porphyrin macrocycle.

Acknowledgment. This work was supported by the National Center for High-Performance Computing and the National Science Council of Republic of China (Grant NSC91-2113-M-005-018).

Supporting Information Available: Computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0617238

---

(12) Levy, D. A.; Orgel, L. E. *Mol. Phys.* **1961**, *3*, 583.