in 50 ml of methanol and 1.3 g of dipyridyl and 1 g of sodium iodide were added under nitrogen. To the resulting solution a solution of 0.55 g of iodine in 20 ml of ethanol was slowly added with mixing. Dark violet crystals were formed which after filtering off were washed several times with small volumes of methanol. *Anal.* Calcd for $[Co(dipy)_2I_2]I$: C, 31.92; N, 7.45; H, 2.16, I, 50.5. Found: C, 31.05; N, 7.24; H, 2.75; I, 51.0.

Preparation of $[Co(dipy)_2Br_2]Br$.—The procedure was the same as for the iodide, an equivalent amount of sodium bromide and bromine being used. *Anal.* Calcd for $[Co(dipy)_2Br_2]Br$: C, 39.60; N, 9.17; H, 2.64; Br, 39.15. Found: C, 39.45; N, 8.95; H, 3.05, Br, 41.5.

Preparation of $[Co(dipy)_2Cl_2]Cl$.—One gram of $CoCl_2 \cdot 6H_2O$, 1 g of lithium chloride, and 1.6 g of dipyridyl were successively dissolved in 50 ml of dry methanol under nitrogen. Gaseous chlorine was then slowly introduced into this solution under cooling for 15 min. The resulting crystals were filtered off and washed with methanol. They were redissolved in ethanol on a water bath and the ethanol was slowly evaporated on the boiling water bath. After a while green needles of the *trans* isomer started to form on the walls of vessel. The hot solution was decanted and the remaining crystals were washed several times with cold ethanol and ether and dried. Further slow evaporation of the solution at room temperature resulted in the formation of violet crystals of the *cis* isomer which were filtered off and washed with ethanol and ether. *Anal.* Calcd for $[Co(dipy)_2Cl_2]Cl \cdot 3H_2O$: C, 45.6, N, 10.53; H, 4.14; Cl, 20.02. Found: C, 45.08; N, 10.40; H, 4.05; Cl, 20.17.

Spectra.—A Cary Model 14 spectrophotometer was used. Infrared spectra were taken on a Perkin-Elmer Model 337 grating infrared spectrophotometer in Nujol mulls.

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Spin Delocalization in γ-Picoline N-Oxide Coordinated with Bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II)[1]

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Proton magnetic resonance evidence for electron spin delocalization in the π orbitals of heterocyclic N-oxides[2,3] and in σ orbitals of heterocyclic amines axially coordinated to nickel(II) and cobalt(II) 2,4-pentanedionates[3,4] has been recently reported. Copper(II) β-diketonates are also known to coordinate with various ligands such as heterocyclic bases to give pentacoordinate[5] and hexacoordinate[6] species in which the added ligands are presumed to be axially disposed. In the present work nmr isotropic shifts of the protons in γ-picoline N-oxide complexed with bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II) [$Cu(CF_3COCHCOCH_3)_2$, herein referred to as $Cu(TFAA)_2$], were obtained and compared with the previous results.

Experimental Section

Bis(1,1,1-trifluoro-2,4-pentanedionato)(γ-picoline N-oxide)-copper(II).—A mixture of 0.37 g (0.001 mole) of $Cu(TFAA)_2$ and 0.11 g (0.001 mole) of γ-picoline N-oxide was dissolved in 14 ml of hot toluene. Heptane (15 ml) was added and the solution allowed to cool slowly. The turquoise-green crystals which separated, 0.40 g, were recrystallized twice from toluene–heptane. After drying *in vacuo* at 55° the product melted 149.5–150°.

Anal. Calcd for $C_{16}H_{15}F_6NO_5Cu$: C, 40.13; H, 3.16; N, 2.93. Found: C, 40.28; H, 3.22; N, 2.69.

Magnetic Moments.—These were obtained by the Gouy method for solids and by the method of Evans[7] for solutions. A diamagnetic correction of 202×10^{-6} cgs unit was made for the 1:1 complex.

Optical Spectra and Equilibrium Constants.—Optical spectra were obtained using a Cary Model 14 recording spectrophotometer. Equilibrium constants were evaluated at about 23° using as solvent chloroform purified immediately before use by washing with concentrated sulfuric acid, water, bicarbonate solution, and water, drying, and distilling. At 14,300 cm^{-1} the molar extinction (ϵ) of $Cu(TFAA)_2$ is 32 l. $mole^{-1}$ cm^{-1}, and that of the complex was taken to be 54 l. $mole^{-1}$ cm^{-1} by extrapolation. For γ-picoline N-oxide $\epsilon \sim 0$ at this frequency.

