experimental geometries of NSF and NSF_3 were used.[2] Straightforward application of the method involves the relation

$$E_R = 0.5[\Phi_{val}(N) - \Phi_{val}(O^+)]$$

where $\Phi_{val}(N)$ is the valence potential in the ground-state molecule and $\Phi_{val}(O^+)$ is the valence potential in the ion, approximated by replacing the N nucleus by the O nucleus. Calculations based on this relation yield $\Delta E_R = 0.8$ eV, a value almost exactly equal to $-\Delta E_B$. Previous studies[30,31] have shown that ΔE_R values calculated by this method are usually too large and must be reduced by a factor of about half to give satisfactory correlations of E_B data. Thus, we conclude in this case that $\Delta E_R + \Delta E_B \leq 0$. The sulfur atom of NSF_3 is surely more positively charged than that of NSF, and therefore $\Delta V > 0$. Hence, the calculations, even allowing for uncertainty in ΔE_R, indicate that $\Delta Q_N < 0$.

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Metal–Nitroxyl Interactions. 41. Comparison of Electron–Electron Spin–Spin Interactions in Spin-Labeled Silver Porphyrins in Fluid Solution, in Frozen Solution, and on Imbiber Beads

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EPR spectra were obtained for three spin-labeled silver porphyrins in fluid solution, in frozen solution, and on imbiber beads. The values of the electron–electron spin–spin coupling constant, *J*, obtained in the three media, were in good agreement, which indicated that the molecular conformations were substantially unchanged by immobilization. Therefore, the values of the interspin distance, *r*, obtained from the rigid-lattice spectra, reflect the geometries of the molecules in fluid solution as well as in the solid state. For a tetraphenylporphyrin that had the spin label attached to the ortho position of one of the phenyl rings, the large solvent dependence of *J* observed in fluid solution persisted in frozen solution. The analysis of the frozen-solution spectra indicated that the change in *J* was accompanied by a change of about 2 Å in the interspin distance. The strong solvent dependence of *J* is consistent with the hypothesis that the solvent influences the molecular conformation and that in some conformations there is weak orbital overlap between the ortho substituent and the porphyrin π system.

Introduction

The determination of molecular structure in fluid solution is a problem of longstanding interest to chemists. Although X-ray crystallography provides detailed information concerning the structure of molecules in the solid state there is always the concern that structures in solution may differ from structures in the solid state. Therefore a structure-dependent observable that can be measured both in the solid and in fluid solution is important as an indicator of whether other parameters measured in the solid state pertain to the structure in fluid solution.

The electron–electron coupling constants, *J*, obtained from the EPR spectra of spin-labeled complexes of slowly relaxing metals in fluid solution, arise from the isotropic exchange interaction between the two unpaired electrons. For small molecules in fluid solution, molecular tumbling averages away the electron–electron splitting due to the anisotropic dipolar interaction that is dependent on the interspin distance. However when molecules are immobilized, the ESR spectra reflect the combined effects of the isotropic exchange and anisotropic dipolar interactions. Thus, analysis of the spectra can provide the value of *J* as well as the interspin distance.[1-3]

We have shown previously that the values of *J* are sensitive to changes in the conformations of the bonds between the metal and the nitroxyl.[1,4-6] Thus, agreement between the values of *J* obtained from spectra run in fluid and frozen solutions indicates that the conformations of the metal–nitroxyl linkage are similar in the two states. In cases where there is agreement between the values of *J* in fluid solution and in the solid states, the value of *r* obtained from the immobilized spectra should also pertain to the fluid-solution structure.

