81600-73-9; *cis*-[Co(en)$_2$(nicH-*O*)$_2$](ClO$_4$)$_3$, 81554-39-4; *trans*-[Co(en)$_2$(nicH-*O*)$_2$](ClO$_4$)$_3$, 81600-76-2; [Co(NH$_3$)$_5$py](ClO$_4$)$_3$, 15351-76-5; [Co(NH$_3$)$_5$(nic-*N*)](ClO$_4$)$_3$, 81554-40-7; [Co-(NH$_3$)$_5$nica](ClO$_4$)$_3$, 15675-82-8; [Co(NH$_3$)$_5$mnic](ClO$_4$)$_3$, 38686-26-9; [Co(NH$_3$)$_5$CO$_3$]NO$_3$, 15244-74-3; [Co(en)$_2$CO$_3$]Cl, 15842-50-9; [Co(NH$_3$)$_5$(nicH-*O*)](ClO$_4$)$_3$, 81554-26-9; [Co(NH$_3$)$_5$(inicH-*O*)]-(ClO$_4$)$_3$, 81554-27-0.

Supplementary Material Available: Figures showing the pD IR titration spectra of [Co(NH$_3$)$_5$(nic-*N*)]$^{2+}$ and [Co(NH$_3$)$_5$(nic-*O*)]$^{2+}$ and the ^{1}H NMR spectra of *cis*- and *trans*-[Co(en)$_2$(nic-*O*)$_2$]$^+$ in the alkyl region (4 pages). Ordering information is given on any current masthead page.

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Concentration- and Solvent-Dependent Electron Paramagnetic Resonance Signals from μ-Nitrido-bis[(5,10,15,20-tetraphenylporphinato)iron]. Solute–Solvent and Solute–Solute Interactions

G. Alan Schick, Eric W. Findsen, and David F. Bocian*

We have been investigating the magnetic properties[1] of the nitrogen-bridged iron porphyrin μ-nitrido-bis[(5,10,15,20-tetraphenylporphinato)iron]$^{2-4}$ [((TPP)Fe)$_2$N]. Unlike the analogous oxygen-bridged porphyrin, which is diamagnetic at low temperatures due to the antiferromagnetic exchange interaction between the two iron ions,[5] ((TPP)Fe)$_2$N has a net spin $S = \frac{1}{2}$ over the temperature range 4–295 K.[1,2] The EPR spectrum of the complex is characteristic of an axially symmetric system with $g_\perp = 2.15$ and $g_\parallel = 2.01$.[1,2] An early EPR study of a solid sample of ((TPP)Fe)$_2$N failed to reveal any nuclear hyperfine structure on either of the two EPR signals.[2] We recently reexamined the EPR spectrum of the complex in a frozen carbon disulfide solution and observed well-resolved ^{14}N nuclear hyperfine splittings on the $g_\perp$ component.[1] We attributed the hyperfine structure to the interaction of the unpaired electron with the nucleus of the bridging nitrogen atom. The frozen-solution EPR spectra also exhibited, however, several signals which were not observed in the spectrum of the solid sample. We were unable to explain the origin of the additional signals at that time.

The appearance of the additional signals in the EPR spectrum of ((TPP)Fe)$_2$N in carbon disulfide suggests that the solvent or solution environment may significantly influence the magnetic properties of the complex. So that the effects of these factors on the EPR signals could be better assessed, the spectrum of the complex has been obtained in various solvents as a function of concentration.

Experimental Section

The ((TPP)Fe)$_2$N complex was prepared and purified as described in ref 2. The identity of the molecule was confirmed by UV–visible and infrared spectroscopy.

