# Electron Spin Exchange between Di-*tert*-butyl Nitroxide and Copper(II)-β-Diketone Complexes

## R. A. Zelonka and M. C. Baird*

*Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada. Received January 25, 1971*

**Abstract:** Solutions of copper(II) trifluoroacetylacetonate and hexafluoroacetylacetonate, $Cu(tfac)_2$ and $Cu(hfac)_2$, in the liquid free radical di-*tert*-butyl nitroxide exhibit $^{19}F$ nmr spectra. Spin relaxation of the copper complexes is achieved by coordination of the nitroxide and rapid electron exchange between solute and solvent molecules. A dark green, labile mononitroxide adduct of $Cu(hfac)_2$ has been isolated and characterized. It is antiferromagnetic, with a room-temperature magnetic moment of 1.05 BM and a singlet–triplet separation of approximately 645 $cm^{-1}$.

In the past decade, nuclear magnetic resonance (nmr) and electron spin resonance (esr) spectroscopy have been complementary techniques in the study of paramagnetic molecules.[1,2] In cases where the electron spin relaxation times are long, well-resolved esr spectra can generally be obtained, but not nmr spectra. On the other hand, if the electron spin relaxation times can be shortened by, for instance, rapid electron exchange between paramagnetic molecules, then nmr spectra can often be observed. In general, much smaller hyperfine interactions can be observed in nmr spectra than in esr spectra. Nmr spectroscopy also has the further advantage that the sign of the coupling can be obtained.

Although most organic radicals in dilute solutions have long electronic relaxation times and have been extensively studied by esr spectroscopy,[3] the relatively short electronic relaxation times of concentrated poly-crystalline[2] and liquid[4,5] radicals are favorable for nmr studies, and a number of stable radicals have been studied by this technique.

More recently, it has been reported[6] that solutions of, for instance, phenoxy radicals in the stable liquid free radical di-*tert*-butyl nitroxide (DBNO) also exhibit nmr spectra. Spin exchange between solute and solvent molecules shortens the electronic relaxation times by averaging the electron spin levels of the solute molecules, and contact shifts can be observed which are not resolved by esr spectroscopy. This work suggested the use of DBNO as a solvent for nmr studies of transition metal compounds, particularly those of chromium(III), high-spin iron(III), and copper(II), which generally have relatively long electron spin relaxation times but which also have zero or small magnetic anisotropies. Thus, dipolar shifts should be negligible in the nmr spectra of coordination compounds of these ions, and the problems often associated[7] with factoring out dipolar shifts can be avoided. While this work was in progress, Wilbur and Kreilick[8] reported investigating the interactions of nitroxide radicals with a number of

paramagnetic transition metal–acetylacetonate complexes. Although the addition of the metal complexes to dilute solutions of the nitroxides did cause broadening of the esr spectra of the nitroxides, it was not possible to distinguish between dipolar or exchange mechanisms.

We have similarly studied the interactions of several paramagnetic acetylacetonates with chloroform solutions of DNBO and have found little or no narrowing of lines in the nmr spectra of the acetylacetonates VO-$(acac)_2$, $Cr(acac)_3$, $Fe(acac)_3$, $Ru(acac)_2$, and $Cu(acac)_2$ and the acetylacetonate derivatives VO(dibenzoylmethanato)$_2$, Fe(dibenzoylmethanato)$_3$, Cu(dibenzoylmethanato)$_2$, and Cu(ethyl acetoacetate)$_2$. Apparently electron exchange, if any, is not sufficient to shorten the electronic relaxation times significantly.

As reported in a preliminary communication,[9] we have, however, found that solutions of Cu(trifluoroacetylacetonate)$_2$, $Cu(tfac)_2$, and Cu(hexafluoroacetylacetonate)$_2$, $Cu(hfac)_2$, in neat DNBO do exhibit $^{19}F$ nmr spectra. Our results appeared to be consistent with an electron spin exchange mechanism between nitroxide molecule and copper ion, and we now report details of our investigations into this system.

