JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 110, NUMBER 7 MARCH 30, 1988

Proton NMR Study of Dehydration of the Silica Gel Surface

Charles E. Bronnimann, Robert C. Zeigler, and Gary E. Maciel*

*Contribution from the Department of Chemistry, Colorado State University,
Ft. Collins, Colorado 80523. Received August 4, 1987*

Abstract: The CRAMPS technique has been used to obtain high-resolution ^{1}H NMR spectra of silica gel samples at different stages of hydration. An untreated sample shows resolvable peaks for physisorbed water and for two distinguishable types of silanol protons. The peak for physisorbed water is easily eliminated by sample evacuation. The moiety giving rise to one of the silanol peaks can be removed by sample evacuation at 500 °C and is identified as hydrogen-bonded silanols. Experiments on spin–lattice relaxation, dipolar dephasing, and spin exchange provide evidence on the proximity of each type of proton to other protons. The results show that both types of silanol protons are physically proximate to each other on the surface.

Silica surfaces play important roles in catalysis, chemical separations, and microelectronic fabrications. ^{29}Si NMR, using cross polarization (CP) and magic-angle spinning (MAS), has been shown to provide valuable information regarding the types of silicon sites present on a silica surface.[1,2] Considerable attention has been focused on determining the number and characteristics of hydroxyl groups on silica surfaces. A variety of techniques, including spectroscopic approaches, have been used to elucidate the nature of surface hydroxyl groups. The most informative spectroscopic technique has been infrared spectroscopy.[3,4]

Proton NMR should, in principle, be an extremely useful tool in the characterization of surface hydroxyls and has been used with some success in certain cases.[5-8] In general, proton NMR experiments on solid samples are encumbered by the severe line-broadening effects of strong ^{1}H–^{1}H magnetic dipolar interactions. If these effects are not too large, because of large ^{1}H–^{1}H internuclear distances and/or fast motional averaging, then sharp ^{1}H NMR resonances can often be achieved by magic-angle spinning (MAS), which also averages the chemical shift anisotropy. For systems in which ^{1}H–^{1}H dipolar line-broadening effects are large, say >20 kHz, another approach is required, either extremely fast MAS[9,10] or multiple-pulse line-narrowing techniques.[11,12] The combination of MAS with multiple-pulse line narrowing (CRAMPS (combined rotation and multiple-pulse spectroscopy)[13,14]) has been used successfully in the study of surface hydroxyls in silica–alumina samples.[8] The present paper addresses in more detail the nature of the surface hydrogens in silica gel. Particular attention is focused on the use of a new class of CRAMPS-based ^{1}H relaxation experiments designed to explore the dipole interaction between the various types of protons distinguished by the ^{1}H CRAMPS technique.

Experimental Section

^{1}H CRAMPS spectra were obtained at 187 MHz on a modified Nicolet NT-200 spectrometer, using the BR-24 pulse sequence.[12] The cycle time for the BR-24 pulse sequence varied between 108 and 144 μs in the experiments of this study, corresponding to a pulse spacing of 3.0–4.0 μs. Magic-angle spinning, at speeds ranging from 2.0 to 3.0 kHz, employed a spinner based on the design of Gay.[15] Samples (ca. 10 mg) were sealed under vacuum in thick-walled 5-mm-o.d. (2-mm i.d.) glass tubes. Repetition delays of 3–6 s and between 64 and 256 repetitions were used to obtain signal-to-noise ratios of at least 100. Chemical shifts were determined by external referencing via substitution of samples containing tetrakis(trimethylsilyl)methane (TTMSM) and are reported here relative to tetramethylsilane (TMS).

The integrated intensities discussed below were obtained by deconvoluting the experimental spectra, using Nicolet software. As the ^{1}H magnetization in the CRAMPS experiment is generated by a single preparation pulse, the intensities obtained from the ^{1}H CRAMPS spectra should accurately reflect quantitation for analytical purposes.

The silica gel employed in this study is S-679 from Fisher.

Results and Discussion

1. Dehydration Studies. Assignment of Spectra. Figure 1 shows the ^{1}H CRAMPS spectra of silica gel in equilibrium with the atmosphere (1A), as well as samples evacuated at 25 °C (1B), 200 °C (1C), and 500 °C (1D). Examination and deconvolution (1A′ and 1A″) of Figure 1A show that there are mainly three contributing peaks. There are two relatively narrow contributing

---

[1] Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 5529.