Electron Spin Resonance.—The spectrum of a powdered sample was obtained using a Varian instrument operating at a frequency of 35 kMcps. The *g* values were obtained directly from the spectrum without recourse to computer construction. A solution spectrum was obtained using a spectrometer frequency of approximately 10 kMcps.

Nuclear Magnetic Resonance.—The proton spectra were obtained in deuteriochloroform, purified by standing over sodium bicarbonate and anhydrous magnesium sulfate and distilling just prior to use with tetramethylsilane as an internal standard. Experimental results were duplicated using $Cu(TFFA)_2$ and independently using a recrystallized sample of the 1:1 γ-picoline N-oxide:$Cu(TFAA)_2$ complex. All solids were dried just prior to use. Some irreversible decomposition of the complex occurred at higher temperatures so variable temperature runs were carried out starting at the lowest temperature using a freshly prepared solution. In all cases the general temperature dependence given in Figure 1 could be repeated, although some broadening of the line widths and downfield shifts of the resonances was always noted after heating the samples even as low as 60°.

Mass Spectrometry.—A fragmentation pattern of the 1:1 $Cu(TFAA)_2$:γ-picoline N-oxide was obtained using an A.E.I. MS 9 spectrometer. The observed copper-bearing fragments, identified by their characteristic copper 63:65 ratio, were in the order of decreasing abundance: $Cu(TFAA)_2$, $Cu(TFAA)_2–CF_3$, $Cu(TFAA)_2–CH_3CO$, a fragment of molecular weight 231, and Cu(TFAA). In all cases the cleavage fragments were also observed.

Bis(1,1,1-trifluoro-2,4-pentanedionato)(γ-picoline N-oxide)zinc(II).—To the hydrate of $Zn(TFAA)_2$ in toluene was added a stoichiometric amount of γ-picoline N-oxide. The water was removed azeotropically. A white crystalline precipitate, mp 135.5–136.5°, was recovered by filtration after standing overnight. The nmr spectrum at 39° showed peaks at 497 (α), 435 (β), 146 (γ-CH_3), 125 (CH_3), and 348 (CH) cps from TMS.

Anal. Calcd for $C_{16}H_{15}F_6NO_5Zn$: C, 39.99; H, 3.14; N, 2.91. Found: C, 40.30; H, 3.42; N, 3.02.

Results

$Cu(TFAA)_2$ interacts with N-oxides to form addition complexes of 1:1 and under some conditions 2:1 stoichiometry. The 1:1 γ-picoline N-oxide:$Cu(TFAA)_2$ complex in its crystalline form has a magnetic moment of 1.94 BM. Its powder esr spectrum was re-

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(1) This research was supported by the National Science Foundation through grant No. N.S.F. GP 3397.

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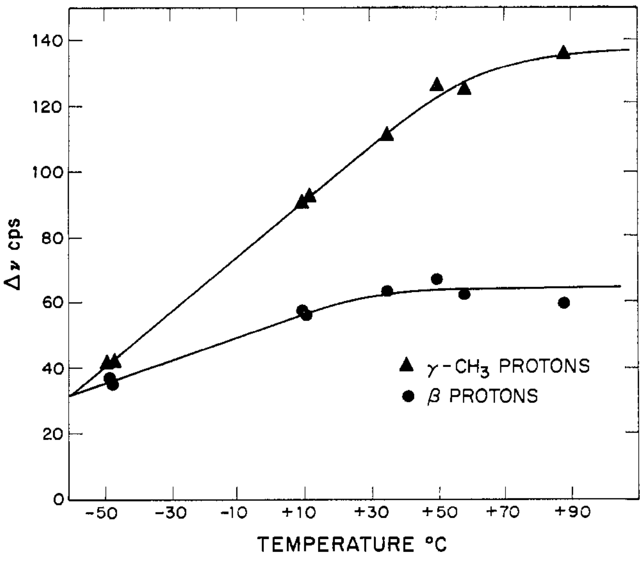

Figure 1.—Variation of nmr isotropic shifts with temperature. Data were obtained from deuteriochloroform solutions 0.135 *M* in $Cu(TFAA)_2$ and 0.40 *M* in γ-picoline N-oxide. The plotted shifts are the observed shifts multiplied by 2.97 to approximate shifts expected for pure 1:1 complex.