The EPR spectra were recorded from frozen solutions or "thin films" at 110 K with a Bruker ER200D X-band spectrometer with a 12-in.
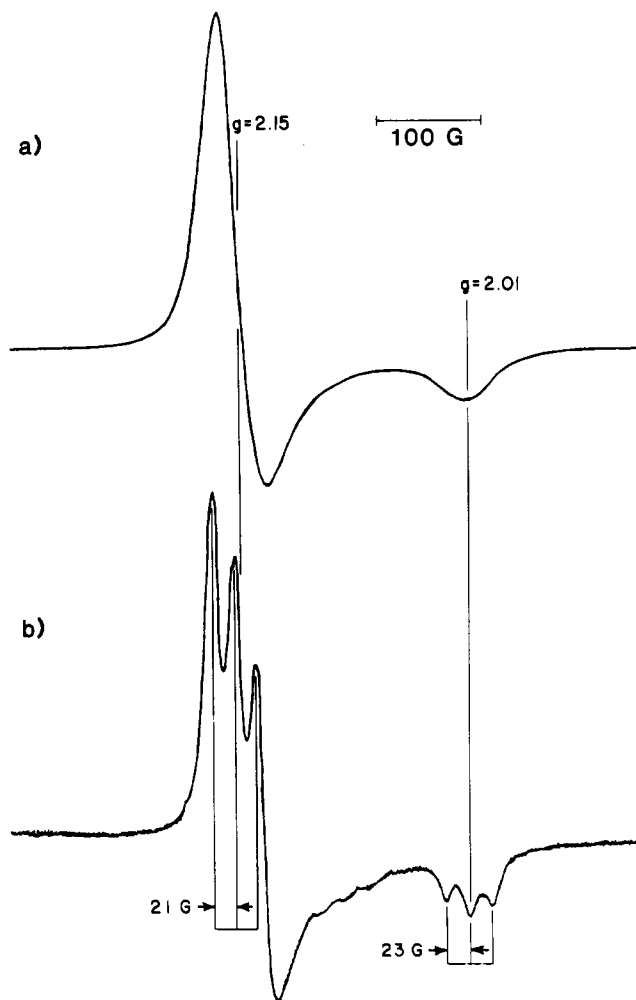
(1) Schick, G. A.; Bocian, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 7982–7984.
(2) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747–1752.
(3) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339–345.
(4) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623–6628.
(5) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1–35.

Figure 1. EPR spectrum of ((TPP)Fe)$_2$N in carbon disulfide at 110 K (concentration 6.7 × 10^{-3} M): (a) broad-line signal obtained from the bulk solution; (b) signal obtained from a "thin film" (see text) of the same solution (modulation amplitude 4 G; microwave power 1.99 mW (a) and 15.7 mW (b)).

magnet. The temperature was controlled with a Bruker ER4111VT liquid-nitrogen variable-temperature system.

The solvents used for the EPR studies (benzene, ethanol, and carbon disulfide) were all spectral grade and displayed no adventitious EPR signals. Thin films of ((TPP)Fe)$_2$N were made by warming the top of an EPR tube containing the complex in a 6.7 × 10^{-3} M carbon disulfide solution and then inverting and righting the tube, allowing the solvent to run down the warm tube and partially evaporate, leaving a film of ((TPP)Fe)$_2$N. The tube was placed in the EPR cavity such that only the thin-film region was in the microwave field.

Results and Discussion

The EPR spectrum of 6.7 × 10^{-3} M ((TPP)Fe)$_2$N in carbon disulfide at 110 K is shown in Figure 1a. The spectrum of the complex at lower concentrations in carbon disulfide and in benzene is similar. The EPR spectrum is characteristic of an axially symmetric system with $g_\parallel = 2.01$ and $g_\perp = 2.15$. The signals exhibit no resolved ^{14}N nuclear hyperfine structure[1] and are similar to those observed for solid ((TPP)Fe)$_2$N.[2] The EPR signals narrow only slightly as the concentration is reduced, and no nuclear hyperfine structure can be resolved at 110 K, even at concentrations where the signal intensity limits the acquisition of the spectrum ($\sim$10^{-5} M). The lack of resolved ^{14}N nuclear hyperfine structure in the spectrum obtained at 110 K is in contrast to the well-resolved structure observed at 50 K.[1]

In order to investigate the possibility that the hyperfine structure in the solutions of carbon disulfide and benzene at 110 K is rendered unobservable by sample aggregation and

inhomogeneity which could occur upon freezing, we have also recorded the EPR spectrum of $((TPP)Fe)_2N$ in an ethanol glass at 110 K. The ethanol glass is optically transparent and shows no evidence of solute precipitation or aggregation. Nonetheless, the EPR spectrum of $((TPP)Fe)_2N$ in the homogeneous medium is nearly identical with that observed in the frozen solutions of carbon disulfide and benzene, displaying no resolved nuclear hyperfine structure.

The EPR spectrum of a thin film of $((TPP)Fe)_2N$ prepared from a 6.7×10^{-3} M carbon disulfide solution is shown in Figure 1b. The spectrum exhibits extremely well-resolved ^{14}N nuclear hyperfine splittings on both the parallel $[A_{\parallel} = 23$ G $(\sim65$ MHz$)]$ and perpendicular $[A_{\perp} = 21$ G $(\sim63$ MHz$)]$ signals. At 110 K there is no evidence of the additional signals we observed in our preliminary EPR study of $((TPP)Fe)_2N$ in frozen solution.[1] The lack of interference from these latter signals allows the observation of ^{14}N hyperfine structure present on the $g = 2.01$ signal.

