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Communications to the Editor

A “Magnetochemical” Series. Ligand Field Strengths of Weakly Binding Anions Deduced from $S = {}^3/_2, {}^5/_2$ Spin State Mixing in Iron(III) Porphyrins

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From magnetism to biology, the spin states of iron are remarkable for the diversity and subtlety of their chemistry.[1] Nowhere is this better illustrated than in iron porphyrin chemistry, where all possible spin states have been systematically investigated and where the underlying importance of spin to hemoprotein function has become widely appreciated.[2,3]

The spin state of an iron atom is determined by the field strength and the symmetry of the surrounding ligands, i.e., the ability of the ligands to split the d orbital energies. In this paper, we show that the unusual phenomenon of admixture of $S = {}^3/_2$ and ${}^5/_2$ spin states in iron(III) porphyrins and related macrocycles provides uniquely sensitive opportunities to rank the ligand field strengths of weakly binding anions. By analogy to the well-known Spectrochemical Series, the resulting hierarchy can be called a magnetochemical series.

The concept of admixed spin states, developed in hemes by Maltempo[4] from the earlier theory of Griffith[5] and explored most recently by Bominaar and Block,[6] is exemplified by the perchlorate complex $Fe^{III}(OClO_3)(TPP)$ (TPP = tetraphenylporphyrinate).[7] Its particular tetragonal ligand field makes the intermediate ($S = {}^3/_2$) and high ($S = {}^5/_2$) spin states of iron very close in energy. Rather than create the commonly observed thermal *equilibrium* between the two spin states (so-called spin crossover), the selection rules of quantum mechanics and spin−orbit coupling allow the two states to mix completely and create a new, discrete, *admixed* ground state. Such admixed $S = {}^3/_2$, ${}^5/_2$ states give rise to magnetic properties that lie along a continuum between the extremes of the pure $S = {}^3/_2$ and $S = {}^5/_2$ states. These include magnetic moments between 3.9 and 5.9 μ_B, EPR $g_\perp$ values (x,y tensors) between 4.0 and 6.0, Mössbauer quadrupole splitting values (ΔE_q) that increase with increasing $S = {}^3/_2$ character, and, for TPP complexes, ^1H NMR $\delta_{pyrrole}$ values which shift dramatically upfield with increasing $S = {}^3/_2$ character. These properties are sensitive reporters of changes in the ligand field strength of X^- in a series of FeX(TPP) complexes. Herein lies the essence of our proposal. The relative field strengths of ligands can be readily ranked if their complexes lie in the admixed spin regime. Elements of this idea can be found in our earlier work[7] and in the NMR studies of Goff,[8,9] but the scope and implications of these observations have not been recognized previously.

The principle is first illustrated for anions X^- in the series FeX(TPP), for which available μ_{eff}, $g_\perp$, ΔE_q, and $\delta_{pyrrole}$ data are gathered in Table 1. Of the four parameters, the most sensitive to the degree of $S = {}^3/_2$, ${}^5/_2$ admixture is the ^1H chemical shift of the eight pyrrole protons on the periphery of the porphyrin macrocycle, $\delta_{pyrrole}$. High-spin species such as FeCl(TPP) have large *down*field shifts (+80 ppm), whereas species approaching pure intermediate spin have *up*field shifts that can be as large as −62 ppm. Such upfield shifts in FeX(TPP)-type species have not been reported previously, and it is interesting to speculate on the upper boundary and how $\delta_{pyrrole}$ scales along the cotninuum. The unliganded species, $Fe(TPP)^+$, which is expected to have a pure $S = {}^3/_2$ spin state, is presently unrealizable because of ligand-like interactions with arene solvent molecules.[13] The trend in $\delta_{pyrrole}$ values gives rise to the following field strength order: $Ag(Br_6CB_{11}H_6)_2^- < CB_{11}H_{12}^- < SbF_6^- < Co(C_2B_9H_{11})_2^- < AsF_6^- < ClO_4^- < C(CN)_3^- < CF_3SO_3^- < BF_4^- < ONC(CN)_2^- < ReO_4^-$. The next most useful parameter is magnetic moment (μ_{eff}), where despite possible solid state effects (e.g., intermolecular magnetic coupling, differing effects of solvation, impurity effects, experimental error, etc.), essentially the same correlation is observed. The lack of extensive data in the $g_\perp$ column of Table 1 arises from poor solubility in a common inert solvent (e.g., toluene) and from signals too broad to achieve an accurate ranking. Available Mössbauer quadrupole splittings, ΔE_q, appear to follow a trend of increasing magnitude with increasing $S = {}^3/_2$ character. There is a remarkable general congruence of derived ligand rankings from the four parameters, even though each has a different physical basis. Small reversals in ligand rankings may result from differing conditions of measurement.

