mations of VI and four conformations of VII. The interspin distances were between 11.5 and 13.5 Å for VI and between 9.3 and 10.2 Å for VII. The electron–electron spin–spin coupling constant J was negative for most of the conformations of VI and positive for most of the conformations of VII. There was no correlation between the values of r and J. The range of conformations accessible to the five-membered nitroxyl rings appears to have a greater impact on the value of the exchange coupling constant J than the range of conformations accessible to the six-membered nitroxyl rings.

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Metal–Nitroxyl Interactions. 37. Single-Crystal EPR Spectra of a Spin-Labeled Copper Complex Containing an Imine–Urea Linkage

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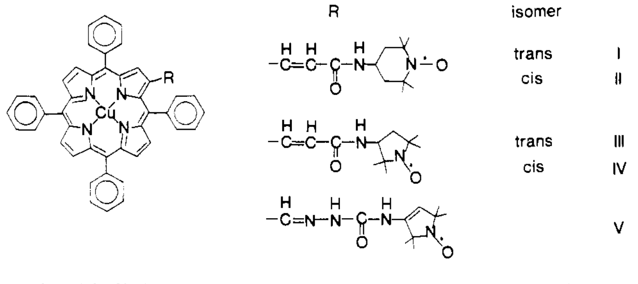
Single-crystal EPR spectra have been obtained for a spin-labeled copper complex containing an imine–urea linkage. Six conformations of the molecule were observed in the zinc tetraphenylporphyrin host. The dependence of the electron–electron spin–spin splittings on the orientation of the crystal in the magnetic field was analyzed to obtain the isotropic exchange and anisotropic dipolar contributions to the interaction. The interspin distance, r, ranged from 10.0 to 14.0 Å. Values of the exchange coupling constant, J, ranged from -81×10^{-4} to $+37 \times 10^{-4}$ cm^{-1}. There was no correlation between the values of r and J. Comparison of the values of r and J for this complex with values obtained previously for spin-labeled copper complexes containing cis and trans acrylamide linkages indicated that isomers with cis and trans conformations of the imine linkage were present in the crystal.

Introduction

In a recent series of reports we have shown that detailed information concerning molecular geometry and electron–electron spin–spin coupling constants can be obtained from the analysis of frozen-solution and single-crystal EPR spectra of spin-labeled transition-metal complexes.[1-5] Substantial differences in the values of the electron–electron spin–spin coupling constants and interspin distances were observed for the cis and trans isomers of complexes I–IV, which have an acrylamide linkage between a metalloporphyrin and a nitroxyl ring.[2,5] In fluid solution a single species was observed in the EPR spectra of V. The lines remained sharp at temperatures as low as –60 °C, which indicated that any dynamic processes occurring in solution that interconverted species with different values of the exchange coupling constant J must have activation energies less than about 8 kcal/mol.[6] The values of J were strongly solvent dependent. It was therefore of interest to determine the conformation of V that was present in solution. We have examined the single-crystal EPR spectra of V doped into a single crystal of zinc tetraphenylporphyrin in order to compare the spin–spin interaction parameters observed for the conformations in the crystal with the values of J observed in fluid solution.



Experimental Section

Compound V was prepared as reported in ref 6. The imine linkage in V is hydrolytically unstable, so the single crystal of zinc tetraphenylporphyrin doped with V was grown in a Kewaunee glovebox under a nitrogen atmosphere. Other aspects of the single-crystal preparation, mounting of the crystal, and data collection were performed as reported in ref 2–4. The angle between the z' axis used for data collection and the z axis of the copper **g** and **a** tensors (α in Figure 1A) was less than 3°, so it was assumed that $x = x'$, $y = y'$, and $z = z'$.

Analysis of EPR Spectra. The analysis of the single-crystal EPR spectra of spin-labeled metal complexes has been discussed previously.[2-5] The electron–electron spin–spin coupling splits each hyperfine component for both of the electrons into an AB doublet. Since there is less nuclear hyperfine splitting of the nitroxyl lines than of the copper lines, it is easier to identify the AB doublets for the nitroxyl lines than for the copper lines, so the initial estimates of the orientation and spin–spin interaction parameters were obtained from the nitroxyl lines. The orientation dependence of the spin–spin splitting of the nitroxyl lines was analyzed with the computer program ROTAN.[2] The adjustable parameters are the isotropic exchange coupling constant J, the interspin distance r, and the orientation of the interspin vector, which is defined by the angles ϵ and η. The values of the spin–spin interaction parameters were then used to simulate the complete experimental spectra. The simulations indicated that the parameters obtained from the nitroxyl lines were in good agreement with the spectra of the copper lines.