## Experimental Section

**Chemicals.** DBNO was prepared by the method of Hoffman, *et al.*[10] Most of the metal acetylacetonates and substituted acetylacetonates were prepared by standard methods,[11] while $Cu(tfac)_2$ and $Cu(hfac)_2 \cdot H_2O$ were purchased from Peninsular Chemresearch Inc. The pyridine and quinoline adducts of $Cu(tfac)_2$ and $Cu(hfac)_2$ were prepared by methods described in the literature,[12,13] as were the compounds $Zn(tfac)_2$[14] and $Zn(hfac)_2 \cdot 2H_2O$.[15] Recrystallization of the latter two compounds from anhydrous acetone gave crystalline materials which, from their infrared spectra, appeared to be anhydrous $Zn(tfac)_2$ and $Zn(hfac)_2$.

**Nmr Spectra.** Proton nmr spectra of solutions of $Cu(acac)_2$ and Cu(ethyl acetoacetate)$_2$ in $CDCl_3$ exhibited broad (width at half-height, $\Delta \nu_{1/2}$, ~100 Hz) bands at approximately $\tau$ 9.1 and 7.0, respectively. The spectra of $Cu(tfac)_2$ and $Cu(hfac)_2 \cdot H_2O$

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similarly contained broad absorptions at approximately $\tau$ 8.2 and 11.1 (intensity ratio 1:3) and at $\tau$ 7.1, respectively. No $^{19}$F nmr spectra could be detected for the latter two complexes. The compounds Zn(acac)$_2$, Zn(tfac)$_2$, and Zn(hfac)$_2$ exhibited CH resonances at $\tau$ 4.53, 4.47, and 4.35, respectively; the first two exhibited CH$_3$ resonances at $\tau$ 8.00 and 8.02, respectively.

Unlike Cu(acac)$_2$, both Cu(tfac)$_2$ and Cu(hfac)$_2$·H$_2$O dissolved readily in neat DBNO, yielding dark green solutions. Although the intense, broad nitroxide resonance masked the proton nmr spectra of the complexes, the $^{19}$F nmr spectra at room temperature exhibited single, broad absorptions at approximately −102 and −80 ppm (i.e., downfield from internal C$_6$F$_6$), respectively. The chemical shifts and line widths were strongly temperature dependent and are listed for the temperature ranges attainable in Table I. The solvent begins to solidify at temperatures below

**Table I.** Line Widths ($\Delta\nu_{1/2}$, ppm) and $^{19}$F Chemical Shifts (ppm downfield from internal C$_6$F$_6$) at Various Temperatures

| Temp, °K | Cu(tfac)$_2$ Chemical shift | $\Delta\nu_{1/2}$ | Cu(hfac)$_2$·H$_2$O Chemical shift | $\Delta\nu_{1/2}$ |
|---|---|---|---|---|
| 345 | −104.6 | 4.46 | a | a |
| 335 | −104.0 | 4.57 | a | a |
| 325 | −103.8 | 4.68 | −82.3 | a |
| 315 | −103.5 | 4.92 | −81.6 | 2.66 |
| 305 | −102.7 | 5.17 | −81.1 | 3.29 |
| 295 | −102.2 | 5.60 | −80.4 | 3.92 |
| 285 | −100.0 | 5.95 | −79.5 | 4.61 |
| 275 | −97.7 | 6.67 | −77.9 | 4.81 |

$^a$ Measurement was made difficult because of decomposition.

275°K, while decomposition of the Cu(tfac)$_2$ and Cu(hfac)$_2$·H$_2$O solutions begins at approximately 340 and 320°K, respectively.

The chemical shifts are also strongly dependent both on the nitroxide concentration and on the presence of other potential ligands. In 4:1 DBNO-tetrahydrofuran solutions, the resonances were broadened by approximately 15% and in 1:1 DBNO-THF solutions, the resonances were too broad to be observed. There was also a noticeable downfield shift of the resonances as the concentration of DBNO decreases.

