Spin Exchange between Paramagnetic Metal Complexes and Aliphatic Nitroxides: ^{19}F Nuclear Magnetic Resonance Spectroscopy of Copper(II) Complexes

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Summary The use of the stable free-radical di-t-butylnitroxide as a solvent makes possible the observation of the ^{19}F n.m.r. spectra of some copper(II) complexes.

ALTHOUGH n.m.r. spectra of solutions of organic radicals usually cannot be observed because of the long electronic relaxation times of the radicals, solutions of, for instance, phenoxy-radicals in the liquid free-radical di-t-butylnitroxide (DBNO) do exhibit n.m.r. spectra.[1] 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 e.s.r. experiments. Wilbur and Kreilick have recently attempted to extend this technique to a series of transition metal acetylacetonates.[2] Some spin exchange between DBNO and cupric acetylacetonate (Cu acac$_2$) and vanadyl acetylacetonate was observed, but DBNO was not found to be generally useful in enhancing the ^{1}H n.m.r. spectra of metal complexes.

We have found that the fluorinated acetylacetonate compounds Cu(hexafluoroacetylacetonate)$_2$ (Cu hfac$_2$) and Cu(trifluoroacetylacetonate)$_2$ (Cu tfac$_2$) dissolve readily in neat DBNO, and although the proton resonances are obscured by the t-butyl line, the solutions exhibit single lines in the ^{19}F n.m.r. spectra at approximately 80 and 102 p.p.m. downfield from internal C_6F_6, respectively. Both resonances broaden on lowering the temperature and on changing the solvent to a 1:1 DBNO–tetrahydrofuran mixture. Solutions of both copper compounds in chloroform, on the other hand, do not show a ^{19}F n.m.r. spectrum. Furthermore, although 10^{-3}M chloroform solutions of both Cu hfac$_2$ and Cu tfac$_2$ exhibit well-resolved e.s.r. spectra in which the copper hyperfine splitting can be observed, the addition of only 10^{-2}M-DBNO to the solution causes severe broadening and loss of fine structure of the copper resonance. Thus in these cases, spin exchange between nitroxide and transition-metal compounds shortens the electronic relaxation times sufficiently that n.m.r. spectra may be observed.

It seems very likely that the mechanism of spin exchange involves the formation of labile copper–nitroxide complexes of the type Cu hfac$_2$, DBNO. The compounds Cu hfac$_2$ and Cu tfac$_2$ are known[3] to be much better Lewis acids to oxygen donors than is the parent compound, Cu acac$_2$, and direct interaction between DBNO and the copper(II) ion might well lead to spin exchange. Similar co-ordination compounds of DBNO with cobalt and palladium are known,[4] and a dark green, crystalline compound can be obtained from Cu hfac$_2$–DBNO mixtures; its i.r. spectrum suggests that it is a simple adduct.

We expect that spin exchange of nitroxides with other paramagnetic transition metal compounds should occur if the metal ion is a good enough Lewis acid to complex the nitroxide.

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