[2] Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1983**, *87*, 5516.

[3] McDonald, R. A. *J. Phys. Chem.* **1958**, *62*, 1168.

[4] Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Marcel Dekker: New York, 1967.

[5] Vega, A. J.; Luz, Z. *J. Phys. Chem.* **1987**, *91*, 365.

[6] Hunger, M.; Freude, D.; Pfeifer, H.; Bremer, H.; Jank, M.; Wendlandt, K. P. *Chem. Phys. Lett.* **1983**, *100*, 29.

[7] Kohler, J.; Chase, D. B.; Farlee, R. D.; Vega, A. J.; Kirkland, J. J. *J. Chromatog.* **1986**, *352*, 275.

[8] Bronnimann, C. E.; Chuang, I.-S., Hawkins, B. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1987**, *109*, 1562.

[9] Dec, S. F.; Wind, R. A.; Maciel, G. E. *Macromolecules* **1987**, *20*, 2754.

[10] Dec, S. F.; Wind, R. A.; Maciel, G. E. *J. Magn. Reson.* **1986**, *70*, 355.

[11] Waugh, J. A.; Huber, L. M.; Haeberlen, U. *Phys. Rev. Lett.* **1968**, *20*, 180.

[12] Burum, D. P.; Rhim, W. K. *J. Chem. Phys.* **1979**, *71*, 944.

[13] Gerstein, B. C.; Pembleton, R. G.; Wilson, R. C.; Ryan, L. *J. Chem. Phys.* **1977**, *66*, 361.

[14] Schnabel, B.; Haubenreisser, U.; Scheler, G.; Muller, R. In Proceedings 19th Congress Ampere; Brunner, H., Hausser, K. H., Schweitzer, D., Eds.; Heidelberg, 1976.

[15] Gay, I. D. *J. Magn. Reson.* **1984**, *58*, 413.

0002-7863/88/1510-2023$01.50/0 © 1988 American Chemical Society

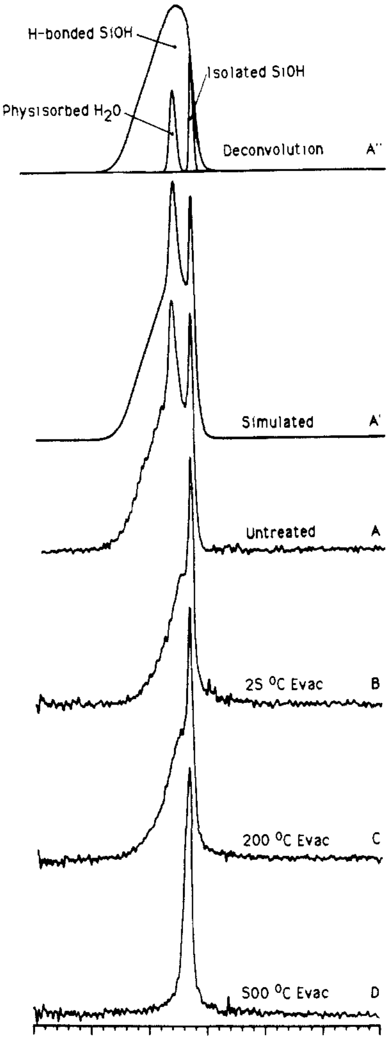

Figure 1. 187-MHz ^{1}H CRAMPS spectra of Fisher S-679 silica gel: (A) untreated; (B) evacuated at 25 °C; (C) evacuated at 200 °C; (D) evacuated at 500 °C; (A″) deconvolution of spectrum A; (A′) computer simulation based on A″.

lines at 1.7 and 3.5 ppm and a broader line centered at about 3.0 ppm in Figure 1, but with a width and a position of maximum that appear to depend upon sample treatment. Evacuation (1.0 × 10^{-2} Torr) of the sample at 25 °C (Figure 1B) leads to a dramatic loss (essentially complete) of intensity at 3.5 ppm. The spectrum obtained on a sample subjected to 200 °C evacuation (Figure 1C) is essentially the same as that from 25 °C evacuation. As there should be essentially no physisorbed water present on the surface after 200 °C evacuation, the 3.5 ppm resonance is assigned to protons in physically adsorbed water. This is qualitatively consistent with previous assignments for water adsorbed on silica moieties.[7,8]

