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Metal–Nitroxyl Interactions. 9. Electron–Electron Coupling in the Copper Complex (3-(*N*-(2,2,5,5-Tetramethylpyrrolin-3-yl-1-oxy)amido)-4,10-dimethyl-5,9-diazatrideca-4,9-diene-2,12-dione)copper(II)

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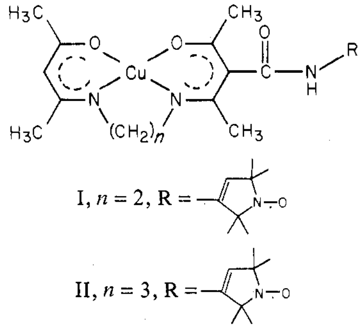
Resolved electron–electron coupling is observed in the room temperature solution EPR spectra of the spin labeled copper complex (3-(*N*-(2,2,5,5-tetramethylpyrrolin-3-yl-1-oxy)amido)-4,10-dimethyl-5,9-diazatrideca-4,9-diene-2,12-dione)copper(II), with values of the coupling constant ranging from 300 G in toluene solution to 415 G in pyridine solution. In most solvents an isomeric form of the complex is also observed which has a value of the electron–electron coupling constant of ~2500 G. The fraction of the complex existing in the isomeric form varies from <5% in Me_2SO solution to ~95% in toluene solution.

Introduction

The interaction of nitroxyl radicals with paramagnetic metal ions provides a means to study interactions between nonequivalent unpaired electrons. The results of metal–nitroxyl interaction studies are pertinent to a wide variety of nitroxyl spin label and spin probe investigations.[1a]

We are investigating a wide range of complexes containing both a paramagnetic metal and a nitroxyl free radical. Among our recent demonstrations of resolved electron–electron spin–spin splitting in electron paramagnetic resonance (EPR) spectra we reported compound I.[1b] In this paper we report the synthesis and EPR spectra of II, in which the ethylene bridge of I has been replaced by a trimethylene bridge yielding a unique opportunity to observe metal electron–nitroxyl electron coupling for two isomers of a compound.



III, $n = 3$, R = Ph

Experimental Section

Physical Measurements. All spectra were obtained in dry purified solvents using freshly prepared solutions. Infrared spectra were recorded in solution or in Nujol mulls on a Perkin-Elmer 337 grating spectrometer or on a Digilab FTS-IR10 Fourier transform spectrometer. Visible spectra were obtained in toluene, CH_2Cl_2, THF, and pyridine solutions on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ϵ in parentheses. Magnetic susceptibilities were measured on a Bruker Faraday balance with 1 μg sensitivity using $HgCo(SCN)_4$[2] and $[Ni(en)_3]S_2O_3$[3] as calibrants. Values of μ_{eff} in Bohr magnetons are given below along with the diamagnetic correction[4a] (χ_{dia}) used in the calculations. A temperature-independent paramagnetism (TIP) of 60×10^{-6} was assumed for copper(II).[1b,5] EPR spectra were run on a Varian E-9 spectrometer as previously described. Spectra were obtained on 1.5×10^{-3} to 1.0×10^{-2} M solutions at power levels well below saturation and modulation amplitudes which did not cause line broadening. The relatively high concentrations were necessary to obtain reasonable signal to noise levels for the "outer" lines in the spectra of the spin-coupled systems (see below). The high concentrations did not appear to have any effect on the line shapes of the "center" lines or on the positions of the "outer" lines. All coupling constants are given in Gauss (1 G = 0.1 mT).

Table I. EPR Parameters for Copper Complex, III

solvent	g_{iso}[a]	$\langle a\rangle_{Cu}$,[b] G	$\langle a\rangle_N$,[c] G	A[d]	B[d]	C[d]
CH_2Cl_2	2.1025	77.8	13.6	19.6	6.2	1.2
toluene	2.1029	77.5	13.5	21.9	7.6	1.5
1:1 THF–CH_2Cl_2	2.1030	76.5	13.6	18.8	7.0	1.2
THF	2.1039	75.5	13.5	20.5	7.1	1.4
Me_2SO	2.1045	75.5	13.3	32.2	21.2	3.7
pyridine	2.1083	70.7	13.5	24.0	12.3	2.4

[a] Relative to DDPH (2.0036). Uncertainty ±0.0007. [b] Uncertainty ±0.2. Value given is for ^{63}Cu. Value for ^{65}Cu is 1.07× the value given. [c] Uncertainty ±0.1. [d] A, B, and C are line-width parameters; see text. Values given are for 100% Lorentzian lines.