In the crystal of ZnTPP doped with V six distinguishable species were characterized. At some orientations of the crystal additional weak lines were observed, which were not assigned. It is likely that these lines are due to additional species with lower populations or

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Table I. g and A Values for the Copper[a,b] and Nitroxyl Electrons[c]

electron	species	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
copper	1-6	2.048	2.048	2.200	24	24	196
nitroxyl	1	2.0084	2.0061	2.0029	7	7	28
nitroxyl	2	2.0089	2.0066	2.0034	7	7	28
nitroxyl	3	2.0085	2.0063	2.0028	7	7	25.5
nitroxyl	4	2.0084	2.0061	2.0026	8	8	28
nitroxyl	5	2.0087	2.0063	2.0032	7.5	7.5	26
nitroxyl	6	2.0085	2.0066	2.0030	10	10	26

[a] The principal values of the porphyrin nitrogen hyperfine coupling tensor were $A_{xx} = 14.6 \times 10^{-4}$, $A_{yy} = 14.6 \times 10^{-4}$, and $A_{zz} = 17.4 \times 10^{-4}$ cm^{-1}. [b] Values are for ^{63}Cu. Both ^{63}Cu and ^{65}Cu were included in the simulations. [c] A values are given in units of 10^{-4} cm^{-1}.

Table II. Orientation and Interaction Parameters[a]

species	A_1	A_2	ϵ	η	r[b]	J[c]	$d_{\parallel}$[c]	population, %
1	10	45	83	−45	14	−68	−15	14
2	10	45	83	−40	14	−81	−15	14
3	152	−20	128	−40	10.5	37	−36	14
4	60	130	115	20	11	0	−32	30
5	150	−20	130	50	10	22	−42	14
6	160	45	55	50	10.5	−48	−36	14

[a] Angles are defined in Figure 1 and are in units of degrees. [b] In angstroms. [c] In units of 10^{-4} cm^{-1}.

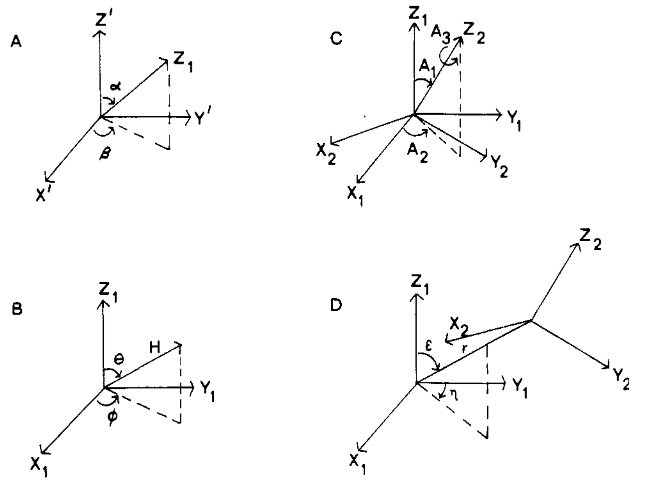


Figure 1. Definitions of the orientation relationships: (A) angles α and β, defining the orientation of the copper z axis relative to the primed axes used for data collection; (B) angles θ and ϕ, defining the orientation of the magnetic field relative to the axes of the copper electron; (C) angles A_1, A_2, and A_3, defining the orientation of the nitroxyl axes relative to the copper axes; (D) angles ϵ and η, defining the orientation of the interspin vector r relative to the copper axes. Throughout the text r is used to denote the magnitude of the interspin vector.

broader lines, but the lines for these species were not resolved at enough orientations to adequately define them. A broad underlying signal was observed in all of the spectra. Similar signals have been seen in the crystals of I–IV, and possible explanations have been discussed.[4]