More detailed geometrical information can be obtained from the analysis of EPR spectra obtained on doped single crystals than from powder samples. However, not all molecules can readily be doped into single crystals. Furthermore, the analysis of single-crystal data is time-consuming. We are therefore exploring the extent to which geometrical information can be

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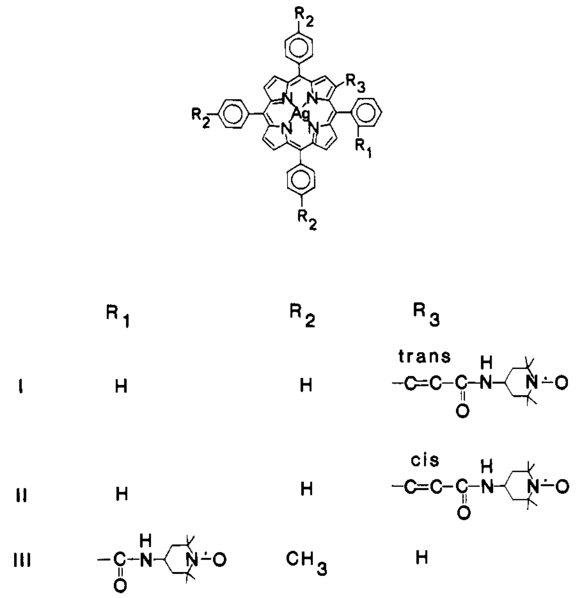
obtained by the analysis of powder spectra. We have recently reported results for spin-labeled complexes of Cu(II),[2,7] vanadyl,[7] and low-spin Co(II).[8] In this paper we report results for spin-labeled Ag(II) complexes I–III.



Experimental Section

Spin-labeled silver porphyrins I–III were prepared as previously reported.[9] EPR spectra were obtained on a Varian E-9 with an E-231 cavity containing a Dewar insert. Spectra were obtained at microwave powers that did not cause saturation and modulation amplitudes that did not cause distortion of the lines. Temperatures were measured with a thermocouple mounted directly above the cavity. *g* values were measured relative to DPPH (2.0036).

Samples on EMCO B-1318S imbiber beads were prepared from 1.0×10^{-3} M toluene or dichloromethane solutions. A 1.0-g quantity of beads was added to 0.3 mL of solution while it was being stirred with a spatula. The mixture was kept under vacuum for about 5 min to remove most of the solvent. The beads were crushed in a mortar and pestle (about 5 min) and transferred to a 4-mm-o.d. quartz EPR tube. The tube was evacuated for 24 h at about 0.1 torr to remove residual solvent. EPR spectra were obtained on evacuated samples.

Computer Simulation of EPR Spectra. Fluid-solution EPR spectra were simulated with the computer program CUNO.[9,10] The sign of J cannot be determined in fluid solution. EPR spectra of the immobilized samples were simulated with the computer program MENO.[2] The Hamiltonian (eq 1) consists of terms for independent electrons 1 (silver) and 2 (nitroxy) as given in eq 2 and an interaction term as given in eq 3. The interaction term includes an isotropic exchange

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{int}} \tag{1}$$

$$\mathcal{H}_i = \sum_{j=x_i,y_i,z_i} (\beta_g S_{ij} H_j + A_j S_{ij} I_{ij}) \qquad i = 1, 2 \tag{2}$$