Preparation of Compounds. (3-(*N*-(2,2,5,5-Tetramethylpyrrolin-3-yl-1-oxy)amido)-4,10-dimethyl-5,9-diazatrideca-4,9-diene-2,12-dione)copper(II), II. The compound was prepared by a method analogous to that reported for I[1b,7] except that trimethylenediamine was used and the reaction time was decreased to 1.5 h; yield 44%. IR: (Nujol mull) ν_{NH} 3400 (broad), $\nu_{CO(amide)}$ 1650 (weak), ν_{CO} and ν_{CN} multiple poorly resolved bands between 1500 and 1600 cm^{-1}; (CH_2Cl_2 solution) ν_{NH} 3400, $\nu_{CO(amide)}$ 1675, ν_{CO} 1560, ν_{CN} 1510 cm^{-1}; (toluene solution) ν_{NH} 3400 cm^{-1} (weak), carbonyl region obscured by solvent. $\mu_{eff} = 2.44\ \mu_B$ (measured at 27 °C, $\chi_{dia} = -265 \times 10^{-6}$). Visible spectrum: (toluene solution) 605 (1.88), 310 (4.49); (CH_2Cl_2 solution) 590 (1.92), 304 (4.43), 240 (4.32); (THF solution) 605 (1.94), 304 (4.34), 237 (4.27); (pyridine solution) 606 (2.00). Anal. Calcd for $C_{22}H_{33}N_4O_4Cu$: C, 54.93; H, 6.91; N, 11.65. Found: C, 55.10; H, 7.04; N, 11.53.

(3-(*N*-Phenylamido)-4,10-dimethyl-5,9-diazatrideca-4,9-diene-2,12-dione)copper(II), III. The compound was prepared by the method used for II except that phenyl isocyanate was used instead of 3-isocyanato-2,2,5,5-tetramethylpyrrolinyl-1-oxy; yield 48%. IR: (Nujol mull) ν_{NH} 3265, $\nu_{CO(amide)}$ 1660, ν_{CO} 1580, ν_{CN} 1510 cm^{-1}; (CH_2Cl_2 solution) ν_{NH} 3400, $\nu_{CO(amide)}$ 1660, ν_{CO} 1560; ν_{CN} 1510; (toluene solution) ν_{NH} 3400 cm^{-1} (broad) carbonyl region obscured by solvent. $\mu_{eff} = 1.75\ \mu_B$ (measured at 27 °C, $\chi_{dia} = -220 \times 10^{-6}$). Visible spectrum: (toluene solution) 605 (2.03), 310 (4.46); (CH_2Cl_2 solution) 590 (2.03), 311 (4.42), 245 (4.42); (THF solution) 605 (2.03), 312 (4.42), 246 (4.46); (pyridine solution) 608 (2.04). Anal. Calcd for $C_{20}H_{25}N_3O_3Cu$: C, 57.33; H, 6.02; N, 10.03. Found: C, 57.42; H, 6.08; N, 9.97.

Computer Simulations. The EPR spectra of compounds II and III were simulated using the computer program CUNO, which has been described in detail.[8] Both ^{63}Cu and ^{65}Cu were included in all calculations. The simulations of the EPR spectra of III provided values of the copper hyperfine coupling constant, $\langle a\rangle_{Cu}$, the nitrogen hyperfine coupling constant, $\langle a\rangle_N$, and the g value of the copper electron as summarized in Table I. Line widths were assumed to vary with copper nuclear spin as $A + Bm_I + Cm_I^2$.[9] The coupling constants and g values obtained for III and the values of these parameters for free nitroxyl

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radicals ($g = 2.0059$, $\langle a \rangle_N' = 14.2 \pm 0.2$ depending on solvent) were used as the initial values in the simulations of the EPR spectra of II. The spectra of II were simulated as mixtures of two species with values of the electron–electron coupling constant, J, 300–415 G (J_1) for one species and 2350–2650 G (J_2) for the second species. The "outer" lines of the AB pattern[8] with J_1 were observed in all solvents though with varying relative intensities. Both the high-field and low-field "outer" lines of the AB pattern with J_2 were observed in toluene solution and the high-field lines were also observed in CH_2Cl_2 and 1:1 THF–CH_2Cl_2. The dielectric loss of the solvents and lower population of this isomer prevented detection of the outer lines with J_2 in the other solvents, though the line shape of the center lines clearly indicated the presence of the second isomer as discussed below.

