

Table II. Effect of the Annealing of  $\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2^a$  at 800 °C

time of anneal, days	$\mu_{\text{eff}}$ , $\mu_{\text{B}}/\text{mol}$ of $\text{CoS}_2$	$\Theta$ , K	time of anneal, days	$\mu_{\text{eff}}$ , $\mu_{\text{B}}/\text{mol}$ of $\text{CoS}_2$	$\Theta$ , K
0	2.10 (2)	94 (2)	8	1.70 (2)	109 (2)
4	1.94 (2)	102 (2)	17	1.73 (2)	112 (2)

<sup>a</sup> Prepared from precursors and heated at 800 °C for 7 days.

$\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2$  was annealed at 800 °C for varying periods of time, and the effective moments are given in Table II. As prepared, the two samples of composition  $\text{Co}_{0.2}\text{Ru}_{0.8}\text{S}_2$  initially gave effective moments of 1.99 and 2.10  $\mu_{\text{B}}$ . It can be seen that at the end of 8 days the measured effective moment of  $\mu_{\text{eff}} = 1.70 \mu_{\text{B}}$  was close to the spin-only value of 1.73  $\mu_{\text{B}}$ . Further annealing up to 17 days did not change the observed effective moment appreciably. The other members of the system after long annealing also gave the effective moment expected for the amount of  $\text{CoS}_2$  present in the composition. It is evident that the observed effective moments are useful in determining the homogeneity of the samples since the X-ray diffraction patterns indicated single-phase formation for all the products reported.

Susceptibility measurements of members of the system  $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$  ( $0.5 \leq x \leq 1$ ), as a function of temperature from 80 to 300 K, gave values that were temperature independent and varied from  $0.8 \times 10^{-4}$  to  $1.1 \times 10^{-4}$  emu/mol.

For pure  $\text{CoS}_2$ , the moment corresponds to approximately one unpaired electron on the cobalt atom, which is present as low-spin Co(II). Goodenough<sup>13,14</sup> has shown that the observed metallic conductivity and ferromagnetic moment are due to partially filled  $\sigma^*e_g$  states. He indicated that, in this compound, the  $\sigma^*e_g$  states constitute a band. The occurrence of an energy difference between the  $t_{2g}$  and  $\sigma^*e_g$  states that is larger than the intraatomic exchange energy gives rise to the low-spin-state configuration of cobalt(II). For the system

$\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ , it was shown that, for compositions where  $x \leq 0.2$ , the 4d electron associated with Rh(4d<sup>7</sup>) are localized and there is a ferromagnetic alignment between Co(3d<sup>7</sup>) and Rh(4d<sup>7</sup>) electrons. For such an interaction to occur, the relative energies of the cobalt 3d and rhodium 4d manifolds must be similar. Magnetic susceptibility measurements for members of the system  $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$  indicate that Ru(4d<sup>6</sup>) is in the low-spin state and hence diamagnetic. The observed moments of the products are due to the amount of Co(low-spin 3d<sup>7</sup>) present. Whereas the 4d electrons of Rh(4d<sup>7</sup>) appear to be localized in the system  $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$ , the observed Pauli paramagnetic behavior for the system  $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$  indicates that, in the absence of localized cobalt electrons, rhodium 4d electrons are delocalized.

### Conclusion

Synthesis of members of the  $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$  and  $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$  systems has been accomplished by the sulfurization of mixtures of  $(\text{NH}_4)_2\text{RuCl}_6$  and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  or  $(\text{NH}_4)_2\text{RuCl}_6$  and  $(\text{NH}_4)_3\text{RhCl}_6$ . The magnetic properties of these systems are dependent on the degree of localization of the 4d electrons. In the presence of Co(3d<sup>7</sup>), rhodium 4d electrons appear to be localized; but if only 4d states are present, then the rhodium 4d electrons are delocalized. Members of these systems are difficult to prepare as single homogeneous products, but magnetic susceptibility measurements can be used to determine when such products are obtained.

