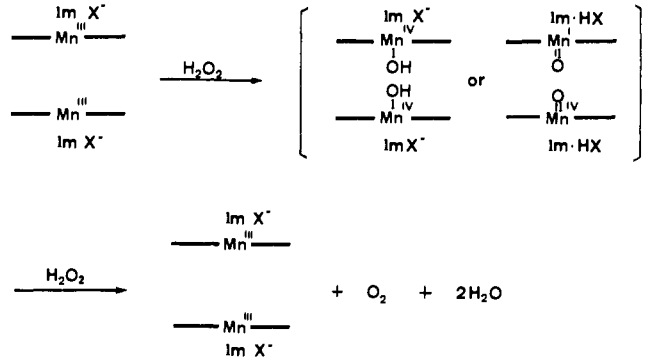
Scheme I



into the cavity. The role of imidazole in H_2O_2-Mn porphyrin systems is reported to be both the acceleration of O-O bond homolysis and the stabilization of an intermediate $Mn^{IV}(=O)$ complex.[8] In marked contrast with **1** and **2b**, biphenylene-linked porphyrin **3** had absolutely no catalase activity even though the predicted metal-metal distance (3.8 Å)[9] is similar to that of the Mn-CAT from *T. thermophilus* (3.6 Å).[3d] This could be explained by formation of the inert μ-oxo dimer, since, after treatment of the reaction mixture of **3** with H_2O_2, the corresponding intramolecular μ-oxo complex was detected by means of FABMS.[10] This had absolutely no catalase activity.

The binuclear center is essential for catalysis, as seen by compounds **2a** and **2b**. The monomanganese complex **2a** has absolutely no catalytic activity. Spectrophotometric analysis[7] revealed that a bis(imidazole) Mn complex did not form, thus confirming that the second Mn porphyrin in the dimer serves to sterically block imidazole ligation to the first one. From these results, two Mn ions are essential and the intermetal distance is important for the development of high catalase activity. In the anthracene-linked porphyrin dimer, this is around 4.5 Å,[9] which is rather longer than the enzymatic one. On the other hand, the turnover rate for *T. thermophilus* enzymes is much larger ($k \approx 10^7$ s^{-1}).[3f]

For clarification of the oxygen evolution mechanism, we used isotopically labeled hydrogen peroxide and analyzed the evolved oxygen by mass spectrometry.[11] When a 1:1 molar ratio of $H_2{}^{16}O_2$-$H_2{}^{18}O_2$ was used, the evolved oxygen was also in a 1:1 molar ratio of $^{16}O_2$ and $^{18}O_2$ and with no ^{16}O-^{18}O detected in the initial stage of the reaction. Furthermore, by kinetic measurement, the initial rate of O_2 evolution was observed to be first order in [**1**] and [H_2O_2]. Thus O_2 evolution proceeds unimolecularly in H_2O_2 at the rate-determining step. Since it has been established that rapid formation of the Mn=O complex occurs by treatment of Mn porphyrins with H_2O_2 in the presence of imidazole,[12] the Mn porphyrin dimer is very likely to form the corresponding bis Mn=O complex, which can reductively decompose and evolve oxygen in unimolecular fashion. This mechanism is also supported by the in situ formation of Mn=O porphyrin dimers and their succeeding rapid reaction with H_2O_2.[13] Thus, we propose a new mechanism for the decomposition of H_2O_2 (Scheme I).

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Supplementary Material Available: Mass spectral charts of evolved oxygen and kinetic data (2 pages). Ordering information is given on any current masthead page.

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(10) After treatment of **3** with H_2O_2, the residual porphyrin showed m/z = 1452 ($M + 2H^+$), 1450 (M^+), instead of the starting porphyrin dimer, m/z = 1435 ($M - 2Cl^- + H^+$). The observed new peaks are assigned to the corresponding intramolecular μ-oxo complex, which regenerates **1** by treatment with a dilute HCl solution.