Results and Discussion

The spin-labeled copper complex, II, was prepared by the reaction of 3-isocyanato-2,2,5,5-tetramethylpyrrolinyl-1-oxy with Cu(batm) analogous to the preparation of I.[1b] The IR spectrum in CH_2Cl_2 solution includes CO and NH stretches characteristic of substituted amides. Complex II and its analogue with a diamagnetic ligand, III, are stable in the solid phase when stored in a desiccator but decompose slowly in solution.

Magnetic Susceptibility. The solid-state magnetic moment of the copper complex with a diamagnetic ligand, III, is 1.75 μ_B which is reasonable for a copper complex with a small orbital contribution.[4b] The solid-state magnetic moment for the spin-labeled complex, II, is 2.44 μ_B which agrees well with the values reported for I[1b] and for spin-labeled copper salicylaldimines.[6] Since a spin-only value of $2^{1/2} \times 1.73 = 2.44$ μ_B would be expected for two independent unpaired electrons, assuming no orbital contribution, the magnetic susceptibility of the spin-labeled copper complex is consistent with a very small ($<kT$) interaction between the copper and nitroxyl electrons in the solid phase. Detailed interpretation of the solid-state susceptibilities must await variable-temperature data.

Electronic Spectra. The electronic spectra of the spin labeled complex, II, and of its analogue with a diamagnetic ligand, III, have essentially identical λ_{max} in a series of solvents suggesting that the electronic structure of the copper complexes is not strongly perturbed by the presence of the spin label. The spectra in the visible region are also in good agreement with the reported values for unsubstituted Cu(batm).[10] However, the d–d band in II is generally broader than in III resulting in a slightly lower value of ϵ. The broadening may reflect the presence of the second species which is observed in the EPR spectra.

The electronic spectra of II and III are quite insensitive to solvent. The energy of the d–d transition is essentially identical in toluene, THF, and pyridine solution, though in CH_2Cl_2 the transition occurs at slightly higher energy.

EPR Spectra. The EPR spectra of the copper complex with a diamagnetic ligand, III, exhibit the typical four-line pattern expected for electron coupling to the copper nucleus ($I = {}^3/_2$). Nitrogen superhyperfine coupling is partially resolved on the high-field ($m_I = -{}^3/_2$) peak. Line width and coupling parameters obtained from the computer simulations of the spectra of III in various solvents are given in Table I. Coupling to other nuclei in the molecule may be present but is not resolved in the spectra, so it is treated only as line broadening in the simulations. As has been done successfully in previous studies of spin-labeled copper complexes,[1,6] it was assumed that similar values of g, $\langle a \rangle_{Cu}$, and $\langle a \rangle_N$ to those found for III would be expected for the spin-labeled complex, II, in the absence of electron–electron coupling.

The influence of solvent on the EPR spectra is clearly indicated by the data in Table I. As the donor strength of the solvent increases, the value of $\langle a \rangle_{Cu}$ decreases and the g value increases. These changes in $\langle a \rangle_{Cu}$ and g are consistent with previous observations on EPR spectra of copper complexes that A decreases and g increases as the strength of the interaction with axial ligands increases.[11,12]

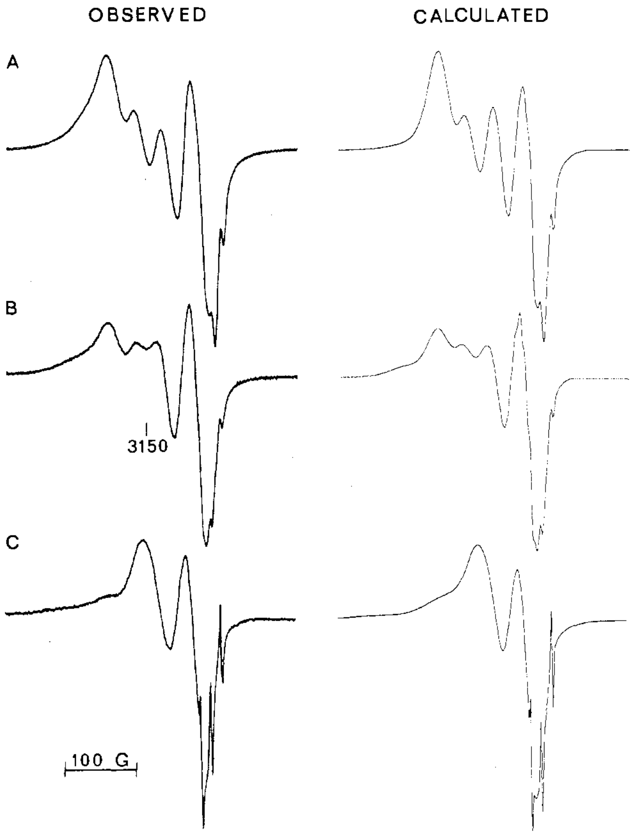


Figure 1. X-Band EPR spectra of the spin-labeled copper complex II and computer simulations (400 G scans, 125 G/min scan rate): (A) toluene solution; (B) THF solution; (C) Me_2SO solution.