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## A Highly Siliceous Structural Analogue of Zeolite Y: High-Resolution Solid-State <sup>29</sup>Si and <sup>27</sup>Al NMR Studies

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Reaction of synthetic zeolite Na-Y with  $\text{SiCl}_4$  vapor at 560 °C yields an essentially aluminum-free faujasite structure, which is highly crystalline and which, when studied by <sup>29</sup>Si NMR spectroscopy with magic-angle spinning, gives a spectrum consisting of a single sharp peak characteristic of regular, Si(4Si), lattice ordering. The <sup>27</sup>Al MAS NMR spectrum of the dry dealuminated material shows two peaks, one corresponding to residual lattice aluminum and one due to  $\text{AlCl}_4^-$ . The <sup>27</sup>Al MAS NMR spectrum of washed dealuminated zeolite Y contains two peaks: one due to residual aluminum still on tetrahedral sites in the lattice and an additional peak due to octahedrally coordinated cationic aluminum in the zeolitic channels. The latter can be successively removed by washing, the intensity of the octahedral peak greatly decreasing. <sup>27</sup>Al NMR is a valuable tool in probing the coordination, quantity, and location of aluminum atoms in chemically treated zeolites.

### Introduction

The catalytic activity of the hydrogenic form of zeolites is known to increase with increasing Si/Al ratio.<sup>2</sup> It is, therefore, desirable to be able to prepare zeolites with high—and preferably variable—silicon contents, especially since thermal

stability increases as zeolites become more siliceous. Considerable efforts channeled in this direction culminated, in the mid-1970s, in the synthesis of zeolite ZSM-5, an active catalyst in a number of reactions.<sup>3</sup>

Probably the most well-established method of preparing highly siliceous faujasites consists of hydrothermal treatment of ammonium-exchanged zeolite Y.<sup>4</sup> Aluminum leaves the

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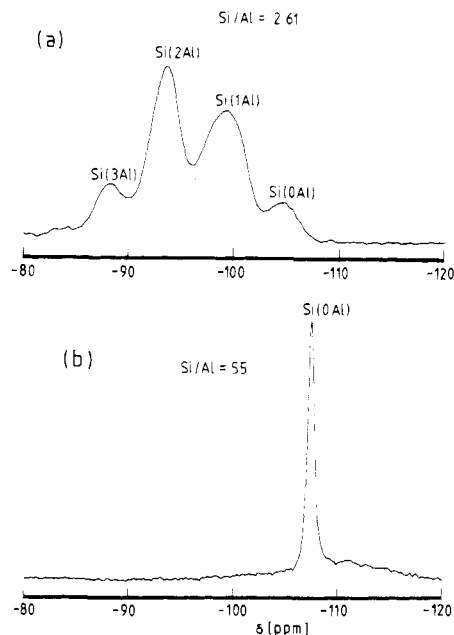
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framework and migrates into interstitial cationic positions; framework vacancies are believed<sup>5,6</sup> to be subsequently reoccupied by silicon. However, a recent study involving sorption measurement of gases by the product<sup>7</sup> showed it to contain a secondary mesopore system with pore radii in the range 15–19 Å. It follows therefore that the silicon which reoccupies empty tetrahedral sites comes not only from the surface or from amorphous parts of the crystals but also from their bulk and that probably the removal of entire sodalite cages is involved. Recently, we threw more light on this using solid-state <sup>29</sup>Si NMR.<sup>8</sup> Repeated hydrothermal treatment of NH<sub>4</sub>-Y followed by extraction of nontetrahedral aluminum and reexchange with ammonium chloride solution yields materials with Si/Al ratios of over 50. The method is, however, lengthy and inconvenient.

Recently a much simpler single-step process of increasing the Si/Al ratio in synthetic faujasites has been reported.<sup>9</sup> It consists of passing silicon tetrachloride vapor at elevated temperature through a bed of anhydrous zeolite Na-Y. A crystalline, virtually aluminum-free faujasite is obtained, formally analogous to microporous silica. Furthermore, the aluminum content of the product can be varied by inter alia altering exposure time to silicon tetrachloride vapor.