Since the two triplets comprising the nitroxyl doublet for a particular species must have the same nitroxyl nitrogen hyperfine splitting, the differences in the hyperfine splittings for the various species at a particular orientation of the crystal (due to the differences in the orientations of the nitroxyl z axes) were useful in assigning the lines. The signals from the six species were distinguished as follows. Species 1 and 2 had the largest values of J, so the spin–spin splittings were larger than for the other species at most orientations of the crystal. The interspin vector was oriented similarly for the two species, but the value of J for species 2 was sufficiently greater than for species 1 that the lines for the two species were resolved. The lines for species 1 were sharper than for species 2. The lines for both species were broader than for the other species so only the lowest and highest field lines were resolved. The preliminary analysis of the orientation of the nitroxyl z axes for these two species was based on the changes in the g value. The value of J for species 3 was smaller than for species 1 and 2, the nitroxyl z axis was in a different quadrant, and the interspin vector was oriented differently. Species 4 had the highest population, and its lines dominated the spectra at many orientations of the crystal. The nitroxyl z axis for species 4 was 60° away from the copper z axis whereas the nitroxyl z axes for the other species were near the copper z axis so the nitrogen hyperfine splitting for species 4 was substantially different than the splittings for the other species at most orientations of the crystal. The nitroxyl z axis for species 5 was oriented similarly to that of species 3, but the value of J was smaller and the interspin vector was oriented differently. The orientations of the nitroxyl z axis and of the interspin vector for species 6 were different than for the other species.

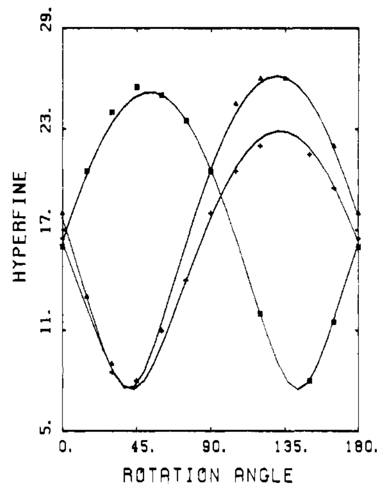


Figure 2. Plots of the orientation dependence of the nitroxyl nitrogen hyperfine splitting in gauss in three orthogonal planes for species 4 of complex V doped into ZnTPP. The experimental data are denoted by the following symbols: (▲) xy plane; (*) xz plane; (+) yz plane. The solid lines are the calculated curves.

The g values and nuclear hyperfine coupling constants obtained from the simulations of the spectra are given in Table I. The parameters obtained for the copper electron are in good agreement with those obtained for the copper electron in I–IV.[2,5] The parameters obtained for the nitroxyl electron are similar to those obtained for the nitroxyl electrons in I–IV.[2,5] An example of the agreement between the observed and calculated orientation dependence of the nitroxyl nitrogen hyperfine splitting is shown in Figure 2.

The angles that define the relative orientations of the axes of the copper and nitroxyl tensors, the dipolar tensor, and the magnetic field direction are shown in Figure 1. The values obtained for these angles and for the spin–spin interaction parameters are ~~given in Table II.~~ The dipolar splittings calculated for the orientation of the crystal at which the magnetic field is parallel to the interspin vector ($d_{\parallel}$) are

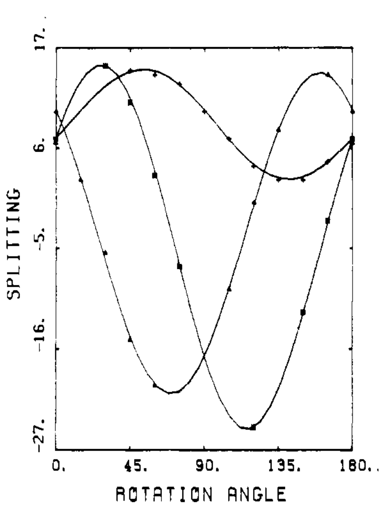


Figure 3. Plots of the orientation dependence of the spin-spin splitting in gauss in three orthogonal planes for species 4 of complex V doped into ZnTPP. The experimental data are denoted by the following symbols: (▲) *xy* plane; (*) *xz* plane; (+) *yz* plane. The solid lines are the calculated curves.