Examination of the EPR spectra of the spin-labeled complex, II, indicates that the spectra are markedly different from those of the analogous complex with a diamagnetic ligand, III. The portion of the EPR spectrum of II occurring near 3150 G is shown in Figure 1 for three solvents. There are two notable features: (1) none of the patterns resemble the usual four-line copper spectra and (2) the appearance of the spectrum is solvent dependent. When the spectrometer gain and modulation amplitude are increased to give an amplification ~100 times greater than that used to record the central portion of the spectrum, weak outer lines are observed at ~2750 and ~3500 G as indicated in Figure 2. The positions of these "outer" lines are consistent with an electron–electron coupling constant, J_1, of ~350 G which is solvent dependent. If, however, very high power levels, gains, and modulation amplitudes are utilized and the spectrum is time averaged, extremely weak lines can be observed at ~5800 G in toluene, CH_2Cl_2, and 1:1 THF–CH_2Cl_2 solutions as indicated in Figure 3. Under the same conditions a signal at ~500 G was observed in toluene solution. These additional lines are characteristic of an additional species with an electron–electron coupling constant of ~2500 G (J_2). The very low intensities of these lines made it impossible to detect them in solvents with higher dielectric loss.

The spectra of both species were interpreted as ABMX spin coupled systems and simulated using the computer program CUNO,[8] as shown in Figures 1–3. A low-intensity, sharp three-line pattern observed on the high-field side of the signals near 3150 G in Figures 1–3 is due to a small amount of a free nitroxyl (1–2%). In toluene solution (Figure 1A) the complex is almost completely in the form of the isomer with the large coupling constant, and the signals at 3150 G appear to be a

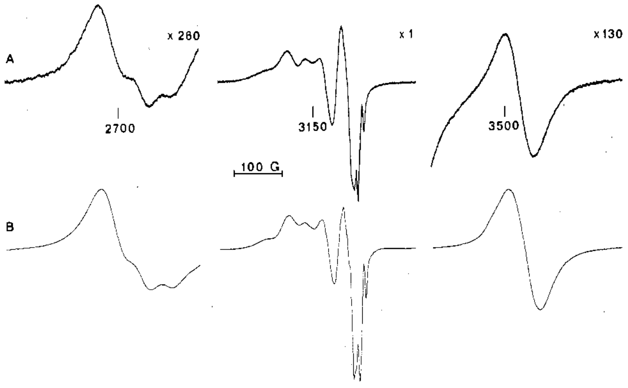


Figure 2. X-Band EPR spectra of the spin-labeled copper complex II in 1:1 THF–CH_2Cl_2 solution and computer simulations: (A) observed spectra (400 G scans, 125 G/min scan rate, 30 mW; center lines, 0.125 G modulation amplitude; outer lines, product of gain and modulation amplitude 260× and 130× greater for low-field and high-field lines, respectively, than for center lines); (B) computer simulations as described in text.

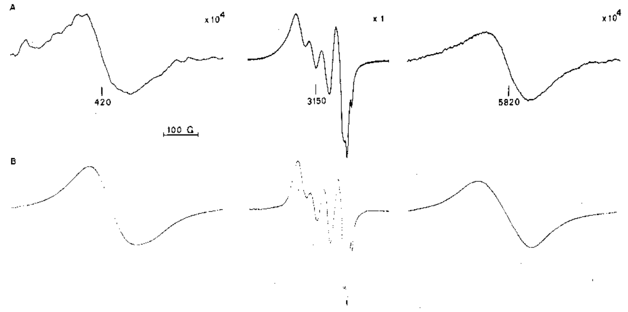


Figure 3. X-Band EPR spectra of the spin-labeled copper complex II in toluene solution and computer simulations: (A) observed spectra (center lines, 400 G scan, 125 G/min rate, 10 mW, 0.10 G modulation amplitude; outer lines, time-averaged spectra of 25 scans, 600 G scan, 250 G/min scan rate, 200 mW, product of gain, modulation amplitude and square root of power level is 1×10^4 greater for outer lines than for inner lines); (B) computer simulations as described in text.