Such a highly siliceous faujasite is of obvious interest as a catalyst and sorbent. The absence of strong electric fields and gradients (the framework is not charged as in parent Na-Y) will probably affect the material's sorption properties for a number of molecules. A high Si/Al ratio indicates that the hydrogen form (obtained from ion exchanging the remaining Na<sup>+</sup> with NH<sub>4</sub><sup>+</sup> followed by thermal decomposition of the ammonium form) may be a strong Brønsted acid. Furthermore, as pointed out by Beyer and Belenykaja,<sup>9</sup> it should be possible to distinguish which proportion of catalytic behavior of faujasite is attributable to high silicon content and which to shape selectivity. In the past, highly siliceous zeolites (such as ZSM-5 or mordenite) were of a framework topology quite different from that of low-silica ones (such as Linde A or X). In other words, we now have faujasites with Si/Al ratios far beyond the range of 1.0–3.0 encountered in zeolites X and Y.

Here, we report some findings relating to the structure and composition of the highly siliceous faujasites obtained by using magic-angle-spinning NMR.<sup>10</sup> We have already published<sup>12,13</sup> a brief note describing some preliminary <sup>29</sup>Si NMR (at 17.88 MHz) and electron microscopic findings. Recently, however, we were able to measure <sup>29</sup>Si spectra at much higher fields (79.80 MHz) and with greatly improved resolution.<sup>17</sup> Further, <sup>27</sup>Al spectra in the solid state could be recorded at 104.22 MHz, thereby revealing insight into the status of aluminum



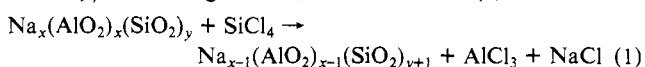
**Figure 1.** <sup>29</sup>Si MAS NMR spectra at 79.8 MHz: (a) parent Na-Y zeolite; (b) sample after treatment with SiCl<sub>4</sub>. Chemical shifts are given in ppm from tetramethylsilane.

in the zeolite before and after the reaction. <sup>27</sup>Al NMR is particularly valuable for highly siliceous zeolites: In the study of Si-Al ordering in synthetic faujasites<sup>14</sup> it was shown that it becomes increasingly difficult to deduce the position of Al atoms via <sup>29</sup>Si NMR as the Si/Al ratio increases, since then mostly Si(0Al) and Si(1Al) building units are present.

#### Experimental Section

Dehydrated Na-Y (Si/Al ratio 2.61) was treated at 560 °C with dry argon saturated (at room temperature) with SiCl<sub>4</sub> for 3 h. Aluminum was successively substituted in the zeolite framework by silicon and removed in part from the crystals in the form of volatile AlCl<sub>3</sub> observed as a white vapor. The zeolite was then flushed, also at 560 °C, with dry argon, and the temperature was gradually reduced. The product was then repeatedly washed with water.

Each step in the substitution reaction, taking Na-Y with an Si/Al ratio of  $y/x$  as starting material, can be written as (1). As indicated



by the NMR data (vide infra), part of the aluminum remains in the solid as NaAlCl<sub>4</sub> formed from the high-temperature reaction of NaCl and AlCl<sub>3</sub>, which gives [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> on contact with water. This, together with the sodium chloride, can be successively removed by washing the product repeatedly with aqueous acid. The aluminum content of the product (by analytical electron microscopy and chemical analysis) is similar to that of the ZSM zeolites. The bulk of the dealuminated product formed is crystalline to X-rays and electrons although some amorphous material may be formed in some cases. High-resolution microscopic images were, in general, very sharp, indicating essentially total retention of structural integrity. It is also highly resistant to heat treatment. Powder diffraction gives lines that are sharper than for the parent zeolite. Their relative intensities, however, are different, which is mostly due to the absence of the cation. For complete dealumination the cubic unit cell constant decreases from 24.68 (Na-Y with Si/Al = 2.61) to 24.31 Å. When the reaction is forced to completion, a broad peak at ca. -112 ppm is observed, possibly due to amorphous silica.

High-resolution solid-state <sup>29</sup>Si MAS NMR spectra were obtained at 79.80 MHz with a Bruker WH-400 narrow-bore spectrometer equipped with a homemade single-frequency probe and a magic-angle spinning attachment.<sup>11</sup> Proton decoupling was not used, and 5-s intervals were allowed between pulse sequences. The spinner assembly was of the Andrew-Beams type;<sup>10</sup> spinners were made of Delrin and had an internal volume of ca. 450 μL. The spinning rate was ca. 3.0–4.0 kHz with compressed air as driving gas. <sup>29</sup>Si chemical shifts

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are given from tetramethylsilane.

