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Explorations in metalloporphyrin stereochemistry, physical properties and beyond

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Abstract

A review of selected portions of our work in the area of porphyrin structure and physical characterization is presented. Topics covered include early work on periodic trends in first row transition metalloporphyrins, a survey of electronic structure of iron derivatives including spin-state trends, ligand orientation effects and the elucidation of unusual low-spin states for iron(II). A discussion of the different types of high-spin iron(II) complexes and the effects of hydrogen bonding is given. A survey of nitric oxide (NO) derivatives is presented as well as a brief introduction into the use of nuclear resonance vibrational spectroscopy for the study of iron porphyrins and heme proteins.

Keywords

Iron porphyrinates; electronic structure; molecular structure; nitrosyl complexes; periodic trends; EPR and Moessbauer spectroscopy

INTRODUCTION

This paper is loosely taken from my Hans Fischer Career award lecture given at ICPP-5 in Moscow. As such, it is not a complete review of all work that has been carried out by me or my collaborators in porphyrin chemistry, but an author chosen selective survey.

My work in porphyrin synthesis and characterization began during my postdoctoral stint in the laboratory of Professor J. Lynn Hoard. Professor Hoard was a distinguished structural inorganic/physical chemist who made seminal contributions in the structural descriptions of icosahedral borides, higher coordination number complexes, uranium complexes, and porphyrin derivatives. I went to Cornell because of an interest in higher coordination chemistry and had a successful first few months characterizing the structures of several *cis*-dioxovanadium (V) complexes [1–3]. Amusingly, none had a coordination number greater than six. During this time, I noted other members of the Hoard laboratory working on porphyrin structures. I went to discuss my next projects with Professor Hoard and made an “offer.” I would now begin work in the area of metalloporphyrins spending part of my time on projects of special interest to him and part of the time on projects of particular interest to me. At this time, I regarded the porphyrin ligand as an extremely versatile ligand for coordination chemistry with any biological issues of secondary importance. I have since recanted. I dedicate this paper to the fond memory of Professor J. L. Hoard (1905–1993).

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DISCUSSION

Discussion with Prof. Hoard about expanding the central hole of the porphyrin core led to the preparation and structural investigation of the tin(IV) complex $[\text{Sn}(\text{TPP})\text{Cl}_2]$.¹ The result was a spectacular success with the structure determined to exceedingly high resolution (0.516 Å) [4]. The core undergoes a substantial radial expansion with Sn–N distances of 2.098 Å, with the Sn centered precisely in the ring center. This was the first time that such a strong porphyrin ring expansion had been demonstrated. Other large changes, relative to a nickel complex, are large increases in the $\text{C}_a\text{--N--C}_a$ angle, opening of the $\text{C}_a\text{--C}_m\text{--C}_a$ angle. The results are summarized in Fig. 1. Other work that was started at Cornell was the beginning of studies of metalloporphyrins with nitric oxide and other species interesting from an inorganic chemistry perspective including periodic trends. These will be described as appropriate in future sections of this paper.

The studies that I wanted to carry out concerning periodic trends were investigations examining how the structures of metalloporphyrins changed as the number of d electrons and the d electron configuration changed. These studies emphasized the first row transition elements from chromium to zinc. A summary of the structural behavior of the necessarily square-planar species is given in Table 1. Two species require additional comment. The structure of $[\text{Mn}(\text{TPP})]$ was observed to have a thermal parameter for manganese that is inconsistent with the precise centering of the metal atom in the porphyrin center at either RT or 118 K as shown in Fig. 2 [6]. This result strongly emphasized the importance of a filled or half-filled $d_{x^2-y^2}$ orbital that leads to an expanded porphyrin core in the structure. The second issue deals with the differing physical properties of four-coordinate $[\text{Fe}(\text{TPP})]$ and $[\text{Fe}(\text{Pc})]$. Later work [8] showed the importance of solid-state intermolecular interactions in defining the precise nature of the $S = 1$ state and that reference should be consulted for details.