four-line pattern with an apparent splitting about half of the value of $\langle a \rangle_{Cu}$ which is observed in the absence of electron–electron coupling. In this solution the "outer" lines of the ABMX pattern can be observed at both low field and high field as shown in Figure 3. The observation of these signals in toluene solution is facilitated by the low dielectric loss of the solvent, the absence of saturation effects up to 200 mW, and the high proportion of the complex present as this isomer. In other solvents such as THF, 1:1 THF–CH_2Cl_2, and pyridine, there are about equal amounts of the two isomers. In these cases the center portion of the spectrum (Figure 1B) is characterized by greater intensity in the middle portion of the grouping of lines as well as to low field of the four-line pattern observed in toluene. The "outer" lines for the isomer with a small electron–electron coupling ($J_1 \sim 360$–415) are clearly resolved in these cases as shown in Figure 2. In Me_2SO solution (Figure 1C) the complex appears to exist almost exclusively as the isomer with a small value of the electron–electron coupling constant ($J_1 = 373$ G). Though up to 5% of the other isomer could be difficult to detect in the computer simulations, there is clearly no major contribution of the four-line pattern observed in toluene solution in the spectrum in Me_2SO solution. There is also much greater intensity in the middle portion of the pattern in Me_2SO than in toluene. Due to dielectric loss of the solvent and smaller populations of the isomer with a large value of the coupling constant, it was not possible to detect either set of "outer" lines for that isomer in some solutions. In simulating the spectra in these cases a value of 2500 G was used for J_2 since the observed values of J_2 in other solvents ranged from 2350 to 2650 G and the line shape calculated for the central portion of the spectrum (around 3150 G) is insensitive to changes of ~100–200 G in J when J is so large.

Table II. Solvent Dependence of the Isomer Populations and of the Electron–Electron Coupling Constants

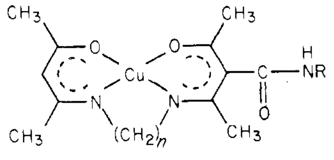
	structure II			structure V		
solvent	J_1,[a] G	%[b]	$\langle a \rangle_{Cu}$	J_2,[c] G	%[b]	$\langle a \rangle_{Cu}$
toluene	300[d]	5	77.5	2650	95	75.0
CH_2Cl_2	365	25	77.8	2350	75	74.0
THF	360	45	75.0	*e*	55	72.0
20:1 CH_2Cl_2–Me_2SO	373	50	76.5	*e*	50	74.0
1:1 THF–CH_2Cl_2	375	55	75.0	2450	45	72.0
pyridine	415	60	71.0	*e*	40	68.0
1:1 Me_2SO–CH_2Cl_2	380	>95	76.5	*e*	<5	
Me_2SO	373	>95	76.5	*e*	<5	

[a] Obtained by computer simulation. Uncertainty ±2 G unless otherwise noted. [b] Based on computer simulation. Uncertainty ±5%. [c] Obtained by computer simulation. Due to broad lines and sloping baseline uncertainty ±25 G. [d] Outer lines for this isomer are weak and partially superimposed on tailing edge of center lines. Uncertainty ±20 G. [e] Outer lines not observed. $J_2 = 2500$ G used in simulations of center lines.

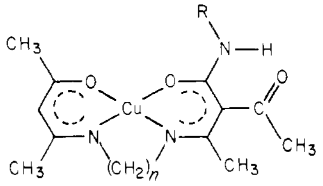
The major uncertainty in determining the relative populations of the two isomers results from uncertainties in the line widths. Since there are so many unresolved lines in the spectra, comparable agreement between observed and calculated spectra can be obtained with isomer populations differing by ±5% provided compensating changes are made in the line widths for the two species. However, even with this uncertainty there are marked changes in the populations of the two isomers as a function of solvent. The populations of the isomers and the values of the coupling constants in various solvents are given in Table II.

The effect of solvent on the value of the electron–electron coupling constant is not the same for the two isomers. Values of J_1 fall in the order toluene < CH_2Cl_2 < 1:1 THF–CH_2Cl_2 while values of J_2 fall in the order CH_2Cl_2 < 1:1 THF–CH_2Cl_2 < toluene. The effect of solvent on the populations of the isomers appears to parallel the hydrogen bonding ability of the solvent. In strongly hydrogen bonding solvents such as Me_2SO, structure II may be stabilized by hydrogen bonding to the solvent. However, in toluene solution where hydrogen bonding to the solvent is much weaker, structure V (see below), which allows for intramolecular hydrogen bonding, is favored. However, it is unlikely that hydrogen bonding is the sole factor since in 20:1 CH_2Cl_2–Me_2SO there is a large molar ratio of Me_2SO to compound which would be adequate for a specific hydrogen-bonding interaction, but the compound still exists as an approximately 1:1 mixture of the two isomers.