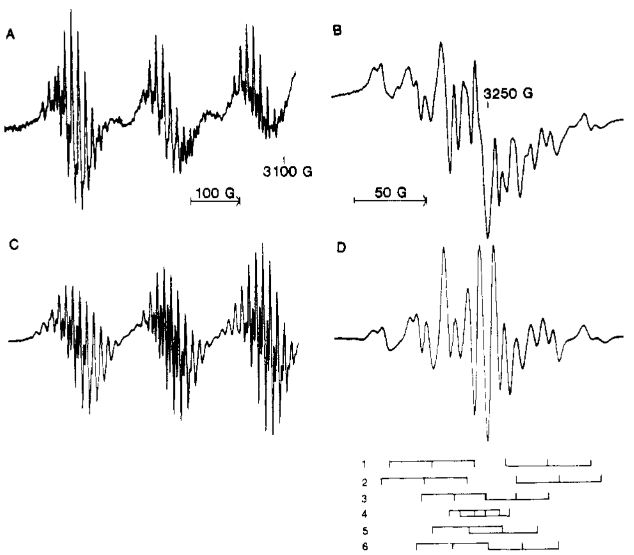


Figure 4. X-Band (9.106-GHz) EPR spectra of complex V doped into ZnTPP obtained at $\theta = 0°$: (A) 600-G scan of the copper lines; (B) 200-G scan of the high-field portion of the spectrum; (C, D) corresponding calculated spectra. The spectra were obtained with 2-G modulation amplitude and 5-mW microwave power. The overall amplification for part A is 5 times that for part B.

also included in Table II. The uncertainties in the parameters are as follows: angles, ±5°; r, ±0.5 Å; J, $\pm 2 \times 10^{-4}$ cm^{-1}. An example of the agreement between the observed and calculated orientation dependence of the spin-spin splitting is shown in Figure 3.

Due to the extensive overlap of the lines in the spectra it was difficult to determine the line widths accurately. Some of the line width variations that can lead to discrepancies between the observed and calculated spectra have been discussed previously.[2-4] Species 1 and 2 had nitroxyl line widths between 5 and 14 G, species 3, 5, and 6 had nitroxyl line widths between 4 and 10 G, and species 4 had the sharpest nitroxyl lines with line widths between 3 and 6 G. The line widths for the copper lines were between 5 and 15 G for species 1-3, 5, and 6 and between 2.5 and 8 G for species 4.

Results and Discussion

Figure 4 shows the EPR spectra of V obtained at $\theta = 0°$. Since the magnetic field is along the copper z axis, the copper g value is equal to g_{zz} and the copper A value is equal to A_{zz}. At this orientation 17 nitroxyl lines were clearly resolved. The zero crossing points calculated for the nitroxyl lines of each of the six species are marked below the simulated spectrum. The nitroxyl nitrogen hyperfine splittings for species 1 and 2 were 29 G, and the spin-spin splittings were 80 and 93 G, respectively. Only the lowest and highest field lines were resolved for these species. The nitroxyl nitrogen hyperfine splitting for species 3 was 22 G, and the spin-spin splitting was 43 G. Its spectrum was an apparent five-line pattern of which the lowest field and two highest field lines were clearly resolved. The other two lines were obscured by the more intense lines from species 4. The nitroxyl nitrogen hyperfine splitting for species 4 was 17 G, and the spin-spin splitting was 6 G, which gave a six-line pattern that was well resolved and dominated the center of the spectrum. The nitroxyl nitrogen hyperfine splitting and the spin-spin splitting for species 5 were both about 24 G, so its spectrum was an apparent four-line pattern. Only the lowest and highest field lines were resolved for this species. For species 6 the nitroxyl nitrogen hyperfine splitting was 24 G and the spin-spin splitting was 48 G. Only the lowest and highest field lines were resolved.