$$\mathcal{H}_{\text{int}} = -JS_1S_2 + \mathcal{H}_{\text{dipolar}} \tag{3}$$

contribution and an anisotropic dipolar contribution. The symbols in eq 1–3 have their usual meanings and are discussed in detail in ref 2. The perturbation calculations were carried to second order. The splitting between the singlet and triplet levels is J, and a negative value of J indicates an antiferromagnetic interaction. *g* values used in the simulations: silver, g_{xx}, $g_{yy} = 2.040$, $g_{zz} = 2.108$; nitroxyl, $g_{xx} = 2.0085$, $g_{yy} = 2.0064$, $g_{zz} = 2.0030$. A values: silver, A_{xx}, $A_{yy} = 28.0 \times 10^{-4}$ cm^{-1}, $A_{zz} = 57.0 \times 10^{-4}$ cm^{-1}; nitroxyl, $A_{xx} = 4.0 \times 10^{-4}$ cm^{-1}, $A_{yy} = 5.0 \times 10^{-4}$ cm^{-1}, $A_{zz} = 31 \times 10^{-4}$ cm^{-1}.[1] For both of the unpaired electrons, the axes of the g and A tensors were assumed to be coincident. Coupling of the silver unpaired electron to four equivalent nitrogens with A_{xx}, $A_{yy} = 23.0 \times 10^{-4}$ cm^{-1} and $A_{zz} = 20.5 \times 10^{-4}$ cm^{-1} was included.[1] Thirty-four values of θ per 180° and 15 values of ϕ per 180° were used in the simulations. The angles that define the relative orientations of the g tensors for the two unpaired electrons and the orientation of the interspin vector are shown in Figure 1. Since the metal g values and A values were axially symmetric, the value of η was set equal to 0. The values of A_1 and A_2 could only be obtained for the spectra in which resolved nitroxyl nitrogen hyperfine splitting was observed. The simulated spectra were more sensitive to changes in the orientation of the nitroxyl hyperfine tensor z axis relative to the interspin vector than to changes in ϵ, A_1, and A_2, individually. The uncertainties in ϵ, A_1, and A_2 were ±20° although the simulated spectra were sensitive to changes in the angle between the interspin vector and the nitroxyl z axis of about 5°. The sign of J can be determined by simulation of the frozen-solution spectra if two conditions are satisfied: (1) the spectra are sufficiently well resolved to unambiguously define the orientation parameters and (2) the dipolar and exchange interactions are of similar magnitude. Most of the spectra reported here met these criteria. In the following discussion if the sign of J is not given, the sign is now known. The uncertainty in the value of J obtained from the frozen-solution spectra was about 5%. Due to the dependence of the dipolar splitting on r^{-3}, the uncertainty in the value of r increased as the value of r increased. For the values of r between 6.5 and 9.0 Å the uncertainty was ±0.3 Å. For the values between 11 and 13 Å the uncertainty was about ±0.5 Å.

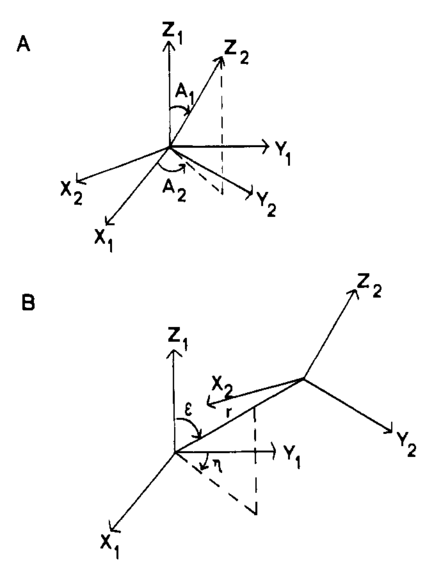


Figure 1. Definitions of the angles that relate the orientations of the nitroxyl hyperfine tensor and the interspin vector to the axes of the silver hyperfine tensor (electron 1): (A) angles A_1 and A_2 defining the orientation of the z axis of electron 2 (nitroxyl); (B) angles ϵ and η defining the orientation of the interspin vector r. Throughout the text, r is used to denote the magnitude of the interspin vector.

Results and Discussion

EPR Spectra of I and II. In fluid solution at room temperature the values of J for spin-labeled silver porphyrin I ranged from 34×10^{-4} to 43×10^{-4} cm^{-1} depending on solvent.[9] In 9:1 toluene–THF solution the value of J increased from 39.8×10^{-4} cm^{-1} at room temperature to 50.7×10^{-4} cm^{-1} at −60 °C (Table I). The spectrum obtained at −180 °C in frozen 9:1 toluene–THF solution is shown in Figure 2B. The simulated spectrum was obtained with $J = -55 \times 10^{-4}$ cm^{-1}, $r = 12.5$ Å, $\epsilon = 90°$, $A_1 = 65°$, and $A_2 = 0°$. This value of J agrees well with the value obtained by extrapolation of the fluid-solution data to the freezing point of the solvent. Thus the conformation observed in frozen solution corresponds to a low-temperature form of the molecule. Since the change in J as a function of temperature was relatively small, it is likely that the conformational change as a function of tem-