The effects of increasing the coordination number to five are summarized in Table 2. Again the importance of whether or not the $d_{x^2-y^2}$ orbital is populated is evident; this is seen in very large out-of-plane displacements for the M(II), Fe(II) and Fe(III), and Zn(II) species. Although the $[\text{Co}(\text{TPP})(1\text{-MeIm})]$ derivative [16] was studied as part of the periodic trends of structure project, it became useful in a discussion by Lynn Hoard and myself of why cobalt(II) porphyrins are a qualitatively acceptable substitute for iron(II) in the oxygen binding proteins myoglobin and hemoglobin [15]. An outgrowth of that discussion was the preparation and structural characterization of $[\text{Co}(\text{TPP})(\text{Me}_2\text{Im})]$, the bulky methyl substituents were expected to lead to a longer axial bond length and a larger out-of-plane displacement of the cobalt(II) [17]. Such effects were indeed found, although the magnitude was somewhat less than originally expected. I believe that the Hoard, Scheidt PNAS paper also had some other benefits. It brought to the fore the need for protein structures to account for possible nonplanar conformations of the porphyrin ring. It also led to my immediate increased involvement in iron porphyrinate chemistry and structure.

The six-coordinate species were also on the periodic trends agenda and a summary of some results is given in Table 3. The early study of the cobalt(II) complex $[\text{Co}(\text{TPP})(\text{Pip})_2]$ [24] showed the significance of a populated d_z^2 orbital; the corresponding bond in the cobalt(II) complex $[\text{Co}(\text{TPP})(\text{Pip})_2]^+$ where this orbital is unoccupied is extremely large [23]. The pattern

¹Abbreviations: C_a , pyrrole alpha carbon; C_β , pyrrole beta carbon; C_m , methine carbon; 4-CNPy, 4-cyanopyridine; 3-ClPy, 3-chloropyridine; Deut, deuteroporphyrin dianion; EPR, electron paramagnetic resonance; Him, imidazole; L, general axial ligand, usually a nitrogen donor; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; 2-MeIm[−], 2-methylimidazolate; Me₂Im, 1,2-dimethylimidazole; 4-Me₂NPy, 4-dimethylaminopyridine; OEP, octaethylporphyrin dianion; Pip, piperidine; Porph, generalized porphyrin dianion; N_p , porphyrin nitrogen atom; Py, pyridine; Pc, dianion of phthalocyanine; PMS, petamethylenesulfoxide; THT, tetrahydrothiophene; TMSO, tetramethylenesulfoxide; TMP, tetramesitylporphyrin dianion; TTP, tetratolylporphyrin dianion; 1-VinIm, 1-vinylimidazole; X, generalized anionic ligand.

is marked in the table by noting which axial bond distances are expected to be long by the criterion of a populated d_z^2 orbital.

The synthetic chemistry of iron porphyrinates was strongly assisted by the availability of important synthetic intermediates. One of the most important of these is the perchlorato-ligated derivative $[\text{Fe}(\text{TPP})(\text{OClO}_3)]$ that is illustrated in Fig. 3. The out-of-plane displacement of the iron(III) center is significantly different from that of either low-spin or high-spin species. Indeed, the molecule has the unusual electronic state of a quantum-admixed intermediate spin state ($S = 3/2, 5/2$). This state leads to unusually large values of the Moessbauer quadrupole splitting value (values greater than 3 mm/s and axial EPR spectra with $g > 4$). The coordinated perchlorate ligand, in addition to being a weak-field ligand that leads to the intermediate-spin state, is also a weakly binding ligand that will be easily replaced even by relatively weak ligands. Marj Kastner in my lab used this complex to prepare the six-coordinate, high-spin complex $[\text{Fe}(\text{PP})(\text{H}_2\text{O})_2]^+$, the first such structurally characterized species [27,29]. It has the iron centered in the porphyrin plane even though the iron is in the high-spin state, this does require that there be radial core expansion consistent with the population of the $d_{x^2-y^2}$ orbital. Of course, once the first of these species was found, unexpected by at least some, many more such species were soon found. These include many derivatives with weakly binding oxygen ligands. Only one similar complex has been found with iron(II), six-coordinate high-spin complexes with tetrahydrofuran as the pair of axial ligands [35,36]. The iron(III) perchlorate intermediate has also been useful in preparing a number of other iron(III) derivatives with weakly coordinating ligands. A limited selection of those along with some additional six-coordinate iron(II) derivatives are given in Table 4.

At this point, a relatively large number of the possible spin-state/coordination number/oxidation state possibilities were known and are summarized in Table 5. With this data Chris Reed and I wrote a review entitled “*Spin State/Stereochemical Relationships in Iron Porphyrins: Implications for the Hemoproteins.*” This review [37], which has been widely cited, is still useful to this day. I have often called this the “The Smith Brothers Paper” because it is short and sweet. The “easy” lesson is that virtually all of iron porphyrin stereochemistry can be deduced, at a rather high level of precision, simply by knowing if the $d_{x^2-y^2}$ and d_z^2 orbitals are populated or not.