The 3.0 and 1.7 ppm peaks remaining after 200 °C evacuation cannot be due to water and are hence assigned to protons of silanol moieties. Evacuation of the sample at 500 °C (Figure 1D) removes the broad peak at 3.0 ppm, leaving only the relatively sharp peak at 1.7 ppm. A peak at 1.7–2.1 ppm has previously been assigned to SiOH moieties of silica or silica-like regions of silica–alumina samples.[8]

The results shown in Figure 1 demonstrate the resolution of two silanol peaks in the ^{1}H CRAMPS spectra of silica gel. It is well-known that hydrogen bonding produces a proton shift to lower shielding and that the magnitude of the low-shielding shift increases with stronger hydrogen bonding.[16,17] Hence, we assign the broad 3.0 ppm line to hydrogen-bonded silanols and the narrow 1.7 ppm line to "isolated" (non-H-bonded) silanols. According to this interpretation, the breadth of the 3.0 ppm line can be ascribed to inhomogeneous broadening associated with a wide distribution of chemical shifts that reflect a wide variety of hydrogen-bonding details and strengths. Corroborating evidence on the natures of the silanol protons giving rise to the 1.7 and 3.0 ppm peaks is obtained by a series of relaxation experiments that combine the CRAMPS solid-sample technique with well-known liquid-sample NMR relaxation methods.

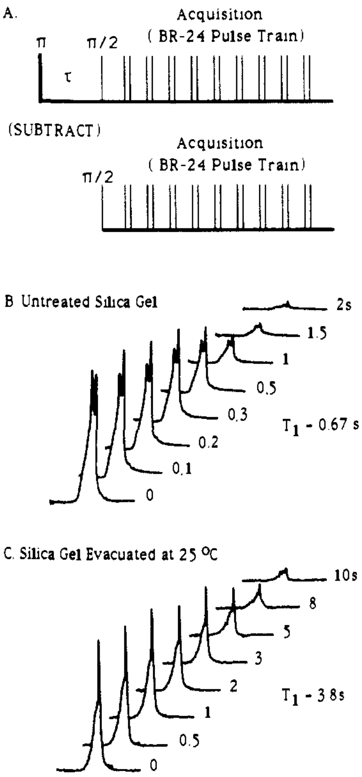

Figure 2. T_1 determination. (A) Pulse sequence, showing individual sequences employed in alternate scans (lower case subtracted from upper case in computer memory). (B) Results for untreated silica gel (showing τ values). (C) Results for sample evacuated at 25 °C (showing τ values).

2. ^{1}H CRAMPS Relaxation Experiments. Measurements of the ^{1}H spin–lattice relaxation time (T_1) of solid samples can provide information on (a) the extent of time dependences (e.g., molecular motion) present in the sample with frequency components at the Larmor frequency and (b) the extent of spin communication, or spin exchange, between different proton spin sets that are resolvable in the spectrum of the sample. Spin exchange can occur either by chemical exchange[18] or by spin diffusion,[19] both of which are chemically relevant from dynamical/structural points of view. Spin diffusion is a concept used in characterizing the process by which resolvable spin sets achieve thermal equilibrium with respect to each other following a perturbation of the system that leaves the different spin sets in different states of nuclear spin polarization. This process depends on mutual spin–spin flip-flops of the following type, where 1 and 2 label individual spins:

$$\begin{matrix}\uparrow & \downarrow & \longleftrightarrow & \downarrow & \uparrow \\ 1 & 2 & & 1 & 2\end{matrix}$$

This flip-flop process is brought about by the magnetic dipole–dipole interaction between spin 1 and spin 2, which in turn depends on structure and dynamics (e.g., the average of the inverse cube of the internuclear distance). If the ^{1}H–^{1}H dipolar interaction

---

(16) Schroter, B.; Rosenberger, H.; Hadzi, D. *J. Mol. Struct.* **1983**, *96*, 301.

(17) Berglund, B.; Vaughan, R. W. *J. Chem. Phys.* **1980**, *73*, 2037.

(18) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic: New York, 1980.

(19) Goldman, M. *Spin Temperature and Nuclear Magnetic Resonance in Solids*; Clarendon: Oxford, 1970.