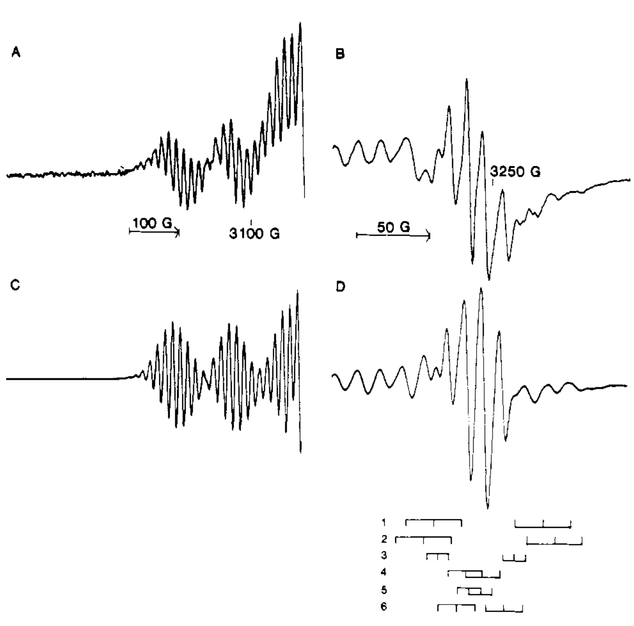


Figure 5. X-Band (9.106-GHz) EPR spectra of complex V doped into ZnTPP obtained at $\theta = 60°$ and $\phi = 0°$: (A) 600-G scan of the copper lines; (B) 200-G scan of the high-field portion of the spectrum; (C, D) corresponding calculated spectra. The spectra were obtained with 2-G modulation amplitude and 5-mW microwave power. There is a 55-G overlap of the spectra in parts A and B. The overall amplification for part A is 4 times that for part B.

Figure 5 shows the spectra of V obtained at $\theta = 60°$ and $\eta = 0°$. The copper g value was 2.087, and the copper hyperfine splitting was 103 G. The zero crossing points calculated for the nitroxyl lines for each of the species are marked below the calculated spectrum. The dominant four-line pattern in the center of the spectrum is due to species 4, which has a nitroxyl nitrogen hyperfine splitting of 11.5 G and a spin-spin splitting of 12 G. There is substantial overlap of the low-field and high-field signals from the other species, and their lines are poorly resolved. Part of the copper spectrum is shown in the low-field portion of Figure 5B at the same scale as the nitroxyl lines. The relative intensities of the copper and nitroxyl lines were well matched by the simulated spectrum. This agreement could not be obtained if the contributions from all the species were not included.

In the crystals of ZnTPP doped with I-IV multiple species were observed, which had different values of the orientation parameters ϵ and η as well as of the spin-spin interaction parameters. These species were attributed to spin-labeled metalloporphyrins that had the spin-labeled side chain attached to different pyrrole carbons.[2,5] The values of η obtained for the six species of V were −45, −40, −40, 20, 50, and 50°. These

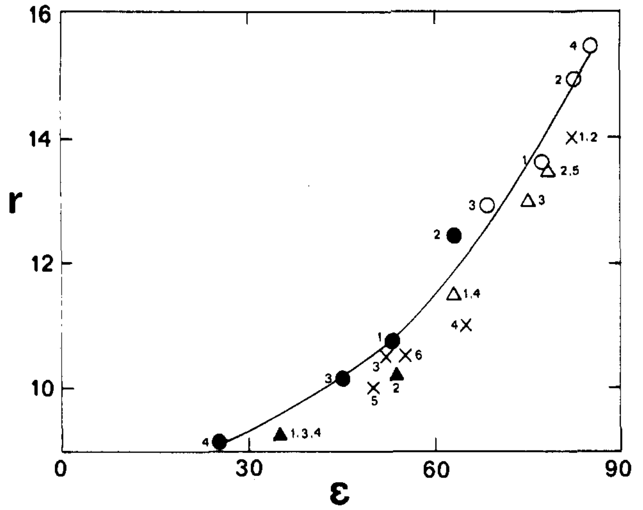
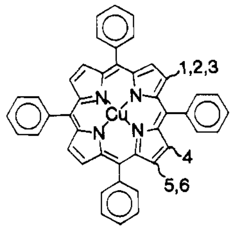


Figure 6. Plots of the values of r and ϵ for spin-labeled complexes I (○), II (●), III (△), IV (▲), and V (×). Each data point is labeled with the number of the species to which it corresponds. The solid line connects the points for complexes I and II.