In order to further investigate the nature of the interactions between DBNO and the copper complexes, the pyridine and quinoline adducts of Cu(tfac)$_2$ and Cu(hfac)$_2$ were prepared. As expected, none of these compounds exhibited a $^{19}$F nmr spectrum in tetrahydrofuran solutions. Of the four adducts, only the quinoline adduct of Cu(tfac)$_2$ was insoluble in neat DBNO. Solutions of the other three complexes in DBNO all exhibited single $^{19}$F resonances which were broader than and shifted downfield from the nonadduct positions. Equimolar solutions of the three adducts and either Cu(tfac)$_2$ or Cu(hfac)$_2$·H$_2$O in DBNO similarly showed only one resonance in their $^{19}$F nmr spectra rather than the two expected for two different species. The chemical shift in each case was intermediate between that of the amino adduct and that of the none or aquo adduct.

DBNO solutions of Zn(tfac)$_2$ and Zn(hfac)$_2$ at room temperature exhibited $^{19}$F resonances at −74.8 and −71.4 ppm, respectively; the corresponding chemical shifts in acetone were −87.8 and −87.0 ppm.

**Esr Spectra.** Room-temperature esr spectra of chloroform solutions of Cu(acac)$_2$, Cu(tfac)$_2$, and Cu(hfac)$_2$·H$_2$O all exhibited the four-line pattern typical[16] of copper(II)-$\beta$-diketonate complexes. The addition of 10$^{-2}$ M DBNO to 10$^{-3}$ M solutions of Cu(tfac)$_2$ and Cu(hfac)$_2$·H$_2$O in chloroform caused severe broadening, with the result that the copper hyperfine structure was completely lost.

**Preparation of Cu(hfac)$_2$·DBNO.** DBNO (0.19 g, 1.26 × 10$^{-3}$ mol) was added dropwise to a solution of Cu(hfac)$_2$ (0.40 g, 8.4 × 10$^{-4}$ mol) in cyclohexane, yielding a deep green solution which was filtered and dried over anhydrous magnesium sulfate to remove any traces of water which might have been present. The solution was again filtered and the solvent was removed under

reduced pressure at room temperature to give a viscous, dark green oil which, on standing for a few minutes, formed needle-like crystals of the product. The crystals were collected and dried in vacuo at room temperature for 1 hr (mp 62–63°). Anal. Calcd for C$_{18}$H$_{20}$CuF$_{12}$NO$_5$: C, 34.76; H, 3.24; N, 2.25; mol wt, 622. Found: C, 34.36; H, 3.08; N, 2.24; mol wt, 425 (37° in chloroform).

The compound is soluble and stable in most common organic solvents at room temperature. The nitroxide ligand seems to be rather loosely bonded, and crystals always have a slight odor of free nitroxide. Perhaps because of partial dissociation of DBNO, solutions at elevated temperatures are not stable and the adduct has not been successfully recrystallized. The solution used for the molecular weight determination decomposed within a few hours at 37°, although solutions in the same solvent at ambient temperatures appeared to be stable for several days at least.

In agreement with the apparently low stability of the copper–nitroxide bond, the mass spectrum of the adduct at 70 eV did not show a parent ion. In contrast to the published[17,18] mass spectrum of Cu(hfac)$_2$, however, the lines corresponding to the ions [Cu(hfac)$_2$]$^+$, [Cu(hfac)$_2$−CF$_3$]$^+$, [Cu(hfac)$_2$−2CF$_3$]$^+$, and [Cu(hfac)$_2$−4CF$_3$]$^+$ were more intense than the CF$_3$$^+$, hfac–CF$_3$$^+$, and hfac$^+$ lines. Apparently, the energy of the ionizing electrons was largely dissipated in breaking the copper–nitroxide bond, thus leaving the remainder of the molecule relatively intact. A weak line which could be assigned to the [(CH$_3$)$_3$C]$_2$NO$^+$ ion was also observed in the spectrum.

The infrared spectrum of Cu(hfac)$_2$·DBNO (Nujol and hexachlorobutadiene mulls) in the region 4000–300 cm$^{-1}$ was essentially a superposition of the spectra of Cu(hfac)$_2$ and DBNO, with only one exception. The band at about 1345 cm$^{-1}$ in the spectrum of the free nitroxide, which has been assigned to the N–O stretching mode,[19] had disappeared and a new, strong band at 1212 cm$^{-1}$ had appeared. Assignment of the latter band to the N–O stretching mode of the adduct is tentative because of the strong hfac bands which also appear in this region. However, it does seem reasonable that the N–O stretching mode of DBNO should decrease on coordination, and we assign the band at 1212 cm$^{-1}$ to this vibrational mode.