solved to give $g_{\parallel} = 2.28$ and $g_{\perp} = 2.08$ as expected for an axially elongated complex.[8] The visible near-infrared spectrum of a Nujol mull showed only a single very broad peak extending from 7000 to 20,000 cm^{-1} with a maximum at 14,400 cm^{-1}. This was resolved, using a computer program,[9] into three Gaussians of about equal intensity centered approximately at 12,000, 14,000, and 16,000 cm^{-1} and assigned to the transitions $A_1 \rightarrow B_1$, $B_2 \rightarrow B_1$, and $E \rightarrow B_1$ expected for a tetragonally distorted d^9 octahedron.[8] From these assignments $g_{\parallel} = 2.28$ and $g_{\perp} = 2.06$ can be calculated assuming a spin–orbit coupling constant of $\lambda = 500$ cm^{-1}. Such a large reduction in λ from the free-ion value is in agreement with other data[10] and has been attributed to a large amount of π bonding in the case of copper acetylacetonate.[11] X-Ray powder patterns showed that this 1:1 complex was free of excess γ-picoline N-oxide, but it was not isomorphous with the corresponding 1:1 γ-picoline N-oxide:$Zn(TFAA)_2$ complex. Attempts to observe the pentacoordinate copper species by mass spectrometry failed, presumably due to vapor-phase dissociation.

In solution the interaction of $Cu(TFAA)_2$ with γ-picoline N-oxide was observed spectrophotometrically. The visible near-infrared spectra of solutions presumed to contain mainly the 1:1 complex were similar to that of the mull. Using a previously described method[5] an equilibrium constant for the formation of the 1:1 complex, $Cu(TFAA)_2 + L = Cu(TFAA)_2L$, was found to be $K = 40 \pm 10$ l. $mole^{-1}$. The large uncertainty in this constant is due to some formation of 2:1 complex at higher γ-picoline N-oxide concentrations which made the exact evaluation of the extinction coefficient of the pure 1:1 complex difficult. The presence of an isosbestic point at 16,300 cm^{-1} for all solutions but those with very high ligand to $Cu(TFAA)_2$ ratios is evidence that only the 1:1 complex and $Cu(TFAA)_2$ are present as the major absorbing species at lower γ-picoline N-oxide:$Cu(TFAA)_2$ ratios. Solutions of the 1:1 complex in deuteriochloroform have a μ_{eff} of 1.95 BM, and the magnetic susceptibility of such solutions was observed to follow a Curie $(1/T)$ relationship from −50 to +60° ruling out antiferromagnetic behavior.

The proton magnetic resonance spectra were observed for the complexes of $Cu(TFAA)_2$ with an excess of γ-picoline N-oxide under conditions of rapid ligand exchange. Isotropic shifts were calculated using as diamagnetic positions those found for the free ligand at the given temperature and concentration, which were approximately those found for the 1:1 $Zn(TFAA)_2$–N-oxide complex. All resonance peaks were significantly broadened owing to the presence of paramagnetic copper(II) making resolution difficult except for widely separated resonances. As a consequence of this broadening the shifts in the α-proton resonances could not be accurately determined. Thus the data presented in Figure 1 include only the β and γ-CH_3 proton resonances.

An electron spin lifetime of $\tau_s \cong 10^{-8}$ sec at room temperature was estimated from the degree of resolution of the copper hyperfine splitting in the esr spectrum of a deuteriochloroform solution containing predominantly the 1:1 γ-picoline N-oxide:$Cu(TFAA)_2$ complex.

Discussion

The isotropic shifts of the γ-picoline N-oxide protons complexed with $Cu(TFAA)_2$ are temperature dependent, but unlike normal isotropic shifts which follow a Curie (T^{-1}) relationship, those observed for the β and γ-CH_3 protons increase with increasing temperature (Figure 1). The ratios of the isotropic shifts for these protons also vary, approaching a constant value β/γ-CH_3 ~ 0.4, at elevated temperatures. This is similar to the ratio previously observed for this ligand complexed with nickel acetylacetonate[2] or $Ni(TFAA)_2$,[12] and therefore at elevated temperatures spin appears to be delocalized into the π orbital of the N-oxide. [This conclusion is further substantiated by solution nmr data on a complex of β-picoline N-oxide and $Cu(TFAA)_2$ which show the α, β-CH_3, and γ proton resonances to be shifted upfield whereas the β proton resonance is shifted downfield.] At low temperatures, very little spin is delocalized in the γ-picoline N-oxide ring and the distribution is not that expected using only the ligand's π orbitals. Such behavior coupled with the Curie behavior of the magnetic susceptibility indicates an equilibrium between at least two paramagnetic species having approximately the same magnetic moments.

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(9) The computer program of H. Stone was used. An alternative decomposition into two Gaussians at 12,800 and 15,500 cm^{-1} gives an equally satisfactory fit to the data.