The difference in the appearance of the bulk solution and thin-film EPR spectra of $((TPP)Fe)_2N$ at 110 K indicates that either second-order magnetic interactions or environmental heterogeneities are significantly greater in the bulk solution than in the film. The independence of the line width from the solute concentration suggests that solvent induced environmental heterogeneity is probably the more important of the two factors for rendering the hyperfine splitting unobservable in the bulk solution. The fact that the spectrum of $((TPP)-Fe)_2N$ in the ethanol glass is similar to that observed in frozen solutions of carbon disulfide and benzene indicates that some solvent-induced heterogeneity exists even in this medium. Recently, Bottomley and Garrett[6] have observed that a small amount of rhombicity is induced in the **g** tensor of $((TPP)-Fe)_2N$ upon freezing solutions of the complex in toluene. It is possible that this type of effect could result in the obscuring of the hyperfine splittings in the bulk solution. This explanation is not, however, altogether satisfactory. Even a small amount of rhombicity should be observable as a broadening of the $g = 2.15$ signal of the complex in bulk solution compared to the thin film. This is clearly not observed. In fact, the $g = 2.15$ signal of the bulk solution appears to be narrower than that of the thin film. It is possible that second-order magnetic interactions also play a role in obscuring the hyperfine structure in the bulk solution. These second-order interactions could be reduced in the thin film by a partial orienting of the molecules during the deposition process.

The ^{14}N nuclear hyperfine splittings we observe on the parallel and perpendicular components of the axial EPR signal of the thin film preparation of $((TPP)Fe)_2N$ are approximately equal $(A_{\parallel} \approx 65$ MHz and $A_{\perp} \approx 63$ MHz$)$ and of nearly the same magnitude as those observed by Bottomley and Garrett[6] for the rhombic EPR signal exhibited by the complex in frozen toluene solution $(A_x = 67.27$ MHz, $A_y = 66.77$ MHz, and $A_z = 66.16$ MHz$)$. These latter workers interpreted the nearly equal hyperfine splittings as being indicative of isotropic ^{14}N hyperfine interaction. They assigned the unpaired electron in the complex to an a_1 molecular orbital, which is predicted by theoretical calculations to be primarily metal centered, 44.5% on each iron (d_{z^2}) and 1.6% nitrido 2s.[7] We agree with this interpretation;[8] however, an alternative explanation for the nearly equal hyperfine splittings is possible and is as
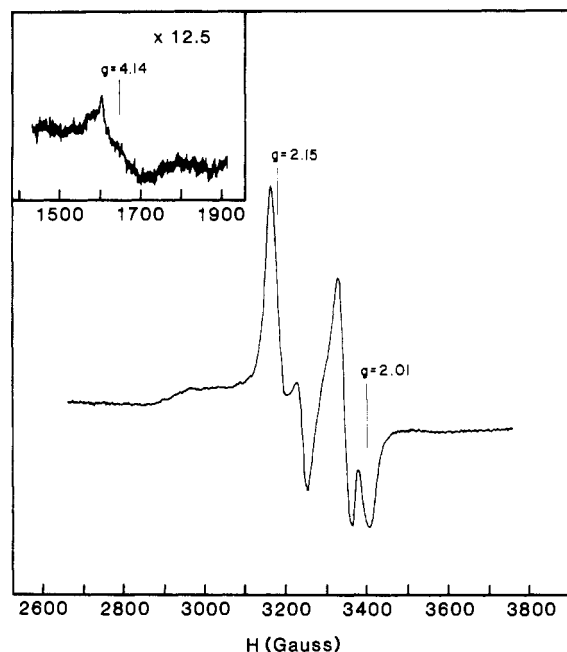

Figure 2. EPR spectrum of $((TPP)Fe)_2N$ in carbon disulfide at 110 K (concentration 7.3×10^{-3} M) (modulation amplitude 4 G; microwave power 1.99 mW). Insert: the low-field region showing the $\Delta m_s = 2$ transitions of the triplet species (modulation amplitude 4 G; microwave power 3.11 mW).
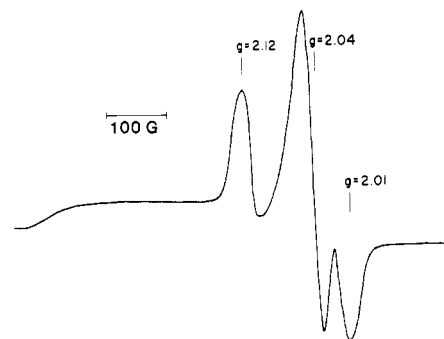