High-resolution solid-state  $^{27}\text{Al}$  MAS NMR spectra were obtained at 104.22 MHz by using the same spectrometer and homemade probe. Chemical shifts were recorded with respect to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  as an external reference, for consistency with previous  $^{27}\text{Al}$  solution studies.<sup>15</sup>

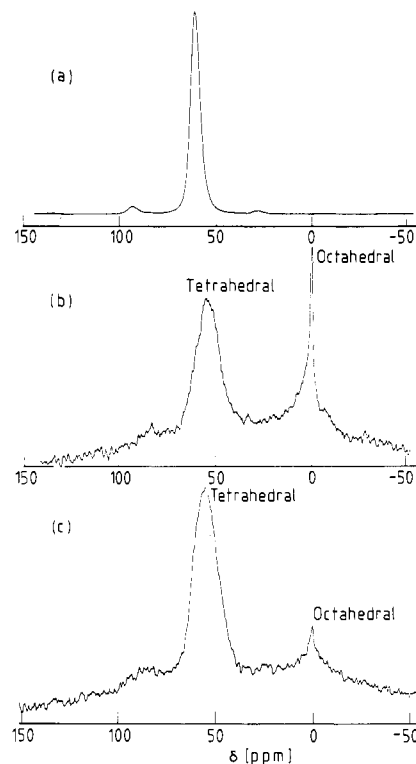
### Results and Discussion

We have examined the parent Na-Y zeolite and the dealuminated final product by high-resolution  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR. A regular dependence of the  $^{29}\text{Si}$  chemical shifts on the number of  $\text{AlO}_4^{5-}$  tetrahedrally linked, via oxygen bridges, to each  $\text{SiO}_4^{4-}$  tetrahedron has previously been demonstrated.<sup>16</sup> For each distinct type of a structural unit, represented as  $\text{Si}(n\text{Al})$  where  $n = 0-4$ , a distinct narrow range of chemical shift was found, with each aluminum substituent being responsible for an ca. 5-ppm low-field shift. We have recently measured these shifts very accurately in zeolites X and Y with a wide range of Si/Al ratios.<sup>17</sup>

Figure 1a shows the  $^{29}\text{Si}$  NMR spectrum of parent zeolite Na-Y. The four peaks correspond, from left to right, with Si(3Al), Si(2Al), Si(1Al), and Si(0Al) ordering of the structural tetrahedra and with chemical shifts of -88.5, -93.7, -99.2, and -105.0 ppm, respectively, each  $\pm 0.3$  ppm, in the intensity ratio of 12.3:37.7:44.2:5.8. It has been demonstrated<sup>14,17</sup> that the ordering of tetrahedral atoms in zeolite Y of this Si/Al ratio does not involve Si(4Al) building units. This is why only four and not five peaks are seen. Figure 1b gives the spectrum for the material that has been dealuminated by using silicon tetrachloride to a Si/Al ratio of 55 (by chemical analysis). The Si/Al ratio in the framework is higher than 55, as  $^{27}\text{Al}$  NMR spectra (see below) indicate that some aluminum is present in octahedral coordination in the zeolitic channels. The chemical shift of the peak of Figure 1b is  $-107.0 \pm 0.1$  ppm, i.e., similar to that found by Lippmaa et al.<sup>16</sup> in quartz. The peak quite clearly represents Si(0Al), i.e., Si(4Si) ordering of tetrahedra, to the exclusion of all other configurations. The hump on the base line arises from the presence of amorphous material (probably silica) in this particular sample. The main peak is very narrow (0.6 ppm at half-height), which indicates high homogeneity and crystallinity, and is one of the narrowest  $^{29}\text{Si}$  peaks we have found in the course of our extensive studies<sup>8,14,17,18</sup> on solid silicates and aluminosilicates.