One of the features of the porphyrin macrocycle that attracted me was the possibility of interesting magnetic behavior. Initially I regarded this as either the stabilization of an unusual coordination number/oxidation state pairing or systems that exhibited spin crossover behavior. The report by Johann Buchler and Allen Hill [38] that the complex $[\text{Fe}(\text{OEP})(3\text{-ClPy})_2]\text{ClO}_4$ exhibited spin crossover behavior with the complex being low spin at lower temperature and an approximate 50:50 spin mixture at room temperature was immediately attractive. We were interested in the possibility of using multiple temperature crystallography in investigating such systems and we applied our recently acquired low temperature device to collect an X-ray data set at 98 K. The structure was clearly that of a low-spin species with equatorial Fe—N_p bond distance average of 1.995 Å and an axial bond distance of 2.031 Å. The complex crystallizes in the triclinic crystal system with required inversion symmetry. These differences were very different when the structure was determined at room temperature. The average equatorial Fe—N_p bond distance of 2.014 Å is clearly near the average expected for low-spin and high-spin forms of the complex. The axial distance and structure was a bit more complicated and we applied a deconvolution process that we term “crystallographic resolution of spin isomers” [39]. The results are depicted in Fig. 4.

Eventually, we also considered and investigated systems with the possibility of spin coupling between magnetic centers including the porphyrin ring (as a π -cation radical) and a small sampling can be found in references [40–47].

During the time that we were analyzing the crystallographic data of $[\text{Fe}(\text{OEP})(3\text{-ClPy})_2]\text{ClO}_4$, I spent several months on sabbatical in the laboratory of Prof. Martin Gouterman at the University of Washington. One of my objectives was to apply Martin's (modern by the standards of the day) charge iterative extended Huckel program to understanding the spin state complexities of iron porphyrinates. Amongst other calculations, we calculated the potential energies of the $[\text{Fe}(\text{Porph})(\text{L})_2]^+$ system as a function of equatorial and axial distances, using values from our experimental determinations of the various types. We reached two wide-ranging conclusions. Conclusion 1: Except for very strong field axial ligands, the energy minima for low-spin, intermediate-spin, and high-spin states are not very different. Conclusion 2: Application of small perturbations to closely related porphyrin systems might lead to differing ground or excited states. These results along with other discussion were published as a book chapter entitled "Ligands, Spin State, and Geometry in Hemes and Related Metalloporphyrins" in the Gray, Lever series on bioinorganic chemistry [48].

Upon my return from the University of Washington, David Geiger and I encountered strong experimental proof of these conclusions. We (serendipitously) obtained a new crystalline polymorph of $[\text{Fe}(\text{OEP})(3\text{-ClPy})_2]\text{ClO}_4$ which had crystallized in the monoclinic crystal system. Both crystalline forms had identical composition but, as we discovered, substantially different solid-state temperature-dependent magnetic susceptibilities. The second phase is not a spin-crossover system, but instead represents the third possible spin state for iron(III), namely a quantum-admixed intermediate spin state [49]. We have found many more examples of N-ligated intermediate-spin systems subsequently [50–52]. The ultimate cause of the difference in spin state arises from differing relative axial ligand orientations that lead to the requirement of long axial bonds as shown in Figs. 5 and 6. This immediately raises the following questions. 1) Are there natural axial ligand orientation preferences? The limiting cases for two axial planar ligands are relative parallel orientations in which the two ligands are in the same and relative perpendicular orientations. 2) Can the axial ligand orientation be controlled and 3) what physical properties are affected? These questions opened up a rich vein of research.

Sarah Osvath prepared the bis-imidazole-ligated iron(III) complex that fortuitously had two distinct iron sites in the crystal. Both had relative parallel oriented imidazole ligands but the absolute orientation of the imidazole ligand in the two sites were roughly 45° apart. This leads to the presence of two distinct EPR spectral features in the solid-state EPR spectrum [53,54]. Both can be described as "classic" rhombic spectra with distinct values for g_x , g_y , and g_z . Values observed were 3.00, 2.2, and 1.47 or 2.84, 2.32, and 1.59. The use of the sterically hindered ligand 2-methylimidazole in $[\text{Fe}(\text{TPP})_2\text{-MeHIm}]_2^+$ leads to a structure in which the two ligands have a relative perpendicular axial ligand orientation and an unusual EPR spectrum with typically only one of the three rhombic values observed and that with a g -value > 3.4 [32,53]. This signal has been called various names, but I prefer the term "large g_{max} ." These differences in the EPR spectra reflect changes in the relative energies of the three lowest lying d-orbitals and is schematically shown in Fig. 7.