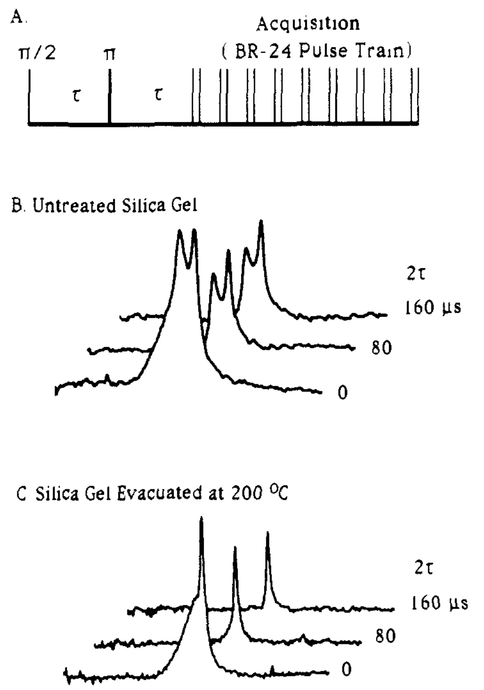

Figure 3. Dipolar dephasing experiment. (A) Pulse sequence. (B) Results for untreated silica gel (showing τ values). (C) Results for sample evacuated at 200 °C (showing τ values).

is strong, resulting in efficient ^1H spin diffusion, then distinguishable ^1H spin sets are in rapid communication and will display a common ^1H T_1 value in a T_1 experiment.

Figure 2A shows the pulse sequence employed in this study for the determination of relevant ^1H T_1 values. This sequence employs ^1H CRAMPS for detection, preceded by a Freeman–Hill modification[20] of a conventional inversion–recovery scheme. Parts B and C of Figure 2 show the experimental results for the untreated silica gel and the sample evacuated at 25 °C, respectively. In each of the two studies, the entire spectrum was found to relax at a common rate. The T_1 value obtained depends strongly on whether or not physisorbed water is present; a 0.67-s T_1 is obtained for the untreated sample and 3.8 s for the evacuated sample. It seems likely (vide infra) that the adsorbed water molecules experience a considerable degree of motion, which provides a relaxation "sink" for all of the protons on the surface. The fact that a common T_1 value was observed for each sample indicates that spin equilibration among the different types of protons is fast, at least on the rather slow time scale of the measured T_1 values. It is not clear from these data alone whether the water protons interact with protons of both silanol species or whether water relaxes one of the silanol species preferentially, while the other silanol relaxes through the spin equilibration with the rapidly relaxing silanol.

Additional information on the relationship between the two types of silanol moieties can be obtained by direct observation of their transverse relaxation behaviors in a dipolar dephasing experiment, which is diagrammed in Figure 3A. In this experiment, the dipolar dephasing that occurs during the period 2τ preferentially attenuates the transverse magnetization of the protons that are most strongly involved in dipolar interactions with other protons. This is analogous to the well-known ^{13}C–^1H dipolar dephasing technique applied routinely in solid-state ^{13}C NMR.[21] Parts B and C of Figure 3 show the results obtained on the untreated and 200 °C evacuated samples, respectively.

Deconvolution of the results shown in both Figure 3B and Figure 3C show that, after 160 µs of dipolar dephasing, the broad silanol peak at 3.0–3.5 ppm is essentially completely gone, a behavior consistent with the interpretation that this peak is due to silanol protons involved in strong dipolar interactions, as would be expected in hydrogen-bonding situations. The small degree of attenuation of intensities of the sharper 3.5 and 1.7 ppm peaks during the dipolar dephasing period shows that ^1H–^1H dipolar effects for these types of hydrogens are much weaker. For the 3.5 ppm peak this can be explained by mobility and/or proton exchange in the physically adsorbed H_2O; for the 1.7 ppm peak, this is a further indication of the "isolated" character of these silanol protons.