six species can be considered to be attached to three pyrrole carbons as sketched in VI. We have arbitrarily kept the values of η between ±90°. However, the Hamiltonian is invariant to inversion, so the orientation $\epsilon = 115°$ and $\eta = 20°$ is indistinguishable from $\epsilon = 65°$ and $\eta = -160°$. The values of η and A_2 are relative to the arbitrary x and y axes used in the data collection since there is no molecular basis for a definition of x and y. Species 1, 2, and 3 have approximately the same values of η, but ϵ is less than 90° for species 1 and 2 and greater than 90° for species 3. Thus species 1 and 2 must have the spin-labeled side chain on the opposite side of the porphyrin plane from the side chain in species 3 or the side chains could be located at the inversion-related locations. There is a similar relationship between the locations of the side chains for species 5 and 6.



VI

The values of r ranged from 10.0 to 14.0 Å, and in view of the inversion symmetry the values of ϵ can be viewed as ranging from 50 to 83°. The values of r are plotted as a function of ϵ in Figure 6 along with the corresponding values for I–IV. There is a consistent correlation between the two parameters.[2,5] This has been attributed to a similarity of conformations for the series of complexes with the values of both ϵ and r increasing as the side chain was forced toward the porphyrin plane by the steric constraints of the single-crystal host. The average value of r for trans isomers I and III was greater than the average value for cis isomers II and IV although there is a region of overlap for the two sets (cf. Figure 6). The additional atom in the linkage between the porphyrin and the nitroxyl for V than for I–IV should cause an increase in the interspin distance, so it is reasonable that the corresponding curve for V would be offset from the curve for I–IV. The values of r for species 1 and 2 clearly fall in the range expected for a trans isomer. The assignments for species 3–6 are more ambiguous if only the values of r and ϵ are considered, but the correlations in Figure 6 indicate that they are more likely to be cis than trans.

For complexes I–IV the values of J for the trans isomers were negative and larger in magnitude than the values of J for the cis isomers, which were positive. The values of J for species 1 and 2 of complex V were large and negative, which is consistent with the conclusion above that these two species are trans isomers. The values of J for species 3–5 are smaller than for species 1 and 2 and have positive signs, which is consistent with assignments as cis isomers. The large negative value of J for species 6 suggests a trans conformation despite the relatively short r. Inspection of CPK molecular models indicated that the values of r for species 1 and 2 (14 Å) were consistent only with an all-trans conformation of the imine–urea linkage but the values of r for species 3–6 (10–11 Å) were consistent with either an all-trans conformation or one containing a single cis linkage and the remainder trans. Thus the single-crystal results indicate the presence of both cis and trans isomers with approximately equal populations.

A neutron diffraction study of urea showed that the molecule, including the hydrogens, was planar.[7] X-ray crystallographic studies of monosubstituted ureas[8,9] and N,N′-disubstituted ureas[10–12] have shown that the urea linkage is planar and has a trans,trans conformation. NMR,[12] IR,[13,14] and dielectric constant[15] measurements indicate that the trans,trans conformation is retained in solution. Thus it seems likely that the urea linkage in V is trans,trans both in solution and in the single crystal. The most likely bond to exhibit cis–trans isomerism is the imine C=N. The activation energy for rotation around C=N bonds is generally lower than for rotation around C=C bonds, but the values usually are in the range of 10–20 kcal/mol.[16] Rotational barriers of this magnitude are low enough that physical separation of isomers at 25 °C would be unlikely but high enough that interconversion would be expected to be slow on the EPR time scale. Due to the hydrolytic instability of complex V little effort was made to separate isomers, and there was no indication during its purification of a tendency to separate into two components. The solution EPR spectra showed a single component with relatively sharp lines over the temperature interval of −60 to +30 °C.[6] The value of J was strongly solvent dependent. As the ratio of chloroform to pyridine was varied at room temperature, the value of J increased continuously from 13×10^{-4} cm^{-1} in chloroform solution to 35×10^{-4} cm^{-1} in pyridine solution.[6] Intermediate values of J were observed in toluene and tetrahydrofuran solution. The magnitudes of these values are similar to those observed for the cis isomer in the single crystal and substantially smaller than the values observed for the trans isomer.