Ken Hatano and Martin Safo pointed out the way to control the axial ligand orientation in iron (III) systems through the use of modest steric hindrance of the axial ligand (various pyridines) and peripheral crowding of the tetraaryl porphyrins, most notably tetramesitylporphyrin. The combination leads to two orthogonal ligand binding pockets on the two sides of the porphyrin plane leading to relative perpendicular orientations of the two pyridine ligands. The use of imidazole as the axial ligand yields compounds with relative parallel orientations as the steric requirements of the five-membered ring are (modestly) less [55,56]. Fig. 8 illustrates the 4-Me₂NPy derivative. Safo prepared a series of pyridines with varying pyridine basicity [57]. Most of these had the large g_{max} signal, and commensurate Moessbauer spectra. But one derivative, the very weakly basic 4-CNPy, had an unusual and unexpected axial EPR spectrum and a Moessbauer spectrum with a small quadrupole splitting constant. We concluded that the

strongly π -accepting character of the 4-CNPy led to the inversion of the d-orbitals as shown in Fig. 9, where the d_{xy} orbital is now the highest in energy of the t_{2g} set. This was confirmed by a study of $[\text{Fe}(\text{TPP})(4\text{-CNPy})_2]^+$ where the steric effects have been largely removed and the observed relative perpendicular orientation can only arise from π -bonding effects [58]. The complex also shows an axial EPR spectrum, consistent with the d_{xy} orbital as the higher energy and singly occupied orbital. This electronic structure is schematically illustrated in Fig. 9.

Additional studies that tried to enforce a relative perpendicular orientation on iron(II) had mixed results. Most systems, including many that are successful in iron(III) yield, in many cases, relative parallel orientations of the axial ligands [60,65]. Very bulky ligands and the use of picket fence porphyrin gave complexes with relative perpendicular orientations in iron(II) species [62,66]. Additional iron(II) and iron(III) studies are detailed in references [61–64].

The importance of the strongly π -accepting character of axial ligands in yielding electronic structure in which the d_{xy} orbital is now the highest in energy in iron(III) is given by the characterization of two isocyanide derivatives [67]. All of the iron(III) species where the d_{xy} orbital is the highest in energy also have strongly ruffled porphyrin cores. This is thought to be the result of the ring distortion required to achieve overlap between the iron d_{xy} orbital and the a_{2u} orbital of the porphyrin.

In what eventually turned out to be an unsuccessful investigation of the Raman spectrum of six-coordinate, high-spin $[\text{Fe}(\text{TPP})(\text{THF})_2]$ with Tom Loehr, Mary Ellison isolated a new crystalline polymorph of the high-spin derivative $[\text{Fe}(\text{TPP})(2\text{-MeIm})]$ [68]. The first report of this complex had substantial disorder of the axial ligand leading to some metrical limitations [69]. The core conformation was also very different. This initial result led us to begin an intensive investigation of the high-spin iron(II) complexes $[\text{Fe}(\text{Porph})(\text{Hind-Im})]$. We find that the complexes can display a wide variety of core conformations, but the displacement of iron from the four nitrogen atom mean plane is relatively constant at $\sim 0.35\text{--}0.36\text{ \AA}$, whereas the iron atom displacement from the 24-atom plane shows larger variation [70,71]. The feature that is the most significant is that the iron(II) appears to be significantly smaller in these imidazole-ligated complexes than those in a series of iron(II) species with an anionic ligand as the axial ligand. These ligands included halides, methoxides and phenolates. This is schematically illustrated in Fig. 10. This immediately suggested to us, among other reasons, that coordinated imidazolate anion would be an interesting system to intensively characterize. The structures of $[\text{Fe}(\text{OEP})(2\text{-MeIm}^-)]^-$ and $[\text{Fe}(\text{TPP})(2\text{-MeIm}^-)]^-$ clearly showed the same pattern as illustrated in Fig. 11. An even more striking feature is the differences in electronic structure as also shown in the figure. Not only are the quadrupole splitting and isomer shift values significantly different, but the sign of the quadrupole splitting constant, obtainable from Moessbauer measurements made in applied magnetic field, are opposite. This can result only from the two structural types of iron(II) also having differently occupied d orbitals [72].