Since stronger field axial ligands such as halides, alkoxides, azide, thiocyanate, η^2-nitrate, thiolates, carboxylates, sulfonates, μ-oxide, sulfate, bisulfate, and teflate ($OTeF_5^-$)[14] all form high-spin complexes in the FeX(TPP) series, they can be grouped at the high-field end of the series but not ranked. However, while it is not possible to form a more extended magnetochemical series from data on tetraphenylporphyrin complexes, the series can be extended to other sequences by changing the macrocycle. Increased tetragonality of the overall ligand field shifts high-spin complexes into the admixed-intermediate-spin regime. This is illustrated by the analogous octaethylporphyrin (OEP), phthalocyanine (Pc), and octaethyltetraazaporphyrin complexes (OETAP), which have progressively increasing *xy* ligand fields. Thus, FeCl(TPP) is high spin, but FeCl(Pc) is admixed[15] and FeCl(OETAP) is pure intermediate.[16] OEP is only a marginally stronger field macrocycle than TPP. Nevertheless, the ^1H NMR spectrum of $Fe(OTeF_5)(OEP)$ hints that $X = OTeF_5^-$ is shifted into the admixed regime.[14] The effect of phthalocyanine is more dramatic. Published μ_{eff} and ΔE_q data on phthalocyanine complexes of the type FeX(Pc)[15] give rise to the sequence $I^- < Br^- < Cl^-$ and also suggest $Br^- \approx Cl_3CCO_2^- \leq CF_3CO_2^-$.

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[1] *Research Frontiers in Magnetochemistry*; O’Connor, C. J., Ed.; World Scientific: Singapore, 1993.

[2] Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.

[3] Mitra, S. In *Iron Porphyrins. Part II*; Lever, A. P. B., Gray, H. B., Eds.; Addison Wesley: Reading, MA, 1983.

[4] Maltempo, M. M. *Q. Rev. Biophys.* **1976**, *9*, 181.

[5] Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, UK, 1961.

[6] Bominaar, E. L.; Block, R. *J. Chem. Phys.* **1991**, *95*, 6712.

[7] Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

[8] Boersma, A. D.; Goff, H. *Inorg. Chem.* **1982**, *21*, 581.

[9] Goff, H. M.; Shimomura, E. T.; Phillippi, M. A. *Inorg. Chem.* **1983**, *22*, 66.

[10] Gupta, G. P.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022.

[11] Bohle, D. S.; Conklin, B. J.; Hung, C.-H. *Inorg. Chem.* **1995**, *34*, 2569.

[12] Ohlhausen, L.; Cockrum, D.; Register, J.; Roberts, K.; Long, G. L.; Powell, G. L.; Hutchinson, B. B. *Inorg. Chem.* **1990**, *29*, 4886.

[13] Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2433.

[14] Kellett, P. J.; Pawlik, M. J.; Taylor, L. F.; Thompson, R. G.; Levslik, M. A.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1989**, *28*, 440 and references therein.

[15] Kennedy, B. J.; Murray, K. S.; Zwack, P. R.; Homborg, H.; Kalz, W. *Inorg. Chem.* **1986**, *25*, 2539.

[16] Fitzgerald, J. P.; Haggerty, B. S.; Rheingold, A. L.; May, L.; Brewer, G. A. *Inorg. Chem.* **1992**, *31*, 2006.