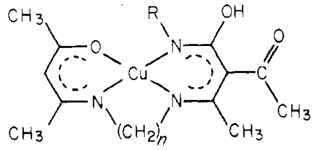
Possible Structures of the Isomers. Nelson et al.[7,13] have considered the possibility of isomerism in the analogues of I with diamagnetic ligands, IV ($n = 2$, R = alkyl, aryl). Species V–VII were considered, but it was found that all of their evidence was consistent with structure IV for a variety of diamagnetic R groups. Since the IR of compound I[1b] is very similar to the IR spectra reported by Nelson et al. for IV,[7] it seems likely that structure I is correct. The IR of compound III is also very similar to that of I and IV,[7] making the structure shown for III a reasonable choice. The assignment of the structures of the two isomers which are observed in the EPR spectra of compound II is less clear-cut. Since the IR of II in CH_2Cl_2 solution includes bands similar to those observed in I,[1b] III, and IV[7] for ν_{NH} and $\nu_{CO(amide)}$, it seems



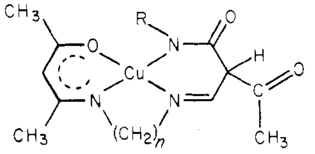
IV



V



VI



VII

reasonable that one isomer of compound II has structure II. One feature that V–VII have in common is that the R group is closer to the copper by two to four bonds than it is in II. In adducts of copper hexafluoroacetylacetonate with pyridine derivatives containing nitroxyl radicals, the electron–electron coupling constant increases substantially as the number of bonds between the copper and the nitroxyl is decreased in a homologous series.[14] Thus it seems likely that the isomer with the smaller value of J (J_1 = 300–415 G) has structure II and the longer Cu–NO distance. Although the structure of the isomer with the larger value of J (J_2 = 2350–2650 G) cannot be made definitively, some evidence is available concerning the plausibility of V–VII. Structures VI and VII both put the pyrrolidine ring of the nitroxyl only two bonds away from the copper. Based on the limited data available[1,14,15] it would seem likely that these short distances would result in $J \gg 2500$ G. VI and VII also both put an additional N in the copper coordination sphere which would potentially be observable in the EPR spectra. However, the lines in the EPR spectra of II are broad enough that nitrogen hyperfine coupling is not resolved and changes could go undetected. One possible reason why isomerism occurs for II but is not observed for IV is that the pyrrolidine ring is more demanding sterically than a methyl or phenyl group. If this were the case then V would appear to relieve steric crowding to a greater extent than either VI or VII. Further, a bulky R group on the donor nitrogen atom as in VI or VII would be expected to force the coordination geometry substantially further away from planarity than in III resulting in decreased values of $\langle a \rangle_{\mathrm{Cu}}$ and increased g values (see below). However, the value of $\langle a \rangle_{\mathrm{Cu}}$ for the second isomer of II was found to be only 2–4 G smaller than for structure II and there was no observable change in g value.

The IR spectra are not as informative as might be expected. An amide N–H band is observed in the IR of II in toluene and CH_2Cl_2 solutions and in Nujol mulls consistent with the presence of structure II. The apparently decreased intensity of the amide N–H band in toluene solution is consistent with the small fraction of II present as structure II in toluene solution. An N–H stretch would also be expected for structure V but could be broadened by hydrogen bonding to the nearby carbonyl group. The region of the IR spectrum from 1500 to 1600 cm^{-1} is poorly resolved in CH_2Cl_2 solution and in Nujol mulls consistent with the presence of more than one species but does not provide detailed information on the nature of the two species. In toluene solution the solvent absorption obscures the carbonyl region. On the basis of these considerations structure V appears to be the most plausible choice for the second isomer of compound II.

The possibility that the two species differ primarily in solvation or in conformation might also be raised. However, the fact that both isomers exist, though in different proportions, in solvents as different in coordinating ability as toluene, CH_2Cl_2, THF, and pyridine makes it seem unlikely that the two isomers observed differ only in axial ligation. The trimethylene bridge in the ligand may adopt a range of conformations, but it seems unlikely that these conformations could give rise to the large difference in J observed for the two isomers if the change in J on going from an ethylene to a trimethylene bridge is as small as discussed below. However, very little is known about the effect of molecular structure and environment on the magnitude of J. Hence the present results are only suggestive, not conclusive, of the nature of the two species yielding the observed EPR spectra.