We have also tried to assay the effects of hydrogen bonding to the N—H proton of a coordinated imidazole, an effect that has been suggested to have biological significance. This has proven to be a difficult task and it seems that the possible effects of hydrogen bonding to the N—H proton of a coordinated imidazole leads to variable effects. One clear-cut case in structure is schematically illustrated in Fig. 12 [73]. Other cases of hydrogen bonding leading to change are much more ambiguous [74].

One of my initial interests was the study of the interaction of nitric oxide (NO) with metalloporphyrins. This was initially a totally curiosity driven project, because at the time NO was simply regarded as a toxic gas. Subsequently to a number of our studies, NO is now recognized as important secondary biological messenger. The first of the nitrosyl derivatives studied was the five-coordinate cobalt derivative, $[\text{Co}(\text{TPP})(\text{NO})]$ [75]. Following my move

to the University of Notre Dame, Mark Frisse developed a neat and simple crystallization method for air-sensitive materials. This was applied to the preparation and characterization of the iron derivative, [Fe(TPP)(NO)] [76]. A bit later on, we were able to prepare analogous Mn, [Mn(TTP)(NO)] [77], and Fe(III), [Fe(TPP)(NO)]⁺ [78], derivatives. As can be seen in Fig. 13, the series has well-defined structural trends, especially the M—N—O angle, the M—N bond distance, and the metal atom displacement out-of-plane. Unfortunately, the structures of the [Co(TPP)(NO)] and [Fe(TPP)(NO)] structures were marred by substantial disorder in the axial ligand position, that was required by the crystallographic symmetry to occupy multiple positions. Some years later, Mary Ellison obtained ordered examples of both the iron[79] and cobalt[80] derivatives of [M(OEP)(NO)]. The iron system was obtained in two different crystalline forms, both of which displayed unusual effects that are directly caused by the NO ligand: an off-axis tilting of the Fe—N bond axis (by several degrees) and an equatorial asymmetry in the Fe—N_p bonds related to the orientation of the the FeNO plane. This phenomenon has now been seen in a number of additional examples [81–83] and is clearly an intrinsic feature of the bonding of NO to iron(II) porphyrins systems where the Fe—N—O angle is in the 140–150° region.

The five-coordinate nitrosyls were an open invitation to a coordination chemist to attempt to satisfy the apparent coordinative unsaturation and add an additional ligand. This experiment showed what was then a still unexpected result. The addition of an imidazole ligand leads to the expected six-coordinate species but the NO ligand exerts a strong structural trans effect. The Fe—N(Im) bond trans to the NO is much longer than expected as illustrated in Fig. 14 [84,85]. The distance is almost 0.2 Å longer than expected in an low-spin iron(II) complex. This trans bond appears quite pliable and is probably the chief feature that enables NO to be a signalling molecule in biology. The effect is seen with other ligands, especially interesting is the piperidine case [86] with two different crystalline forms and two different trans bond distances. These complexes showed that the NO stretching frequency is a remote trans bond detecting system [86]. This has been further demonstrated in a series of temperature-dependent crystal structures and IR investigation [87]. There are other effects on the structure around iron on the addition of the sixth ligand that have been summarized in references [87–89]. We have also characterized additional iron(III) species, especially six-coordinate species and the original references include the following [90–94]. The nitrosyl derivatives were also the original impetus for my laboratory beginning to explore and develop the new vibrational technique NRVS (nuclear resonance vibration spectroscopy). NRVS is a synchrotron-based vibrational spectroscopic method that yields the complete vibrational spectrum of a Moessbauer-active probe nucleus. In simple terms NRVS combines nuclear excitation and molecular motion [95–98]. We have used the method to explore iron species where the ⁵⁷Fe nucleus is the target and the complete, isotope-sensitive vibrational spectrum is available. Only those modes that involve motion of the iron atom will be observed. The selectivity, along with the fact that there are no selection rules, means that iron vibrations that are not observable by IR or resonance Raman spectroscopy will be accessible by NRVS. NRVS absorptions are related to the classical Moessbauer absorption between the nuclear ground state and the nuclear excited state wherein the energy of the observed transition is the energy of the classical absorption plus or minus the energy of the vibrational quantum of the vibration being observed. A schematic of the method's basis is shown in Fig. 15. The intensity of these absorptions is much less than that of the standard Moessbauer absorption. This feature and the fact that the energy differences are so small requires the use of X-rays from a third generation synchrotron source and an extremely high resolution monochromator for the incident beam. The availability of all frequencies with iron motion means that assigning spectra is a difficult task. We have pioneered in the use of oriented single crystal measurements in order to assign NRVS spectra. Theoretical calculations, especially the spectral predictions of density function theory calculations have also aided in the spectral assignments.