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Table I. Electron-Electron Coupling Constants[a] and Interspin Distances for Spin-Labeled Silver Porphyrins

compd	solvent	temp, °C	J, 10^{-4} cm^{-1}	r, Å
I	9:1 toluene-THF	20	39.8	
		0	43.1	
		−30	47.4	
		−60	50.7	
		−180	−55	12.5
	9:1 toluene-CH_2Cl_2	20	38.8	
		−180	−50	12.5
	imbiber beads	20	−40	12.5
		−180	−45	12.5
II	9:1 toluene-THF	20	~10[b]	
		−180	+12	11.0
	imbiber beads	20	+12	11.0
		−180	+12[c]	11.0[c]
III	toluene	20	~1000[d,e]	
	CH_2Cl_2	20	~1000[d]	
	2:1 toluene-CH_2Cl_2	−180	~−700[d]	6.9
	pyridine	20	120[e]	
	9:1 toluene-THF	−180	±40	8.8
	imbiber beads	20	~−700[d]	6.7
		−180	~−700[d]	6.7

[a] The sign of J can not be determined from the fluid-solution spectra. [b] Large line widths cause uncertainty in the value of J. [c] The spectra were poorly resolved so there is greater uncertainty for these values than for the other values. [d] These values of J are sufficiently large that small changes have little impact on the simulated spectra. Uncertainty is $\pm 200 \times 10^{-4}$ cm^{-1}. [e] Value taken from ref 9.

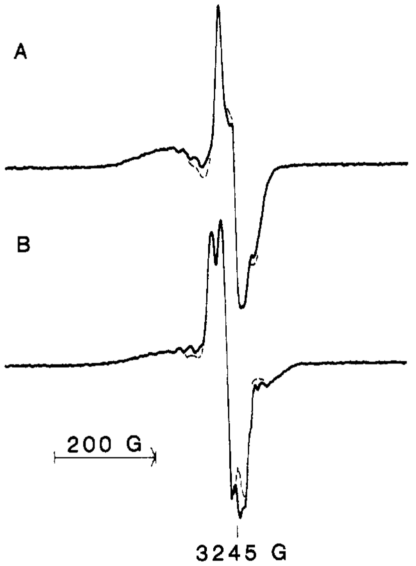

Figure 2. 800-G scans of the X-band EPR spectra of spin-labeled silver porphyrins II (A) and I (B) in 9:1 toluene–THF solution at −180 °C obtained with 1-G modulation amplitude and 0.5-mW microwave power. The dashed lines indicate regions in which the simulated spectra do not overlay the experimental curves.

perature was also relatively minor. The value of J in a frozen 9:1 toluene–CH_2Cl_2 solution (-50×10^{-4} cm^{-1}; Table I) was slightly smaller than the value in 9:1 toluene–THF solution although the interspin distance was 12.5 Å, within experimental error, for both solvent mixtures. To obtain a rigid-lattice spectrum of the compound in a conformation which matched that at room temperature in fluid solution as closely as possible, spin-labeled silver porphyrin I was immobilized on imbiber beads. The value of J for I on the solid substrate at room temperature was -40×10^{-4} cm^{-1}, which agrees well with the values obtained in fluid solution. Cooling the imbiber-bead sample to −180 °C resulted in an increase in the value of J to -45×10^{-4} cm^{-1}. The increase in J with decreasing temperature paralleled the results obtained in fluid solution although the change in J for the immobilized sample was not as large as in fluid solution. The results obtained for I on imbiber beads are consistent with observations for other spin-labeled metal complexes.[7] Although the imbiber beads interact sufficiently strongly with metal complexes to provide immobilized EPR spectra, the interaction is sufficiently weak to permit some conformational changes as a function of temperature.[7] The weak interaction with the substrate also permits examination of the complex approximately as it existed in the fluid solution from which the sample was prepared.