Although the $^{19}$F nmr spectrum of a chloroform solution showed a broad ($\Delta\nu_{1/2} \sim 11$ ppm) resonance at −90.3 ppm, the X-band esr spectrum of polycrystalline Cu(hfac)$_2$·DBNO at 77°K showed no absorptions over the range 0–10,000 G. Similarly, the esr spectrum of a 10$^{-2}$ M solution of the complex in carbon tetrachloride at room temperature could also not be detected. In the latter case, only weak lines attributable to dissociated nitroxide and Cu(hfac)$_2$ could be detected. On adding 4 × 10$^{-2}$ M pyridine to the solution of Cu(hfac)$_2$·DBNO, the nitroxide lines grow rapidly in intensity. A broad copper(II) resonance, presumably attributable to the bispyridine adduct of Cu(hfac)$_2$,[20] also developed, but was not analyzed.

The optical spectra of carbon tetrachloride solutions of Cu(hfac)$_2$, DBNO, and Cu(hfac)$_2$·DBNO in the range 250–800 m$\mu$ are shown in Figures 1 and 2. As mentioned above, addition of DBNO to a pale green solution of Cu(hfac)$_2$·H$_2$O or anhydrous Cu(hfac)$_2$ resulted in the immediate development of a deep green color. This deepening of the color was a result of the approximately eightfold increase in intensity of the low-energy band envelope in the visible region of the spectrum, and has also been noted in the Cu(hfac)$_2$–pyridine system.[20] The only other major change occuring on the combination of the two components is the growth of a low-intensity band at about 370 m$\mu$.

Magnetic susceptibilities were determined in solution using the Evans method[21] and magnetic moments were calculated using the formula

$$\mu_{\text{eff}} = 2.84[(\chi_{\text{M}} - N\alpha)T]^{1/2}$$

where $\chi_{\text{M}}$ is the molar susceptibility corrected for the diamagnetic susceptibilities of the ligands and $N\alpha$ is the temperature-independent paramagnetism of copper(II), about 60 × 10$^{-6}$ cgs/mol.[22]

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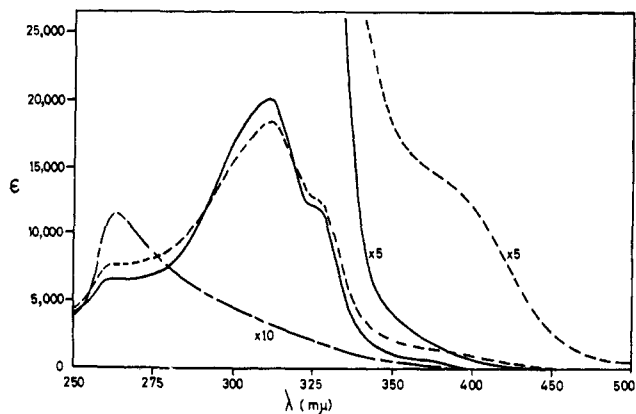
Figure 1. Optical spectra of Cu(hfac)₂ (——), DBNO (- - -), and Cu(hfac)₂·DBNO (-----).
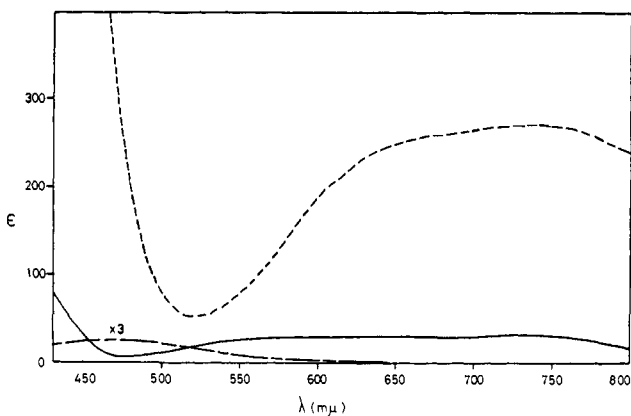


Figure 2. Optical spectra of Cu(hfac)₂ (——), DBNO (- - -), and Cu(hfac)₂·DBNO (-----).