Figure 3. Rhombic EPR spectrum obtained by subtracting the signals of the species observed at low concentrations in bulk solution (Figure 1a) from those observed at high concentrations (Figure 2). The subtraction was performed with the assumption that the $g = 2.15$ signal is entirely due to the low-concentration species.

follows. The anisotropic hyperfine is very large $(A_{aniso} \approx 43$ MHz$)$, and the isotropic hyperfine is approximately half as large and negative $(A_{iso} \approx -21$ MHz$)$.[9] This interpretation, although plausible, is not particularly satisfying for several reasons. The electron would have to be highly localized in a nitrogen 2p orbital in order for the anisotropic hyperfine to be 43 MHz. The anisotropic hyperfine interaction for a pure p orbital on nitrogen is 47.5 MHz;[9] thus, the amount of nitrido 2p character would have to approach 90%. This value is unrealistically large and inconsistent with recent molecular orbital calculations on $((TPP)Fe)_2N$, which predict that the orbital containing the unpaired electron is at most 25.7% nitrido 2p.[7] Also, if the electron is localized in an orbital of primarily nitrido 2p character, the isotropic contribution to the hyperfine should be positive, not negative.[9-12]

(6) Bottomley, L. A.; Garrett, B. B. *Inorg. Chem.* **1982**, *21*, 1260.
(7) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328–3341.
(8) In ref 1 we state that the magnitude of the ^{14}N hyperfine interaction is indicative of the unpaired electron being localized in an orbital with substantial nitrido character. This interpretation was based on the fact that hyperfine structure could only be observed on the perpendicular component of the EPR signal, implying a substantial anisotropic hyperfine coupling. The observation of the hyperfine structure on the parallel component of the signal reported in the present work requires that we modify our earlier interpretation.

(9) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972.
(10) Hamilton, C. L.; McConnell, H. M. "Structural Chemistry and Molecular Biology"; Rich, A., Davidson, N., Eds.; W. H. Freeman: San Francisco, 1968; pp 115–149.
(11) Chien, J. C. W. *J. Chem. Phys.* **1969**, *51*, 4220–4227.

At concentrations greater than 7×10^{-3} M in carbon disulfide, new signals appear in the EPR spectrum of ((TPP)-Fe)$_2$N at $g = 2.12$ and 2.04 (Figure 2). The $g = 2.01$ signal is more intense relative to the 2.15 signal than in the spectrum recorded on lower concentration samples. Also, a broad shoulder is observed on the low-field side of the $g = 2.15$ signal. The spectrum obtained for the new species by subtracting the powder pattern of the species observed at low concentrations (with the assumption that the $g = 2.15$ signal is entirely due to the latter species) is shown in Figure 3. The resulting powder pattern is similar to that expected for a simple rhombic ($g = 2.12$, $g = 2.04$, and $g = 2.01$) system, except for the broad shoulder near $g \approx 2.20$. These new signals which are observed at high concentrations are similar to (although not identical with) those reported in our preliminary EPR study of ((TP-P)Fe)$_2$N.[1,13] The details of the appearance of the EPR spectrum of ((TPP)Fe)$_2$N at high cncentrations in carbon disulfide are quite sensitive to the exact concentration and rate of cooling. Some solute precipitation and aggregation are apparent upon freezing the nearly saturated solutions. In all of the preparations at high concentration, a signal is observed at $g = 4.14$. This signal is characteristic of a triplet species and suggests that the new signals which appear in the EPR spectrum are due to ((TPP)Fe)$_2$N molecules which form aggregates in which first-order magnetic interactions occur between two of the $S = {}^1/_2$ spin centers.

We have attempted to determine the separation and relative orientation of the interacting molecules in the aggregate unit by performing computer simulations of the triplet EPR spectrum using the theoretical procedures developed by Smith and Pilbrow[14–18] to describe two coupled $S = {}^1/_2$ spin centers. Unfortunately, the separation and relative orientation for the two spin centers cannot be determined unambiguously. The computer simulations do show, however, that the $\Delta m_s = 2$ transition of the triplet species can only be calculated at the observed value of $g = 4.14$ if the **g** tensor of *each* of the interacting molecules is rhombic with the values $g = 2.12$, $g = 2.04$, and $g = 2.01$ (Figure 3). Interactions between two spin centers with axially symmetric **g** tensors ($g_\perp = 2.15$ and $g_\parallel = 2.01$) or between one molecule with the axially symmetric **g** tensor and another with the rhombic tensor result in calculated $\Delta m_s = 2$ transitions at $g = 4.27$ and $g = 4.21$, respectively.