The observation of $r = 12.5 \pm 0.5$ Å for the spectra of I obtained under a variety of conditions is consistent with the hypothesis that the small changes in J correspond to relatively small changes in the molecular geometry. Since the acrylamide linkage is expected to be relatively rigid, the molecular conformation would not be expected to show large variations under the conditions examined. When I was doped into a single crystal of $ZnTPP(THF)_2$, the values of J were between -18×10^{-4} and -35×10^{-4} cm^{-1} and r was between 11.5 and 13.0 Å.[1] Although these values are similar to the ones observed in fluid and frozen solutions, the smaller values of J for some of the sites and the range in the values of r suggest that steric constraints of the host may have influenced the conformation of the acrylamide linkage.

In fluid solution the values of J for spin-labeled silver porphyrin II ranged from 5×10^{-4} to 19×10^{-4} cm^{-1}.[9] The spectrum of II in frozen 9:1 toluene–THF solution at −180 °C is shown in Figure 2A. Comparison with the spectrum of I in Figure 2B indicates that the total spread of the nitroxyl lines in Figure 2A is smaller than in Figure 2B, which indicates weaker spin–spin interaction for II than for I. Also, the nitroxyl outer line at about 3300 G in the spectrum of I (Figure 2B) is absent from the spectrum of II (Figure 2A). The simulation of the spectrum in Figure 2A was obtained with $J = +12 \times 10^{-4}$ cm^{-1}, $r = 11.0$ Å, $\epsilon = 45°$, $A_1 = 90°$, and $A_2 = 0°$. The shape of the simulated spectrum was very sensitive to the value of r, the orientation of the z axis of the nitroxyl tensor, and the sign of J. A spectrum obtained on imbiber beads was similar to the one shown in Figure 2A, which indicates that the conformation in frozen solution was similar to the conformation on imbiber beads and presumably also similar to the conformation in fluid solution. When II was doped into $ZnTPP(THF)_2$, the values of J were between $+8 \times 10^{-4}$ and -12×10^{-4} cm^{-1} and the values of r were between 9.5 and 12.0 Å.[1] The positive values of J were observed for the conformations with the larger values of r. The values of r and J observed in frozen solution and on imbiber beads agree well with the extended conformations observed in the single crystal. This suggests that the steric constraints of the host had a significant impact on the conformations at some of the other sites in the crystal. The considerable variation in the values of J observed in the single crystal is also consistent with this conclusion. Thus data obtained in frozen solution and on imbiber beads may correspond more closely with solution conformations than data obtained from single crystals if the host exerts a significant steric influence.

EPR Spectra of III. The spectra of III in fluid solution were strongly dependent on solvent. In noncoordinating solvents the value of J was about 1000×10^{-4} (Table I). Since the g-value difference between the silver and nitroxyl electrons in fluid solution was relatively small, the simulated spectra at X-band and Q-band changed relatively slowly as J increased for values of J greater than about 500×10^{-4} cm^{-1}.[9] Thus, there is considerable uncertainty in these large values of J. In coordinating solvents the value of J decreased to about 100×10^{-4} cm^{-1}. It was proposed that coordination of the solvent to the silver caused a change in the conformation of the ortho substituent.[9] It was therefore of interest to determine whether the frozen-solution spectra could provide information con-

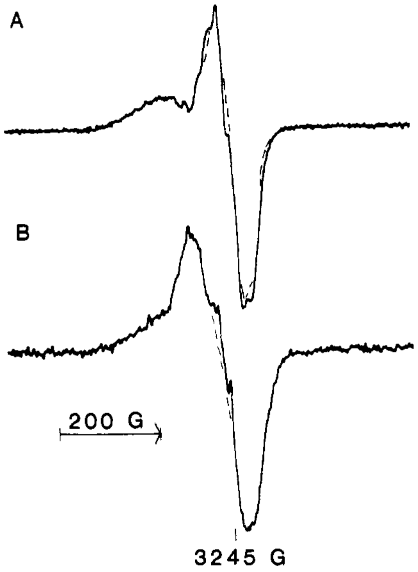

Figure 3. 800-G scans of the X-band EPR spectra of spin-labeled silver complex III at −180 °C obtained with 2-G modulation amplitude and 0.1-mW microwave power: (A) spectrum in 9:1 toluene–THF; (B) spectrum in 9:1 toluene–CH_2Cl_2. The dashed lines indicate regions in which the simulated spectra do not overlay the experimental curves.