For the cis and trans isomers I and II the values of J observed in fluid solution were similar to the values observed in the zinc tetraphenylporphyrin single crystal.[2] The range of values of J observed for III and IV in the same host was larger than had been observed for I and II, and the values were larger than had been observed in fluid solution.[5] These differences may be due to the variety of conformations that are accessible to the saturated five-membered nitroxyl ring in III and IV. It is likely that the variations in the conformations of the

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unsaturated five-membered nitroxyl ring in V will be smaller than for the saturated ring. In four X-ray crystallographic studies of this nitroxyl ring, the ring was found to be planar.[17-20] Thus the comparison of results in fluid solution and in the single crystal may be more reliable for molecules containing the unsaturated nitroxyl than for molecules containing the saturated nitroxyl. If this is true, then the results obtained for V in the single crystal indicate that the species present in fluid solution is the cis isomer. One can speculate that steric effects in the crystal increase the relative stability of the trans isomer. In the single crystal the values of J for the cis isomer ranged from zero to 37×10^{-4} cm^{-1}. These differences are presumably due to small differences in the overall conformation of the spin-labeled side chain. The strong solvent dependence of the value of J for V in fluid solution may indicate that different solvents stabilize slightly different conformations of the side chain.

Conclusions

Single-crystal EPR spectra of V doped into zinc tetraphenylporphyrin indicated the presence of six conformations of the molecule. The interspin distances were in the range 10.0–14.0 Å, and the electron–electron spin–spin coupling constant ranged from -81×10^{-4} to $+37 \times 10^{-4}$ cm^{-1}. A comparison of the values of r and J with those obtained previously for similar molecules suggested that three of the conformations had a cis-imine linkage and three had a trans-imine linkage. Comparison of the values of J obtained in the single crystal with values obtained in fluid solution suggested that the isomer present in fluid solution may have a cis-imine linkage.

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Proton Transfer and Nucleophilic Displacement Reactions of Copper(II) *N*,*N'*-Diglycylethylenediaminate

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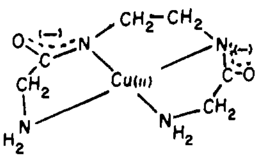
The reaction of $CuH_{-2}DGEN$ with TRIEN and EDTA proceeds through nucleophilic and proton-transfer-limited pathways. The rate constant with trien (650 M^{-1} s^{-1}) is more than 4 orders of magnitude less than that observed for the analogous triglycine complex, but the reaction with H_3O^+ ($k = 1.6 \times 10^7$ M^{-1} s^{-1}) is similar to that observed for other copper polypeptide complexes.

Introduction

Copper(II) reacts with *N*,*N'*-diglycylethylenediamine in basic solution to form a neutral complex in which the two amide protons are ionized.[1] The mode of coordination of the ligand to copper is through the two terminal amine groups and the two deprotonated amide nitrogens. The deprotonated complex is designated as $CuH_{-2}DGEN$ (structure I). Deprotonation is virtually complete above pH 9.



I

The displacement of short-chain polypeptide complexes from nickel(II) and copper(II) by multidentate ligands such as triethylenetetramine (TRIEN) and ethylenediaminetetraacetate (EDTA) proceeds through a number of parallel paths. These can be dissociative,[2,3] proton-transfer limited,[2-5] proton-transfer assisted,[5-9] and nucleophilic.[8,10,11]

The kinetics and mechanism for the reactions of $CuH_{-2}DGEN$ with TRIEN and EDTA have been investigated in this study. The reactions exhibit several parallel paths, which include dissociative, general-acid catalytic, and nucleophilic routes.

Experimental Section

Diglycylethylenediamine was synthesized by the method of Gill and Cottrell.[12] The melting point of the dihydrochloride salt was 246 °C. A stock copper solution, 0.0975 M, was prepared from twice recrystallized $Cu(ClO_4)_2$ and standardized by EDTA titration. Ionic strength was maintained at 0.10 M with $NaClO_4$. Sodium borate and Tris were used to maintain constant pH. pH values were converted to hydrogen ion concentration with the extended Debye–Hückel relationship.

Solutions of $CuH_{-2}DGEN$ were prepared by dissolving an analytically weighed portion of DGEN in double-distilled water followed

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