EPR Power Saturation. EPR microwave power saturation studies also provide evidence of metal–nitroxyl interaction. In the absence of saturation effects a plot of signal amplitude vs. the square root of the microwave power, $P^{1/2}$, is linear. Linear plots of amplitude vs. $P^{1/2}$ were observed for the copper complex with a diamagnetic ligand, III. For nitroxyl radicals, plots of amplitude vs. $P^{1/2}$ typically show deviation from linearity at power levels greater than 1–2 mW.[6] However in the spin-labeled copper complex, II, plots of signal amplitude vs. $P^{1/2}$ for both "inner" and "outer" lines in toluene and 1:1 THF–CH_2Cl_2 solution were linear over the accessible range of power levels (up to 200 mW). The relaxation behavior of the "nitroxyl" electron has clearly been substantially altered by interaction with the "copper" electron.

Comparison with Previous Results. The value of J for structure II ranges from ~300 G in toluene to 415 G in pyridine. The value of J for the spin-labeled copper complex I is also solvent dependent, but the pattern is very different. For II, extremes of J occur in toluene and pyridine solution while for I the values of J in these solvents fall in the middle of the observed range of J's. For I the extreme values are observed in THF and Me_2SO whereas the values of J in these solvents are in the middle of the range observed for II. Thus, even for two compounds as similar as I and II, the effect of solvent on J follows different patterns for the two compounds.

Since the only difference between I and structure II is the length of the alkyl chain between the two nitrogens, it is of interest to compare the values of J for I and II. J is consistently smaller for II than for I.[1b] Distortion of the copper complex away from planarity toward tetrahedral geometry has been observed to cause an increase in g value and decrease in $\langle a \rangle_{\mathrm{Cu}}$.[16] Comparison of the values for I[1] and II shows that g values for II are greater than for I and $\langle a \rangle_{\mathrm{Cu}}$'s for II are less than for I, indicating that II is more distorted from planarity than I. For approximately square-planar Cu^{2+}, the unpaired electron would be expected to be in $d_{x^2-y^2}$. Overlap of the ligand orbitals with $d_{x^2-y^2}$ may be decreased by distortion away from planarity thereby making the electron–electron coupling smaller for II than for the less distorted I. Further studies are necessary, however, before a relationship between J and distortion from planarity can be established.

In our previous report on the electron–electron coupling in I it was noted that in toluene solutions at low temperatures a second species was observed with J ~3000 G.[1b] In light of the results obtained for II it is likely that the second species is an isomeric form of I analogous to V. Apparently the isomerism is much less favorable for I than for II since no trace of the second isomer of I was observed in solvents other than toluene.

The values of J_2 observed for the proposed isomer V are substantially larger than the values we have previously reported for spin-labeled copper complexes[1,6,14,17] except for those where the nitroxyl-containing ring is attached to a coordinated nitrogen.[1,14] Further studies are underway to elucidate the factors which influence the magnitude of electron–electron coupling in room-temperature solution on EPR spectra.

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Registry No. II, 68212-96-4; III, 68212-97-5; V, 68212-98-6; Cu(batm), 40771-94-6; phenyl isocyanate, 103-71-9; 3-isocyanato-2,2,5,5-tetramethylpyrrolinyl-1-oxy, 68212-42-0.

References and Notes

(1) (a) S. S. Eaton and G. R. Eaton, *Coord. Chem. Rev.*, **28**, 207 (1978); (b) D. L. DuBois, G. R. Eaton, and S. S. Eaton, submitted for publication.

(2) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958); H. St. Rade, *J. Phys. Chem.*, **77**, 424 (1973); D. B. Brown, V. H. Crawford, J. W. Hall, and W. E. Hatfield, *ibid.*, **81**, 1303 (1977).

(3) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

(4) (a) A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York, N.Y., 1968, pp 5–7; (b) *ibid.*, pp 34–36, 38.

(5) E. A. Boudreaux and L. N. Mulay, Eds., "Theory and Applications of Molecular Paramagnetism", Wiley, New York, N.Y., 1976; B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959); R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).

(6) D. L. DuBois, G. R. Eaton, and S. S. Eaton, *J. Am. Chem. Soc.*, **100**, 2686 (1978).

(7) P. N. Howells, J. W. Kenney, J. H. Nelson, and R. A. Henry, *Inorg. Chem.*, **15**, 124 (1976).

(8) S. S. Eaton, D. L. DuBois, and G. R. Eaton, *J. Magn. Reson.*, in press.

(9) H. McConnel, *J. Chem. Phys.*, **25**, 709 (1956); D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960).

(10) R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960).

(11) R. Barbucci, P. Paoletti, and M. J. M. Campbell, *Inorg. Chim. Acta*, **10**, 69 (1974).