cerning the conformational changes that accompanied the changes in the value of J. The spectra of III in frozen toluene–CH_2Cl_2 solution and frozen toluene–THF solution are shown in Figure 3, parts B and A, respectively. The spectrum in Figure 3A shows partially resolved spectral regions corresponding to silver transitions at lower field and nitroxyl transitions at higher field, analogous to the spectra in Figure 2. These features indicate relatively weak spin–spin interaction. By contrast the silver and nitroxyl transitions in the spectrum in Figure 3B overlap extensively as expected in the presence of relatively strong spin–spin interaction. The simulation of the spectrum in Figure 3A was obtained with $J = +40 \times 10^{-4}$, $r = 8.8$ Å, $\epsilon = 45°$, $A_1 = 170°$, and $A_2 = 75°$. As a result of the relatively short interspin distance and the small value of J, dipolar coupling dominated the spin–spin interaction and comparable simulated spectra were obtained with positive and negative values of J. The simulation of the spectrum in Figure 3B was obtained with $J = -500 \times 10^{-4}$ cm^{-1}, $r = 6.9$ Å, $\epsilon = 25°$, $A_1 = 120°$, and $A_2 = 85°$. Thus the large changes in J as a function of solvent occur in frozen solution as well as in fluid solution. Furthermore, the data from the frozen-solution spectra indicate that the change in J concides with a substantial change in the conformation of the molecule. A spectrum of III obtained on a sample of imbiber beads prepared from a CH_2Cl_2 solution was similar to that shown in Figure 3B. The agreement between the values of J in fluid solution and frozen solution and the similarity of the spectra obtained by the two methods of immobilization indicate that the immobilized spectra reflect the behavior of the complex in solution.

Comparison with Other Ortho-Substituted Porphyrins. Walker and Benson observed that the thermodynamic and electrochemical properties of a zinc tetraphenylporphyrin containing an amide substituent at the ortho position of one of the phenyl rings were anomalous relative to those of complexes containing similar substituents at the meta or para positions.[11] They proposed that the ortho substituent interacted with the porphyrin π system. An X-ray structure of the complex indicated that none of the atoms of the substituent were within unusually short distances of the π system.[12] However, a weak orbital interaction could not be ruled out.[12] Hambright and co-workers observed that the four isomers of a tetraphenylporphyrin with an amide substituent on the ortho position of each of the phenyl rings were less basic and had electrochemical properties different from those of analogous porphyrins with the same substituents at the meta or para positions.[13] They also proposed interaction between the ortho substituent and the π system. In a series of spin-labeled copper porphyrins including the copper analogue of III, we observed substantially larger values of J for the ortho-substituted porphyrins than for the meta- or para-substituted analogue.[14] The values of J for most of the ortho-substituted complexes were markedly smaller in coordinating solvents than in noncoordinating solvents. The possibility of a weak orbital overlap between the ortho substituent and the π system that was highly dependent on molecular conformation was proposed. The spectra of spin-labeled silver porphyrin III in frozen solution in the presence and absence of coordinating solvent indicate that the decrease in the value of J was accompanied by an increase in the interspin distance and changes in the angles that define the orientation of the interspin vector and the nitroxyl z axis. Such changes support the hypothesis that the strength of the metal–nitroxyl interaction for the ortho-substituted porphyrins depends on weak orbital interactions that are strongly dependent on molecular conformation. Thus, there appears to be a growing body of evidence based on several physical properties that, in some conformations, ortho substituents on tetraphenylporphyrins interact with the porphyrin π system via weak orbital overlap.

Conclusions

For complexes in which there is agreement between the values of J obtained from spectra in fluid solution and in an immobilized form, the values of r obtained from the immobilized spectra reflect the conformation in fluid solution. If the spectra in fluid solution are temperature dependent, the use of imbiber beads to immobilize samples can provide information on the conformations of molecules at room temperature. The application of these techniques to the spectra of spin-labeled porphyrin III indicates that the large changes in J that had been observed previously in fluid solution are due to substantial changes in the molecular geometry.

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