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(13) Treatment of **2b** in CH_2Cl_2 with *m*-chloroperbenzoic acid (mCPBA) at -30 °C in the presence of MeIm gave the corresponding Mn=O porphyrin dimer (cf. ref 14). Addition of H_2O_2 to the resultant solution showed the instantaneous disappearance of the Mn=O complex (403 nm) and simultaneous regeneration of the Mn^{III} complex (463 nm). A similar operation using manganese *meso*-tetramesitylporphyrin indicated only slow disappearance of the Mn=O complex even in the presence of an excess amount of H_2O_2. For efficient O_2 evolution from H_2O_2, two high-valent Mn ions are essential.

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Proton NMR Spectra without Spin-Spin Splittings

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Complete homonuclear decoupling of NMR spectra has been a long-sought goal[1-5] since it promises direct observation of chemical shifts without the overlap problems associated with spin-spin splitting. We propose a new variation of two-dimensional spectroscopy that displays only proton chemical shifts in one frequency dimension and separated spin multiplet structures in the other. It is an extension of the method of *J*-spectroscopy[6] which calculates the Fourier transform of the spin-echo modulation[7] observed in homonuclear coupled spin systems. Previous approaches to this problem have been complicated by severe distortions of the line intensities[1-3] or very unfavorable line shapes.[8] We show that a one-dimensional spectrum may be recorded which consists only of singlet responses at the chemical shift frequencies, with no fine structure due to proton-proton splittings. These resonances are in the pure absorption mode with intensities proportional to the number of equivalent protons at each site. This mode of display is analogous to the usual practice for natural-abundance carbon-13 spectra recorded with broadband proton decoupling.

We modify the usual spin-echo pulse sequence[1,6] to include a 30-ms adiabatic pulse[9] followed by a 90° pulse at the end of the evolution period. This destroys certain components of the echo modulation by dispersing the corresponding spin isochromats in the spatial inhomogeneity of the radio-frequency field. This alters the character of the spin multiplet structure and permits a pure absorption-mode presentation. We use symmetry[10,11] to simplify the two-dimensional spectrum. There is a plane of symmetry through the $F_1 = 0$ axis and each spin multiplet pattern possesses local C_4 symmetry,[11] making it possible to employ a "symmetry filter" which suppresses all signals lacking a C_4 rotation axis. In practice two consecutive local symmetrizations are performed (with respect to the 45° and 135° diagonals) by examining intensities at symmetrically related frequency coordinates and substituting

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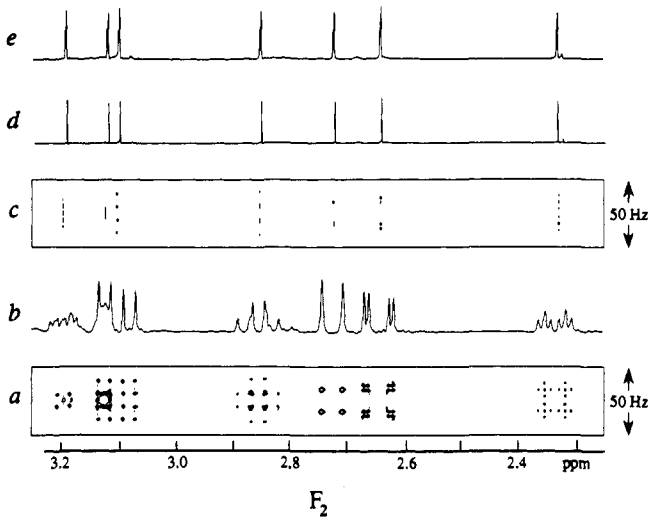

Figure 1. (a) Part of the two-dimensional J-spectrum of strychnine recorded by the new method; (b) projection onto the F_2 axis; (c) after symmetrization and suppression of the splittings in the F_2 dimension; (d) projection onto the F_2 axis; (e) after reimposition of the instrumental line width. Note the uniformity of the intensities.