NRVS spectral data and assignments have now appeared for five-coordinate [Fe(TPP)(NO)] [99,100] and [Fe(TPP)(2-MeHIm)] [101]. The study of several six-coordinate carbonyl derivatives, [Fe(Porph)(CO)(Im)], all with an imidazole as the trans ligand has provided new information about the nature of the Fe—Im vibration that is not seen in the resonance Raman spectra of these species [102,103]. Similar observations have been made for six-coordinate nitrosyl derivatives; these studies also have provided an emendation concerning the nature of the Fe—N and Fe—N—O stretch and bend [104,105]. Normal coordinate analyses of the spectra for four-coordinate complex [Fe(OEP)] have also appeared [106,107].

In addition to the work that has been described here, I would like to point out other reviews that have appeared [108–111]. Further, I would take notice of two bodies of work that have not been discussed in this paper, work on the other oxynitrogen-ligated porphyrins (the ligands NO₂[−] and NO₃[−]) [112–124] and the work on the characterization of π -cation radical complexes [125–139].

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Fig. 1. Diagram illustrating the effects of the core expansion in [Sn(TPP)(Cl)₂]. Top value of each pair is for [Sn(TPP)(Cl)₂] and the lower value is from [Ni(Deut IX DME)].

Fig. 2. ORTEP diagram of the structure of [Mn(TPP)] determined at room temperature (outer ellipsoids) and 118K (inner ellipsoids) showing the centering of the Mn atom. Note the extensive thermal motion of the Mn out of the porphyrin plane at both temperatures.

Fig. 3. Diagram on the left side illustrating the structure of [Fe(OEP)(OCIO3)] and on the right comparing the structural differences between the high-spin, intermediate-spin, and low-spin structures of five-coordinate iron(III)porphyrinates.

Fig. 4. Thermal ellipsoid plots of [Fe(OEP)(3-ClPy)₂]ClO₄ at 98 and 293 K. The plots at 293 K show the result of the "crystallographic resolution of spin isomers."

Fig. 5.
 Diagram illustrating differences between the two crystalline forms of $[\text{Fe}(\text{OEP})(3\text{-ClPy})_2]\text{ClO}_4$.

Fig. 6. Diagram Illustrating the effect of axial ligand orientation on the axial bond distances in iron (III) species.

Fig. 7.
Differences in d orbital energy as a function of relative ligand orientation.

Fig. 8.
ORTEP diagram of [Fe(TMP)(4-Me₂NPy)₂]⁺.

Fig. 9.
Diagram illustrating the change in d orbital energy ordering.

Fig. 10. Differences in coordination geometry between imidazole-ligated high-spin iron(II) and high-spin iron(II) with anionic ligands.

Fig. 11. Structural differences between five-coordinate imidazole- and imidazolate-ligated iron(II) porphyrinates.

Fig. 12.
Effects of hydrogen-bonding on one iron site in $[\text{Fe}(\text{TPP})(2\text{-MeHIm})]2.2\text{-MeHIm}$.

Fig. 13.

Trends in MNO structure as a function of electron count. Derivatives shown include manganese, both formal oxidation states of iron(III) and -(II), and cobalt.

Fig. 14.
Diagram of [Fe(TPP)(NO(1-MeIm))] showing the long bond trans to the NO.

What is NRVS?

Fig. 15.

Diagram illustrating the essential features of NRVS. The transitions illustrated in the left hand portion show (left to right) Moessbauer modulated by electron and magnetic effects, the classic transition between the nuclear ground state and the nuclear excited state, and transitions whose energies are modified by the vibrational quanta in the excited state leading to transitions whose energies are either less than or greater than the classical Moessbauer energy. The right hand portion symbolically depicts a NRVS spectrum.