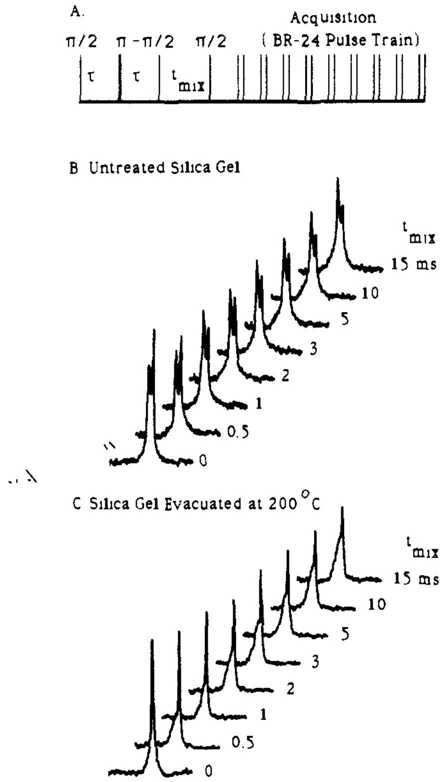

Figure 4. Spin-exchange experiment. (A) Pulse sequence. (B) Results for untreated silica gel (showing t_{mix} values). (C) Results for sample evacuated at 200 °C (showing t_{mix} values).

A third type of ^1H CRAMPS relaxation experiment that we have employed to examine this system is one designed to display spin exchange directly. Figure 4A shows the pulse sequence employed, essentially a 1-dimensional Fourier transform (1D FT) solid-sample ^1H CRAMPS analogue of the 2D FT spin-exchange (NOESY) experiment[22] that is commonly used for liquid samples. In this experiment, a dipolar dephasing period, 2τ, is used to create a difference in spin polarization between proton types that experience different degrees of ^1H–^1H dipolar dephasing. Then the ^1H magnetizations corresponding to these different polarizations are placed along the H_0 direction for a "mixing period", t_{mix}, during which ^1H spin diffusion occurs prior to detection. In the present case a τ value of 80 µs was employed to greatly diminish the ^1H spin polarization of the 3.0 ppm resonance of strongly coupled silanol protons, leaving the polarizations of other protons only slightly attenuated.

Parts B and C of Figure 4 display the results of the ^1H CRAMPS spin-exchange experiment carried out on the untreated silica gel and a sample evacuated at 200 °C. The results are displayed as a function of t_{mix}. For a zero mixing time, the results are essentially the same as those obtained in the dipolar-dephasing experiment with τ = 80 µs. Qualitatively, one can see from Figures 4B and 4C that substantial spin exchange among the different types of protons is observed for mixinng periods as short as 500 µs and that a very high degree of equilibration occurs by about 2–3 ms of mixing. Chemical exchange at such a rate would broaden the ^1H CRAMPS peak beyond the observed line width. Hence, we conclude that the spin equilibration occurs by spin diffusion arising from mutual dipolar coupling. These observations

---

(20) Freeman, R.; Hill, H. D. W. *J. Chem. Phys.* **1971**, *54*, 3367.

(21) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

(22) Jeener, J.; Meier, B. H.; Backmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

are especially apparent for the dehydrated sample (Figure 4C), for which qualitative trends can be seen even without computer deconvolution. For that sample, the apparent spin diffusion efficiency between the two types of silanol protons implies that there are substantial dipolar interactions between these two spin sets. Although a true calculation of internuclear distances would require a detailed model of structure and dynamics at the surface, a crude estimate from these data indicates a mean distance between the hydrogen-bonded and isolated silanol protons of less than 10 Å.

Deconvolution of the results given in Figure 4B indicates that ^{1}H spin diffusion between the water protons and silanol protons is almost nonexistent on the microsecond-to-millisecond time scale of this experiment and that spin diffusion between the two types of silanol protons occurs with a rate that is comparable with that in the evacuated sample (Figure 4C). The combination of these results and those of the T_1 measurements implies that, for the untreated silica gel sample, ^{1}H spin diffusion between the physisorbed water and surface silanols occurs with a correlation time, τ_c, such that $1\ \mathrm{s} > \tau_c > 15\ \mathrm{ms}$.

3. Comparisons with IR Results. The ^{1}H CRAMPS spectra reported here are consistent with the results from previous infrared spectroscopic studies of silica gel. McDonald[3] reported O–H stretching absorbances for physisorbed water, hydrogen-bonded SiOH groups, and isolated SiOH groups in the IR spectrum of fumed silica. Several different types of hydrogen-bonded silanols were observed in the IR spectra, consistent with the variety of coupled silanols observed in the ^{1}H CRAMPS spectra. In both the IR and CRAMPS spectra the physisorbed water peak disappears when the silica is evacuated at 25–30 °C. While most of the IR absorbance associated with the hydrogen-bonded silanols disappeared upon evacuation at 500 °C, a weak absorbance, which was assigned to weakly hydrogen-bonded silanols, remained. These weakly hydrogen-bonded silanols may not be resolved in the CRAMPS spectrum of the silica sample evacuated at 500 °C, or they may not be present in the study reported here, since the sample was evacuated for 16 h, in contrast to the 30-min evacuation used in the IR study.