While the room-temperature magnetic moment of Cu(hfac)₂·H₂O in chloroform solution is 1.88 BM, very close to the spin-only value, the magnetic moment of Cu(hfac)₂·DBNO is very low at room temperature (1.05 BM) and is temperature dependent (see Figure 3). The compound appears to be antiferromagnetic, suggesting that the electronic structure involves a singlet ground state and a thermally accessible triplet excited state. The equation

$$\chi_M = \frac{N\beta^2 g^2}{3kT}\left[\frac{3}{3 + \exp(-J/kT)}\right] + N\alpha$$

has been derived[22] to explain the magnetic properties of individual copper ions in a number of copper acetate dimers, where two copper(II) ions, each with a spin of $^1/_2$, interact to form a complex with a singlet ground state and a thermally accessible triplet excited state. This equation cannot be applied directly to Cu(hfac)₂·DBNO, since it would only give the magnetic susceptibility of half the molecule. However, using an average $g$ value (2.14) for copper-(II) complexes[16] in the modified equation

$$\chi_M = \frac{N\beta^2 g^2}{3kT}\left[\frac{6}{3 + \exp(-J/kT)}\right] + N\alpha$$

we calculate a singlet–triplet separation, $-J$, of $645 \pm 20\text{ cm}^{-1}$.

**Instrumentation.** Nmr spectra were run on a Bruker HX-60 spectrometer with internal lock, esr spectra on a Varian V450Z spectrometer with auxiliary equipment, infrared spectra on a Beckman IR-10 infrared spectrometer, mass spectra on a Jeolco JMS-OISC high-resolution mass spectrometer, and optical spectra on a Unicam SP820 spectrophotometer. Melting points were deter-
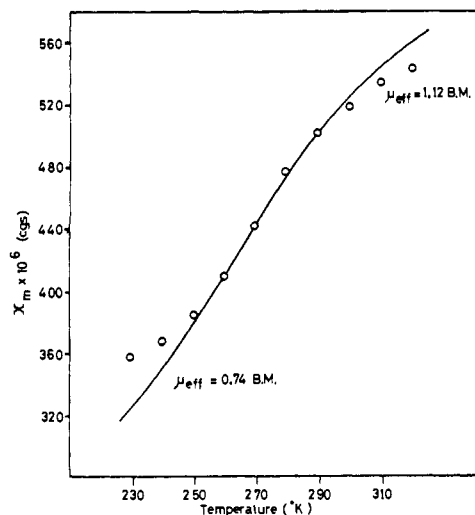


Figure 3. Temperature dependence of the magnetic moment of Cu(hfac)₂·DBNO (O) and theoretical temperature dependence for $J = -645\text{ cm}^{-1}$ (——).

mined using a Gallenkamp melting point apparatus and molecular weights using a Hewlett-Packard Model 302B vapor pressure osmometer.

## Discussion

In the previous section, it was shown that addition of $10^{-2}$ M DBNO to a $10^{-3}$ M chloroform solution of Cu-(hfac)₂ causes severe broadening of the esr signal of the copper complex accompanied by loss of the copper hyperfine splitting. Furthermore, although ¹⁹F nmr spectra of Cu(tfac)₂ and Cu(hfac)₂·H₂O in chloroform solution cannot be detected, solutions of the complexes in neat DBNO do exhibit ¹⁹F resonances. The chemical shifts of Cu(tfac)₂ and Cu(hfac)₂·H₂O are approximately proportional to the temperature, and extrapolation to $T = \infty$ yields limiting chemical shifts of approximately $-119$ and $-103$ ppm, respectively.

The line widths are also temperature dependent, increasing with decreasing temperature. Furthermore, on dilution of or addition to the solutions of oxygen- or nitrogen-containing compounds which can coordinate to the copper, the resonances of both copper compounds broaden and shift to lower field.