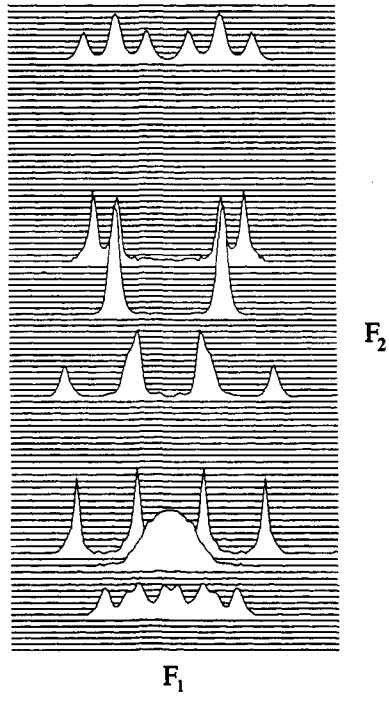

Figure 2. Stacked trace display of the spectrum shown in Figure 1c. For clarity of reproduction only every tenth trace is shown.

the lower intensity at both locations.[12] This operation is carried out on a 50-Hz square data matrix centered on the coordinates $F_1 = 0$, $F_2 = x$ Hz, where x is incremented to scan through all data points along the F_2 axis. After symmetrization, the total integrated signal intensity within the 50-Hz test square remains at a low value unless x has reached a center of C_4 symmetry. Once this center has been identified, all signals within the test region are projected onto a single F_1 trace passing through the center of symmetry, giving the spin multiplet pattern for that particular chemical site. Overlap between adjacent multiplets is handled by subtracting the symmetrized multiplet patterns from the raw experimental data one at a time, if necessary by a gradual iterative procedure.[4]

Projection of each separated multiplet trace onto the F_2 axis gives a single sharp peak at the chemical shift frequency. The height represents the integrated intensity from the chemical site in question; ideally, all intensities would be equal for single-proton sites. The symmetrization operation is very sensitive to the F_2 frequency, so these lines are artifically narrow, essentially only one data point wide. This does not imply a comparably high resolving power for overlapping responses, and to emphasize this point, a Gaussian line width has been imposed (by repeated 1:2:1 convolution) on the final chemical shift spectrum. Although the symmetry filter works well for first-order coupling, strong coupling distorts the intensities and slightly displaces the apparent chemical shifts.

Experimental tests were carried out on the 400-MHz proton spectrum of strychnine recorded on a Varian VXR-400 spectrometer; a region between 2.3 and 3.2 ppm is examined in Figure 1. Each chemically distinct site has J-splittings in both dimensions (Figure 1a) with local C_4 symmetry. Figure 1b shows the projection on the F_2 axis, giving a trace essentially identical with the conventional (coupled) high-resolution spectrum. The spin–spin splitting in the F_2 dimension may be suppressed (Figure 1c) once the symmetry centers (Figure 1d) have been located. Note the uniformity of the intensities. Figure 1e shows the chemical shift spectrum with a 1.2 Hz instrumental line width reimposed. The information is perhaps most effectively displayed as a stacked-trace plot (Figure 2) with the individual spin multiplets in the F_1 dimension and the chemical shifts in the F_2 dimension.

Acknowledgment. We thank James Keeler for illuminating discussions and for information about the adiabatic pulse scheme[9] prior to publication.

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Synthesis and Structural Characterization of a Novel Cluster with a Ga–P Framework

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Recent investigations in this laboratory concerning the formation of novel quasi-aromatic rings such as $(RBPR')_3$,[1] $(RAlNR')_3$,[2] and $(GeNR)_3$,[3] (R and R' = variety of bulky alkyl or aryl groups) have suggested that similar rings comprising exclusively heavier main-group elements could be isolated as stable entities. This goal has been partially realized through the synthesis of the zinc–sulfur ring systems $(RZnSR')_3$[4,5] which possess almost planar Zn_3S_3 arrays.[4,5] In addition, the synthesis of an organogallium–arsenic cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ ($R = CH_2SiMe_3$) has given grounds for confidence that the proposed unsaturated rings can be synthesized if the appropriate substituents were selected.[6] As part of an experimental program designed to attain this objective, we report here on the synthesis and characterization of the novel gallium phosphide cluster species $[Ga_4(Trip)_3\{P(1\text{-}Ad)_4\}P(H)(1\text{-}Ad)]$, **1** [1-Ad = 1-adamantyl, Trip = 2,4,6-(*i*-$Pr)_3C_6H_2$].

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