The ^{1}H CRAMPS technique is a valuable complement to IR spectroscopy, since in NMR the observed area of a given peak is directly proportional to the number of protons giving rise to that peak, and a wide variety of NMR relaxation experiments can be used to study the geometrical arrangements and dynamics of protons on the silica surface.

Conclusions

The results of this study show that state-of-the-art ^{1}H CRAMPS NMR techniques, including various kinds of relaxation experiments, are capable not only of distinguishing structurally different types of hydroxyl moieties on a silica surface but also of addressing the issue of proximity of one type relative to the others. Two distinctly different types of silanol groups are identified, and it is found that the hydrogen-bonded types are the ones that are eliminated first by thermal dehydration. More detailed studies of this type, especially in conjunction with ^{29}Si MAS NMR and IR experiments, should greatly enhance the quality of knowledge in this area.

Acknowledgment. Support from National Science Foundation Grant CHE-8610151 and use of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE-8616437, are gratefully acknowledged.

Registry No. Silanol, 14475-38-8.

Catecholate LMCT Bands as Probes for the Active Sites of Nonheme Iron Oxygenases[1]

D. D. Cox,[†] S. J. Benkovic,[‡] L. M. Bloom,[‡] F. C. Bradley,[†] M. J. Nelson,[§] L. Que, Jr.,*[†] and D. E. Wallick[‡]

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Central Research and Development Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898. *Received July 3, 1987*

Abstract: A series of $[\mathrm{Fe^{III}L(catecholate)}]$ complexes has been synthesized to correlate the energies of catecholate-to-Fe(III) charge-transfer transitions with the nature of the iron coordination environment. L is a tetradentate tripodal ligand, $\mathrm{N(CH_2X)_3}$, where X can be phenolate, carboxylate, pyridine, or benzimidazole, or a combination thereof, and the resulting ternary complexes are high-spin ferric based on their EPR spectra. The complexes exhibit two ligand-to-metal charge-transfer (LMCT) bands in the 400–900-nm spectral region; these are shown to be catecholate-to-Fe(III) charge transfer in nature by resonance Raman studies. The LMCT bands systematically shift to lower energy as oxyanionic ligands on the tripod are replaced by neutral nitrogen ligands, which is consistent with the increased Lewis acidity of the metal center. These observations have been used to gain insight into the iron coordination environment of rat liver phenylalanine hydroxylase and soybean lipoxygenase, both of which form catechol complexes in their Fe(III) forms. The catechol complexes of these enzymes exhibit spectral features that are similar to those of the synthetic catecholate complexes. Based on the energies of the observed catecholate LMCT bands, it is proposed that the iron sites in phenylalanine hydroxylase and lipoxygenase resemble that of the tripod with two pendant pyridines and one carboxylate. These observations should complement other approaches for deducing the metal coordination environment in oxygenases which lack a visible chromophore, i.e., ligand-field spectral studies which provide information on coordination number and geometry, and EPR studies with NO and ^{17}O-labeled ligands which provide information on the binding of exogenous ligands.

There has been recent growing interest in the active site structure of the nonheme iron oxygenases and how the coordination chemistry of the iron center relates to the enzymatic function.[2,3] Our understanding of the mechanism for oxygen activation by these enzymes is rudimentary compared to that for the heme-containing oxygenases because of the paucity of information regarding the nature of their active sites. Some of these enzymes, such as catechol 1,2-dioxygenase,[4] protocatechuate 3,4-di-

---

[†] University of Minnesota.

[‡] Pennsylvania State University.

[§] E. I. du Pont de Nemours.

(1) Contribution No. 4415 from the Central Research and Development Department, E. I. du Pont de Nemours & Co.

(2) Que, L., Jr. *Struct. Bonding* (*Berlin*) **1980**, *40*, 39–72.

(3) Que, L., Jr. *Adv. Inorg. Biochem.* **1983**, *5*, 166–199.

0002-7863/88/1510-2026$01.50/0