Our results appear to be consistent with a rapid electron exchange between DBNO and the copper complexes similar to the exchange between nitroxides and organic radicals observed by Kreilick.[6] Certainly rapid exchange of electrons between nitroxide and copper(II) ion should cause loss of the copper hyperfine splitting in the esr spectrum. It is also reasonable that dilution of DBNO solutions with tetrahydrofuran would have the effect of slowing the exchange, with the result that the electron spin levels of the copper complexes are not effectively averaged and the nmr lines are broadened. Without going into the exchange mechanism at this point, it is likely that the added nitrogen donors would coordinate the axial positions of the copper β-diketonates. Thus the nitroxide would possibly be prevented from approaching the copper atom very closely, and electron exchange would again be hindered.

Difficulty does arise, however, in attempting to explain the temperature dependence of the chemical

shifts. According to the presently accepted theory,[1,2] contact and dipolar shifts should be inversely proportional to temperature and should approach the diamagnetic positions at high temperatures. As is indicated in Table I, the chemical shifts of Cu(tfac)₂ and Cu(hfac)₂ do *not* approach the diamagnetic positions (taken as −74.8 and −71.4 ppm for Cu(tfac)₂ and Cu(hfac)₂, respectively); in fact, they diverge from these positions to extrapolated values of −119 and −103 ppm, respectively. An explanation for this apparently anomalous behavior is offered below.

In their earlier work, Wilbur and Kreilick[3] found that the interactions of nitroxides with Cu(acac)₂ and VO(acac)₂ appeared to be stronger than those with a number of six-coordinate acetylacetonates. They pointed out that the four- and five-coordinate complexes have open coordination sites which could lead to "a smaller interaction distance of a greater exchange coupling."

Our finding that the strength of the copper–nitroxide interactions (as shown by the line-width studies) decreases in the order Cu(hfac)₂, Cu(tfac)₂ > Cu(acac)₂ is completely in accord with this view. The compounds Cu(hfac)₂ and Cu(tfac)₂ are known[23] to be better Lewis acids than is Cu(acac)₂, presumably because of the inductive effect of the fluorine atoms. It is also likely that Cu(hfac)₂ is a better Lewis acid than is Cu(tfac)₂.

Nitroxides may be considered as derivatives of the inorganic radical nitric oxide, and their structures can be rationalized in terms of the resonance hybrids[19]



A            B
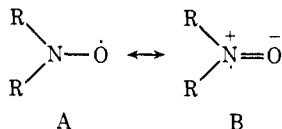
The combination of bond length data, dipole moments, and infrared and esr spectra has been interpreted in terms of a nitrogen–oxygen bond order greater than one[24] and, in any case, both structures A and B are potential oxygen donor ligands.

There have been several examples reported in the literature of nitroxides behaving as Lewis bases. Razuvaev, *et al.*,[25] treated benzene solutions of aluminum and gallium trihalides with the stable nitroxide 2,2,6,6-tetramethyl-4-piperidone 1-oxide. They found that the original triplet in the esr spectrum of the nitroxide disappeared and was replaced by complex signals which were interpreted in terms of hyperfine splittings of both the nitrogen and the metal atoms. Wood and co-workers[26] similarly treated cobalt(III) corrinoids with the same radical and obtained materials which, from their esr spectra, appeared to be 1:1 adducts.

Apparently, the only well-characterized nitroxide complexes which are known are the cobalt(II)[27] and palladium(I)[28] compounds reported by Beck and co-

workers. The cobalt compounds appear to be tetrahedral 2:1 di-*tert*-butyl nitroxide complexes of stoichiometry CoX₂(DBNO)₂ (X = Cl, Br, I). They have magnetic moments which obey the Curie–Weiss law and which suggest the presence of only one unpaired electron per molecule. Thus there appears to be complete coupling of the two odd electrons of the nitroxides with two of the normally (in high-spin cobalt(II) complexes) unpaired electrons of the metal ion. The esr spectrum of the polycrystalline compounds were typical for $S = \frac{1}{2}$ species; in benzene solution, the compounds tended to dissociate slightly and weak lines for the free nitroxide were observed.