0002-7863/96/1518-3281$12.00/0

Table 1. Parameters in FeX(TPP) Admixed $S = {}^3/_2, {}^5/_2$ Spin Complexes Used for Field Strength Ranking

anion	μ_{eff} (μ_B), 300 K	ΔE_q (mm s^{-1}) 4.2 K	ΔE_q (mm s^{-1}) room temp	$g_\perp$ (vs DPPH)	^{1}H $\delta_{\mathrm{pyrrole}}$ (ppm)	ref
$Ag(Br_6CB_{11}H_6)_2^-$	4.1	*a*	*a*		−62.0 (CD_2Cl_2)	this work
$CB_{11}H_{12}^-$	4.2	4.12		4.15		10
			3.77		−58.5 (C_6D_6)	this work
SbF_6^-	4.1	4.29				10
					−49 (C_6D_6)	this work
$Co(C_2B_9H_{11})_2^-$	4.0		3.69	∼4.2 (C_7H_8)	−48.5 (C_6D_6)	this work
					−44 (C_7D_8)	
AsF_6^-	4.25		3.25		−31.5 (C_6D_6)	this work
ClO_4^-	5.2	3.5		4.75		7
					13.0 ($CDCl_3$)	8
			2.79		27.7 (C_6D_6)	this work
$C(CN)_3^-$	5.4	*b*	*b*	5.2	24.0 ($CDCl_3$)	8
					28.2 (C_7D_8)	
$CF_3SO_3^-$	5.5			4.3 ($CHCl_3$)	39.3 ($CDCl_3$)	8
			2.39	∼5.4 (C_7H_8)	47.9 (C_6D_6)	this work
BF_4^-			1.6		56.2 ($CDCl_3$)	this work
$ONC(CN)_2^-$	5.3			5.6 (C_7H_8)		11
ReO_4^-	5.5		1.32 (78 K)			12
	5.76[c]			∼5.8 (C_7H_8)	61.5 ($CDCl_3$)	this work
					66.7 (C_6D_6)	this work

[a] Data unobtainable due to X-ray absorption by bromine atoms. [b] Crystal structure shows six-coordination, thereby invalidating a comparison to five-coordinate species of the type FeX(TPP), at least for data gathered in the solid state. Quoted data are for solution where five-coordination is likely. [c] μ_{eff} obtained for a diamagnetic correction of the macrocycle of -700×10^{-6} cgs emu/mol compared to the one used in ref 12 (-442×10^{-6}).

In summary, the concept of admixed spin states leads to the following qualitative magnetochemical ranking of ligand field strength for iron(III): $Ag(Br_6CB_{11}H_6)_2^- < CB_{11}H_{12}^- < SbF_6^- < Co(C_2B_9H_{11})_2^- < AsF_6^- < ClO_4^- < C(CN)_3^- < CF_3SO_3^- < BF_4^- < ONC(CN)_2^- < ReO_4^- < OTeF_5^- < I^- < Br^- < Cl^-$. Some ligands are ranked for the first time, and the method is particularly useful for the weaker binding and weaker field anions.

The traditional ranking of ligand field strengths is the Spectrochemical Series, derived primarily from the electronic spectroscopy of octahedral Co(III) complexes.[17] A magnetochemical series differs in a number of ways, most fundamentally by being a ground state property. This gives rise to greater sensitivity and to differences in ordering. For example, from the d−d absorptions of $[Co(NH_3)_5X]^{2+}$, a spectrochemical series $Br^- < Cl^- \lesssim ClO_4^- \lesssim ReO_4^-$ is evident.[18] The iron-based magnetochemical series gives $ClO_4^- < ReO_4^- < Br^- < Cl^-$ with much clearer differentiation. The different ordering may reflect the greater importance of π-donation from 2p oxyanions to d^5 iron(III) relative to $(t_{2g})^6$ cobalt(III) (where the d_π orbitals are filled) and/or the role of spin−orbit coupling. It is our hope that the qualitative observations of this paper will stimulate new interest in the definition and parametrization of ligand field strength in low-symmetry molecules and in the more quantitative aspects of spin state mixing. Admixed spin states of other multiplicites have yet to be discovered.

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(17) Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1938**, *13*, 388. Jorgenson, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, 1962.

(18) The $\lambda_{\max}$ values for $X = Br^-, Cl^-, ClO_4^-$, and ReO_4^- are 542, 530, ∼530, and 532 nm, respectively. See ref 17 and the following: Harrowfield, J. M.; Sargeson, A. M.; Singh, B.; Sullivan, J. C. *Inorg. Chem.* **1975**, *14*, 2864. Lenz, E.; Murmann, R. K. *Inorg. Chem.* **1968**, *7*, 1880.