The lowering of the symmetry of the **g** tensor from axial to rhombic which occurs in the interacting ((TPP)Fe)$_2$N molecules suggests that there is a weak electrostatic interaction between the molecules in the oligomeric unit, in addition to the magnetic dipole–dipole coupling which results in the triplet EPR signal. Although our computer simulations of the triplet spectrum do not allow the unambiguous determination of the relative orientation of the two molecules, certain geometries would seem to be more consistent with the rhombicity in the **g** tensor. For example, the interactions between the phenyl groups on neighboring molecules situated side-by-side or side-by-side and rotated 90° with respect to one another could result in a slight distortion of the Fe–N–Fe linkage from linearity. Such a distortion would break the degeneracy of

the e_1 molecular orbitals[7] and mix d_{xz} (d_{yz}) character into the a_1 (d_{z^2}) orbital which contains the unpaired electron, resulting in a rhombic **g** tensor. A separation between the bridging nitrogen atoms on adjacent molecules in a side-by-side structure of ~ 9 Å would be close enough for substantial steric interactions to occur.[4] A simple stacked structure would seem to be less likely since this structure would not maintain the symmetry between the halves of the unit were the constituents to have a rhombic **g** tensor. The fact that simple monomeric tetraphenylporphyrins *do not* form dimeric species in solution also suggests that a stacked structure is unlikely.[17–19] Presumably, the bulky phenyl groups prevent the face-to-face approach of the porphyrin macrocycles. Thus, the structural features which are unique to the ((TPP)Fe)$_2$N unit must be the dominant factor in the interaction rather than features which are common to both simple monomeric and dimeric tetraphenylporphyrins.

Registry No. ((TPP)Fe)$_2$N, 59114-43-1.

(19) (a) White, W. I. "The Porphyrins"; Dolphin, D. E., Ed.; Academic Press: New York, 1978; Vol. V, pp 303–339. (b) Scheer, H.; Katz, J. J. "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 399–524.

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A Reinvestigation of the Kinetics of the Co(CN)$_5$OH$_2^{2-}$–N$_3^-$ Reaction

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The earliest[1] kinetic measurements of the reactions of Co(CN)$_5$OH$_2^{2-}$ with N$_3^-$ or SCN$^-$ yielded pseudo-first-order rate constants, k_{obsd}, that varied with the anion concentration, [X$^-$], according to eq 1. At 40.0 °C and ionic strength 1.0 M

$$k_{obsd} = k_1[X^-]/((k_2/k_3) + [X^-]) \qquad (1)$$

(NaClO$_4$), values of k_1 and k_2/k_3 were 1.4×10^{-3} s^{-1} and 1.7 M, respectively, for N$_3^-$ (pH 6.4) and 2.0×10^{-3} s^{-1} and 3.9 M, respectively, for SCN$^-$ (pH 3.4).[2] The functional dependence of k_{obsd} with respect to [X$^-$] and the reasonable agreement between the values of k_1 for the azide and thiocyanate systems were interpreted on the basis of an S$_N$1 mechanism for the reactions under consideration.[1]

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(12) Dickinson, L. C.; Chien, J. C. W. *J. Am. Chem. Soc.* **1971**, *93*, 5036–5040.
(13) The concentration of ((TPP)Fe)$_2$N is given as 0.1 mg/mL in the caption of Figure 2 of ref 1. This value is in error and should read 10 mg/mL.
(14) Dunhill, R. H.; Pilbrow, J. R.; Smith, T. D. *J. Chem. Phys.* **1966**, *45*, 1474–1481.
(15) Boas, J. F.; Dunhill, R. H.; Pilbrow, J. R.; Srivastava, R. C.; Smith, T. D. *J. Chem. Soc. A* **1969**, 94–108.
(16) Price, J. H.; Pilbrow, J. R.; Murray, K. S.; Smith, T. D. *J. Chem. Soc. A* **1970**, 968–976.
(17) Boyd, P. D. W.; Smith, T. D.; Price, J. H.; Pilbrow, J. R. *J. Chem. Phys.* **1972**, *56*, 1253–1263.
(18) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173–278.

(1) Haim, A.; Wilmarth, W. K. *Inorg. Chem.* **1962**, *1*, 573.
(2) The values of k_1 and k_2/k_3 given in the present paper differ from those given in ref 1. The values reported in ref 1 had been obtained by a graphical procedure. The values reported in the present paper were obtained by nonlinear least-squares calculation.