The palladium complexes were diamagnetic and were of the general formula [XPdDBNO]₂ (X = Cl, Br). Their infrared spectra suggested the presence of bridging halogens, but the structures are otherwise not known.

Aside from an unstable, uncharacterized adduct of copper(II) perchlorate with 2,2,6,6-tetramethylpiperidine nitroxide,[29] no other nitroxide coordination compounds have been prepared. In none of the above cases is the mode of coordination of the nitroxide known, although both O bonding and π bonding have been suggested, *i.e.*



C                D
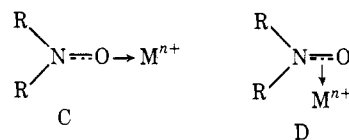
Although both modes of bonding are possible and may exist in different systems, the observation that the nitrogen hyperfine splittings in the esr spectra of nitroxide radicals coordinated to diamagnetic metal ions are increased relative to the splittings of the free radicals suggests that structure C is a more valid representation of the bonding. Coordination by the oxygen would increase the importance of resonance hybrid B, thus increasing the unpaired electron spin density on the nitrogen atom and hence the nitrogen hyperfine splitting.

Attempts to prepare DBNO coordination compounds with Cu(tfac)₂ and Cu(hfac)₂ were successful only in the latter case. Deep green crystals of Cu(hfac)₂·DBNO are easily obtained from cyclohexane if the anhydrous copper complex is used. Preparations using the hydrate Cu(hfac)₂·H₂O yielded a deep green material which crystallized less readily. Although the latter product has an infrared spectrum identical with that of Cu(hfac)₂·DBNO, it also has a weak esr spectrum in the solid state which is characteristic of a spin = $\frac{1}{2}$ species. Although we have not investigated the possibility, it is quite possible that water can attack the coordinated DBNO, yielding a complex containing copper(II) and a diamagnetic ligand which would exhibit an esr spectrum.

Conclusive evidence that the complex Cu(hfac)₂·DBNO does exist as written and is not a rearranged product of a reaction between the nitroxide and the copper complex is given both by the observation of the Cu(hfac)₂⁺ ion in the mass spectrum and by the fact that the

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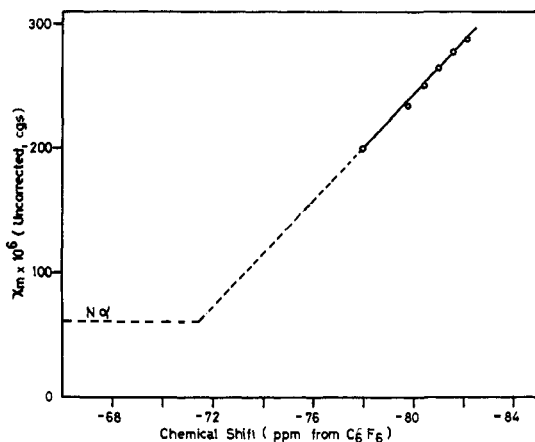(29) C. M. Paleos, N. M. Karayannis, and M. M. Labes, *Chem. Commun.*, 195 (1970).

Figure 4. Plot of uncorrected molar susceptibility of $Cu(hfac)_2 \cdot$ DBNO vs. $^{19}F$ chemical shifts.

nitroxide can be displaced from the adduct and detected by esr. The optical spectrum of $Cu(hfac)_2 \cdot$ DBNO, shown in Figures 1 and 2, is typical of the spectra of monoadducts of $Cu(hfac)_2$. The approximately eight-fold increase in the intensity of the low-energy d–d transition band envelope (Figure 2), for instance, is reminiscent of the similar increase on formation of the pyridine adduct.[20] The apparent decrease in $\nu_{NO}$ in the infrared spectrum of $Cu(hfac)_2 \cdot$ DBNO provides further evidence, albeit somewhat ambiguous, that the complex does contain a coordinated nitroxide molecule.