It is significant that the position of the Si(0Al) peak in Figure 1a does not exactly coincide with the Si(0Al) peak in Figure 1b, their chemical shifts being -105.0 and -107.0 ppm, respectively. This effect is due to the aluminum atoms (and possibly their accompanying cations), which are further away than the first tetrahedral coordination shell. Meier and Moeck<sup>19</sup> have shown that each structural tetrahedron in the faujasite structure has *nine* second-nearest tetrahedral neighbors (while there are always four nearest neighbors, by definition of tetrahedral coordination). This number,  $N_2$ , of second coordination shell members, varies from 8 to 12 between different zeolite structures. In the parent Na-Y zeolite in Figure 1a each Si(0Al) silicon atom has, on average, four Al atoms as second-nearest tetrahedral neighbors, while dealuminated zeolite Y in Figure 1b has none.

$^{27}\text{Al}$  is a quadrupolar nucleus with spin of  $5/2$ . The ( $m = 1/2$ )  $\leftrightarrow$  ( $m = -1/2$ ) transition for such a nucleus is not affected by quadrupolar interaction to first order and is usually the only transition observed. It is, however, affected by quadrupolar interactions to second order; and at moderate fields these dominate the spectra, obscuring any chemical shift effects that might be related to short-range structure. The second-order quadrupolar term is, however, *inversely* proportional to the



**Figure 2.**  $^{27}\text{Al}$  MAS NMR spectra at 104.22 MHz: (a) parent Na-Y zeolite (the two signals of low intensity, equidistant from the central peak, are spinning sidebands); (b) sample after treatment with  $\text{SiCl}_4$  and moderate washing (chemical shifts of the peaks are, from left to right, 54.8 and 0.2 ppm); (c) a similar sample as in (b), but after extensive washing (chemical shifts are 54.9 and 0.0 ppm). All shifts are from  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ .

magnetic field strength, whereas the chemical shift dispersion is *directly* proportional to it. It follows that chemical shift effects are best observed at as high a field strength as possible, when they make the maximum contribution to the spectrum. The MAS spectra in the present work were recorded at 104.2 MHz, corresponding to a proton frequency of 400 MHz. Figure 2a gives the  $^{27}\text{Al}$  spectrum of the parent Na-Y. A single, relatively narrow signal is seen with a chemical shift of 61.3 ppm corresponding to tetrahedrally coordinated aluminum. This result is in agreement with the value reported by Freude and Behrens,<sup>20</sup> considering the frequency dependence of the interaction and difference in frequency between this experiment and the present work. Figure 2b gives the  $^{27}\text{Al}$  spectrum of the dealuminated sample, the  $^{29}\text{Si}$  spectrum of which was given in Figure 1b. This time there are two peaks: a broader one corresponding to aluminum still remaining in tetrahedral sites (at  $54.8 \pm 0.2$  ppm) and a sharp one with a chemical shift of  $0.2 \pm 0.2$  ppm corresponding unmistakably to Al in octahedral coordination. The latter peak is clearly generated by aluminum that has been removed from the framework but has not been removed by washing.  $^{27}\text{Al}$  spectra obtained on dry dealuminated samples *before* the first washing showed a peak at -1.05 ppm corresponding to aluminum in octahedral sites and an intense peak at 100.8 ppm. This latter shift is close to the value of 95.9 ppm observed for  $\text{Li}^+\text{AlCl}_4^-$  and is assigned to the tetrachloroaluminate anion  $\text{AlCl}_4^-$  formed by the high-temperature reaction of NaCl and  $\text{AlCl}_3$  formed during the dealumination step (eq 1). On washing, this peak disappears and the peak assigned to octahedral aluminum appears. The width at half-height of the tetrahedral peak in dealuminated Na-Y is much greater than in the parent material (1428 Hz as compared with 560 Hz), which indicates

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a distribution of immediate environments for the aluminum atoms remaining in the framework. Comparison of parts b and c of Figure 2 shows that most, but not all, of the octahedral aluminum can be removed by washing subsequent to  $\text{SiCl}_4$  treatment. Such octahedral aluminum that still remains may be neutralizing the negative framework charge brought about by the presence of tetrahedral aluminum. An ion-exchange equilibrium can be established during washing between  $\text{Na}^+$  and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  competing for the cationic sites. Inspection of Figure 2c would suggest that most of the framework charge is neutralized by sodium and the remainder by  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  (note that one octahedral Al atom balances the charge of three tetrahedral Al atoms). The poorer signal-to-noise ratio in Figure 2b,c in comparison with that of Figure 2a is due to the much lower concentration of aluminum in these samples. Another striking feature of the spectra in Figure 2 is the large

change in the chemical shift of the tetrahedrally coordinated aluminum, 54.8 ppm in the dealuminated Na-Y as opposed to 61.3 ppm in the parent material. The origin of this effect is at present under investigation.