Table 1

Periodic Trends (d-electron configuration) Four-Coordinate M(II)

Metal Ion	M—N _p , Å	Spin State	Molecular Symmetry	Reference
d ⁴ Cr	2.003	2	C _i	5
d ⁵ Mn	>2.082	5/2	C _i	6
d ⁶ Fe	1.972 1.966	1 1	<i>S₄-Ruf</i> <i>S₄-Sad</i>	7 8
d ⁷ Co	1.949	1/2	<i>S₄-Ruf</i>	9
d ⁸ Ni	1.928	0	<i>S₄-Ruf</i>	10
d ⁹ Cu	1.981	1/2	<i>S₄-Ruf</i>	11
d ¹⁰ Zn	2.036	0	C _i	12

Table 2

Periodic Trends (d-electron configuration) Five-Coordinate M(II) and -(III)

Metal, Axial Ligand	M—N _{pr} , Å	Ct...N, Å	M...Ct, Å	M—N _{ax} , Å	Spin State	Reference
d ⁴ Mn-Cl	2.008	1.990	0.27	2.373	2	13
⁵ Mn-1-Melm	2.128	2.065	0.56	2.192	5/2	14
d ⁵ Fe-X	2.067	2.015	0.47	various	5/2	many
d ⁶ Fe-2-MeHIm	2.086	2.044	0.42	2.161	1	15
d ⁷ Co-1-Melm	1.977	1.973	0.13	2.157	1/2	16
d ⁷ CoMe ₂ Im	1.985	1.979	0.15	2.216	1/2	17
d ¹⁰ Zn-1-Melm	2.068	2.025	0.42	2.106	0	18

Table 3

Periodic Trends (d-electron configuration) Six-Coordinate M(II) and -(III)

Metal Ion Complex	M—N _p , Å	M—Ax, Å	Spin State	Reference
d ⁴ Cr [Cr(TPP)(Py) ₂]	2.027	Normal, 2.13	1	19
d ⁴ Mn [Mn(TPP)(1-Melm) ₂] ⁺	2.017	Long, 2.308	2	20
d ⁵ Fe [Fe(TPP)(Hlm) ₂] ⁺	1.989	Normal, 1.974	1/2	21
d ⁶ Fe [Fe(TPP)(1-Vinlm) ₂]	2.001	Normal, 2.004	0	22
d ⁶ Co [Co(TPP)(Pip) ₂] ⁺	1.978	Normal, 2.060	0	23
d ⁷ Co [Co(TPP)(Pip) ₂]	1.987	Long, 2.436	1/2	24
d ⁸ Ni [Ni(TMPyP(Hlm) ₂)] ⁴⁺	2.038	Long, 2.160	1	25

Table 4

Periodic Trends (d-electron configuration) Six-Coordinate High- and Low-Spin Fe

Complex	M—N _p , Å	M—Ax, Å	Spin State	Reference
d ⁵ Fe(S-ligand) [Fe(TPP)(PMS) ₂] ⁺	1.982	2.341	1/2	31
d ⁶ Fe(S-ligand) [Fe(TPP)(THT) ₂]	1.996	2.338	0	31
d ⁵ Fe(N-ligand) [Fe(TPP)(2-MeHIM) ₂] ⁺	1.970	2.012	1/2	32
d ⁵ Fe(N-ligand) [Fe(OEP)(2-MeHIM) ₂] ⁺	2.041	2.275	5/2	33
d ⁶ Fe(N-ligand) [Fe(TPP)(1-VinIm) ₂]	2.001	2.004	0	22
d ⁵ Fe(O-ligand) [Fe(TPP)(H ₂ O) ₂] ⁺	2.045	2.095	5/2	29
d ⁶ Fe(O-ligand) [Fe(TPP)(THF) ₂]	2.057	2.351	2	35

Table 5

Summary of known iron(II) and iron(III) species.

Oxidation State	Low Spin	Intermediate Spin	High Spin
Fe(III)	[Fe(Porph)(NO)] ⁺ [Fe(Porph)(L) ₂] ⁺	[Fe(Porph)(OCIO ₃)] [Fe(Porph)(L)] ⁺ [Fe(Porph)(L) ₂] ⁺	[Fe(Porph)(X)] [Fe(Porph)(L)] ⁺ [Fe(Porph)(L) ₂] ⁺
Fe(II)	[Fe(Porph)(CO)] [Fe(Porph)(L) ₂]	[Fe(Porph)]	[Fe(Porph)(L)] [Fe(Porph)(X)] ⁺ [Fe(Porph)(THF) ₂] ⁺