The antiferromagnetism of $Cu(hfac)_2 \cdot$ DBNO suggests considerable electron exchange between DBNO and the copper ion. As outlined in the Experimental Section, the magnetic properties can be interpreted in terms of a singlet ground state and a thermally accessible triplet excited state, the singlet–triplet separation being 645 $cm^{-1}$. The exchange interaction is more than twice that of the copper acetate dimer (260 $cm^{-1}$),[22] although it is considerably less than the apparently complete electron pairing in the cobalt(II) complexes, $CoX_2$-$(DBNO)_2$.[27] It is possible that the strong exchange interaction would give rise to both a short spin–lattice relaxation time and a large zero-field splitting, either of which could account for the lack of an esr spectrum in the solid state.

Since only averaged $^{19}F$ resonances were observed in the nmr spectra of mixtures containing $Cu(hfac)_2 \cdot H_2O$ (or $Cu(tfac)_2$), DBNO, and pyridine, exchange between free and complexed DBNO is rapid on the nmr time scale. We have also shown that a strong electron exchange interaction exists when the nitroxide is coordinated to a copper atom. Thus, in solutions of $Cu(hfac)_2$ or $Cu(tfac)_2$ in DBNO, the appropriate conditions for the observation of nmr spectra quite clearly exist, i.e., rapid electron exchange between solute and solvent with the concomitant shortening of the electron spin–lattice relaxation times of the former.

The antiferromagnetism of $Cu(hfac)_2 \cdot$ DBNO provides an explanation for the anomalous temperature dependence of the $^{19}F$ isotropic shifts. Since only the

paramagnetic triplet state can cause contact and dipolar shifts, the isotropic shifts should be proportional to the population of the triplet state, i.e., to the magnetic susceptibility of the complex.[30] A plot of molar susceptibility of $Cu(hfac)_2 \cdot$ DBNO (uncorrected for the diamagnetic susceptibility of the ligands) vs. isotropic shift over the temperature range 275–325°K is indeed linear (Figure 4) and extrapolates to a chemical shift of $-71.5$ ppm at a molar susceptibility corresponding to the temperature-independent paramagnetism of copper(II), $60 \times 10^{-6}$ cgs/mol.[22] This agrees surprisingly well with the chemical shift of $-71.4$ ppm for $Zn(hfac)_2$.

Similar temperature dependences of isotropic shifts have been observed in the proton nmr spectra of a series of substituted iron(III)–dithiocarbonate complexes.[31] The magnetic properties of these complexes have been interpreted in terms of a $^2T_2$ ground state and a thermally accessible $^6A_1$ excited state. A very fast rate of conversion between the two states exists, giving rise to very effective electronic relaxation and hence to well-resolved nmr spectra. Interpretation of the isotropic shifts in these iron systems is complicated by the fact that both of the thermally populated states are paramagnetic.

Although dipolar contributions to the $^{19}F$ nmr spectra are probably negligible because of the small magnetic anisotropics of copper(II) complexes,[32] quantitative estimations of spin densities from the observed dipolar shifts would be very difficult. Qualitatively, it is seen that the $^{19}F$ contact shifts are much larger than the proton contact shifts of $Cu(acac)_2$ and $Cu(tfac)_2$, as is expected if the fluorine atoms exert a significant inductive effect on the copper. The greater shifts and line broadening with $Cu(tfac)_2$ than with $Cu(hfac)_2$ can be explained if a decreased electronic exchange interaction between the nitroxide and $Cu(tfac)_2$ is assumed. The singlet–triplet separation would be decreased, the triplet state would be more highly populated, and the molar susceptibility would be higher. The assumption seems reasonable, since $Cu(hfac)_2$ should be a better Lewis acid than $Cu(tfac)_2$.

It seems likely that the use of paramagnetic solvents to study the nmr of transition metal complexes will prove to be generally useful in systems where the solvent can coordinate directly to the metal ion. The use of more basic stable free radicals, containing nitrogen donor atoms for instance, may prove more fruitful than will the use of nitroxides.

(30) To state the case differently, both magnetic susceptibility and isotropic shifts are theoretically inversely proportional to temperature and thus should be proportional to each other.

(31) R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *J. Chem. Phys.*, 45, 2688 (1966).

(32) B. R. McGarvey, *Transition Metal Chem.*, 3, 180 (1966).