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## Correlations of Axial Ligand Field Strength and Zero-Field Splittings in the Carbon-13 NMR Spectra of Five- and Six-Coordinate High-Spin Iron(III) Porphyrin Complexes

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Carbon-13 NMR spectra have been recorded for complexes of high-spin iron(III) porphyrins in which the axial anionic ligand has been varied. The  $(\text{Me}_2\text{SO})_2$  complexes of high-spin iron(III) tetraphenylporphyrins ( $(\text{TPP})\text{Fe}^{\text{III}}$ ) and natural-derivative porphyrins have also been examined. Replacement of a single anionic ligand with two solvent ligands induces striking changes in carbon-13 NMR spectra, with changes in the phenyl ortho-carbon and meso-carbon signals of  $(\text{TPP})\text{Fe}^{\text{III}}$  on the order of several hundred ppm. This explains the seemingly anomalous upfield and downfield meso-proton shift values for five- and six-coordinate species. Results are interpreted in terms of unpaired spin delocalization through both  $\sigma$ - and  $\pi$ -type molecular orbitals, with a predominant  $\pi$  mechanism of Fe $\rightarrow$ porphyrin "back-bonding" in six-coordinate complexes. A contribution from porphyrin  $\rightarrow$  Fe charge transfer places large unpaired spin density at the meso-carbon atom of five-coordinate species. Modulation of the meso-position spin density by differing axial anionic ligands is apparent in variable NMR chemical shift values for the phenyl and meso-carbon atoms of  $(\text{TPP})\text{FeX}$  complexes. Phenyl shifts show a positive correlation with the zero-field splitting parameter,  $D$ , as measured by far-infrared and magnetic methods. A correspondence is also apparent between meso-carbon NMR shift values and Fe(III)/Fe(II) redox potentials. These observations suggest the ligand field strength of the axial ligand dictates the magnitude of unpaired spin density at the meso position, with larger downfield shifts associated with weaker field ligands. On this basis the following ordering of ligand field strength is offered for high-spin iron(III) porphyrins:  $\text{F}^- > \text{OPh}^- > \text{OPh}(\rho\text{-NO}_2)^- > \text{N}_3^- \approx \text{OAc}^- > \text{NCS}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ .

### Introduction

The high-spin state of iron(III) porphyrins results as a consequence of having either one or two weak-field ligands coordinated at the iron center. The best characterized five-coordinate species are those with a single anionic ligand, in which case the iron atom is raised typically 0.5 Å from the porphyrin plane.<sup>1,2</sup> The distorted-square-pyramidal environment serves to perturb the electronic properties of high-spin iron(III) particularly in the form of inducing large zero-field splitting. Coordination of extremely weak-field ligands such as perchlorate ion results in admixture of the  $S = 3/2$  state with the high-spin state.<sup>3-5</sup> Bisligated high-spin iron(III) porphyrin complexes may be generated through the action of weak-field coordinating solvents (i.e., dimethyl sulfoxide, tetramethylene sulfoxide, water, or alcohols) on certain five-coordinate adducts.<sup>6-10</sup> Core expansion allows placement of

the iron atom in the plane of the porphyrin, and the resulting geometry about the iron center is one of pseudooctahedral symmetry. As such, the electronic properties of this six-coordinate complex might be expected to differ from those of the five-coordinate anion-bound derivative.

Both five-coordinate and six-coordinate high-spin iron(III) porphyrin prosthetic groups are found in hemoproteins. Examples include horseradish peroxidase, which seemingly has only a histidine axial ligand in the resting form, and metmyoglobin, which has histidine and water ligands.<sup>11</sup> It is therefore relevant to ask how mono- or bisligation, as well as the nature of the axial ligand(s), might influence the reactivity, electronic structure, and electron-transfer characteristics of high-spin iron(III) porphyrin complexes. Various physical techniques have been utilized in attempts to answer such

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