(12) T. Ogata, T. Fujisawa, N. Tanaka, and H. Yokoi, *Bull. Chem. Soc. Jpn.*, **49**, 2759 (1976); A. W. Addison, M. Carpenter, L. K.-M. Lau, and M. Wicholas, *Inorg. Chem.*, **17**, 1545 (1978).

(13) R. P. Eckberg, R. A. Henry, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **16**, 2977 (1977); R. P. Eckberg, J. H. Nelson, J. W. Kenney, and P. N. Howells, *ibid.*, **16**, 3128 (1977).

(14) P. M. Boymel, J. R. Chang, D. L. DuBois, D. J. Greenslade, G. R. Eaton, and S. S. Eaton, *J. Am. Chem. Soc.*, **99**, 5500 (1977); P. M. Boymel, G. R. Eaton, and S. S. Eaton, to be submitted for publication.

(15) G. R. Eaton, *Inorg, Nucl. Chem. Lett.*, **8**, 647 (1972).

(16) H. Yokoi and A. W. Addison, *Inorg. Chem.*, **16**, 1341 (1977).

(17) G. A. Braden, K. T. Trevor, J. M. Neri, D. J. Greenslade, G. R. Eaton, and S. S. Eaton, *J. Am. Chem. Soc.*, **99**, 485 (1977).

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Potential Energy Models for Nonbonding and Bonding Interactions in Solid Chlorine

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The observed crystal structure of chlorine at low temperature was used to derive optimized potential energy parameters. Seven potential energy models were tested. The types of energy considered were Buckingham (exp-6) nonbonded, dipolar, quadrupolar, and partial-bonded energy between molecules as represented by a Morse function. The best potential energy model included (exp-6), dipolar, and partial-bond energies. The effective dipole corresponded to point charges of ±0.09 e on the chlorine atoms. The partial-bond energy was about 1–2.7% of the molecular dissociation energy; the best model showed partial bonding which contributed 16% of the total lattice energy.

Introduction

Intermolecular potential energy models for crystalline chlorine have been studied for many years. Yamasaki[1] used a Lennard-Jones (6-12) potential and quadrupole interactions to describe the crystal structure. She determined that a hypothetical cubic structure (space group *Pa*3) has a lower energy than the observed orthorhombic structure (space group *Cmca*). In order to explain the stability of the orthorhombic structure she assumed a partial covalent bond existed between different chlorine molecules. This partial bond corresponded to the observed shortest intermolecular distances of 3.32 Å between chlorine atoms in different molecules. Nyburg[2] showed that a hexagonal structure (space group *Pbm*2) was also predicted by a (6-12) potential model as being more stable than the observed structure. Although the addition of a point quadrupole potential failed to predict the orthorhombic structure, Nyburg found that a finite quadrupole model was successful. The point charges of this quadrupole model were placed at the nuclei and at more than 1.6 Å outside the nuclear positions. The location of effective charges lying so far outside the nuclear positions seemed inherently unreasonable.

Hillier and Rice[3] focused attention on possible partial bonding in the orthorhombic structure by molecular orbital calculations including charge-transfer stabilization. They concluded that charge transfer may contribute about 25% of the cohesive energy but nevertheless failed to predict the observed orthorhombic structure. Nyburg[4] made an extended Hückel molecular orbital calculation on assemblies of chlorine molecules including d-orbital involvement. Although the EHMO energy was only about 5% of the cohesive energy, it was sufficient to stabilize the observed orthorhombic structure. The EHMO energy was found to destabilize the *Pa*3 and $P\bar{6}m2$ structures. English and Venables[5] gave consideration to the possibility of monoclinic space group *C*2/*c*, in addition to the three other space groups mentioned previously. They found that a (6-12) plus point quadrupole potential could not explain the observed structure. They concluded that partial intermolecular bonding stabilizes the observed structure.

Dumas, Vovelle, and Viennot[6] returned to the use of the partial-bond model of Yamasaki, plus (6-12) or (exp-6) nonbonded potentials with no quadrupole potential. They obtained reasonable agreement with the observed lattice vibrational frequencies. However, their potential does not fit the static structure (see the B + M model below). Grout, Leech, and Pawley[7] criticize this work of Dumas et al. on the grounds that a preliminary minimization of the lattice energy was not done. Starr and Williams[8] also determined that such a preliminary minimization was necessary to accurately calculate lattice frequencies.

In this paper we examine the ability of several potential models to predict the lattice constants and molecular tilt in the orthorhombic space group. It transpires that an inter-