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The spin distribution data combined with the spectral data suggest that the low-temperature form is a high symmetry penta- or hexacoordinate species in which the unpaired electron resides principally in a metal orbital which does not overlap with the N-oxide's annular π system. The high-temperature form may be a pentacoordinate species of low symmetry or alternatively a "tetrahedral" structure in which one TFAA acts as a monodentate group with the other coordination site being occupied by an N-oxide. Either of these alternatives would be favored at high temperatures by entropy considerations and is consistent with some fraction of an unpaired electron being located in metal orbitals which allow delocalization into the π system of the N-oxide.

From the observed line widths a mechanism for the nuclear spin relaxation can be deduced. Thus the transverse relaxation time of the proton, T_2, which is inversely related to the line width is given by eq 1,[13] in which ω_s is the electronic Larmor precession frequency.

$$\frac{1}{T_2} = \frac{S(S+1)g^2\beta^2\gamma_I{}^2}{15r^6}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s{}^2\tau_c{}^2}\right] + \frac{S(S+1)A^2}{3h^2}\left[\tau_e + \frac{\tau_e}{1+\omega_s{}^2\tau_e{}^2}\right] \qquad (1)$$

Under conditions for which the broadening due to spin delocalization is small the second term involving A, the hyperfine coupling constant, can be neglected. The correlation time τ_c is defined by the relationship $\tau_c{}^{-1} = \tau_s{}^{-1} + \tau_r{}^{-1}$, where τ_r is the rotational correlation time. This quantity can be independently approximated for a spherical particle by the Debye expression, $\tau_r = 4\pi\eta r^3/3kT$, where η is the viscosity of the solution and r is the effective radius of the sphere. Since $\tau_s \cong 10^{-8}$ sec was independently determined by an esr experiment, τ_c can be evaluated and compared with the magnitudes of its components. Using the line-width data taken from the system described in Figure 1 (for the γ-CH_3 protons in a pure 1:1 complex ($\langle r^1\rangle_{av}{}^{1/6}$ = 7.13 A, $1/T_2 = 270$ sec^{-1}, $T = 284$°K) a value of $\tau_c = 3.4 \times 10^{-10}$ is calculated. This compares with $\tau_r = 3.2 \times 10^{-10}$ for a particle of radius 5.5 A calculated using the Debye equation. As this radius is approximately that of the β-diketone ring system, these calculations strongly indicate that nuclear relaxation is effected by the fluctuating magnetic field seen by the proton caused by the tumbling of the complex in solution. Such a mechanism is also supported by the increase in line width with decrease in solution temperature. These data contrast with the nuclear relaxation mechanism previously postulated for Ni(II) and Co(II) complexes[14] which have much shorter electron spin relaxation times.

Corrections for pseudo-contact shifts cannot be made because the exact geometry of the complex for which delocalization is being observed is unknown. However, using the geometric factors for the 2:1 Ni-$(AA)_2$-N-oxide complex[2] and the g tensor anisotropy found for the solid $Cu(TFAA)_2$-γ-picoline N-oxide complex, pseudo-contact shifts of -5, -6, and -3 cps can be estimated at 39° for the α, β, and γ-CH_3 protons of this ligand coordinated along the fourfold axis of a square pyramid.

Acknowledgment.—We thank Professor J. Turkevich and Dr. J. Karra for performing the epr experiments and Dr. E. B. Miller for the mass spectrometry experiments.

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[13] This and other equations are discussed in the review by D. R. Eaton and W. D. Phillips in "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh Ed., Academic Press Inc., New York, N. Y., 1965, p 103. This equation neglects the g tensor anisotropy which can also contribute to the relaxation of the proton spin: H. Sternlicht, *J. Chem. Phys.*, **42**, 2250 (1965). However, for systems with small anisotropies the contribution from this mechanism is small and can be ignored.

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The Alkali Metal Salt Catalyzed Disproportionation Reactions of Alkyldisilanes

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The alkali metal salt catalyzed disproportionation reactions of disilane in 1,2-dimethoxyethane have been recently investigated.[1] The first step in these reactions is a base-catalyzed disproportionation similar to those found for other silyl compounds[2-5]

$$xSi_2H_6 \xrightarrow{\text{salt}} xSiH_4 + (1/x)(\text{-}SiH_2\text{-})_x \qquad (1)$$

The relative catalytic effectiveness for the disilane disproportionations were KH > LiD > LiCl. For the metal hydride reactions a second, slower reaction also occurred (M = K or Li)

$$(1/x)(SiH_2)_x + MH \longrightarrow MSiH_3 \qquad (2)$$

This reaction was faster with KH than with LiD.

In this note we report the extension of these reactions to a number of alkyldisilanes.

Experimental Section

The cleavage reactions were carried out at room temperature in 100-ml round-bottom flasks which were fitted with either Teflon needle valves or stopcocks and ground joints to allow for transfer of reactants and volatile products between standard vacuum systems and the reaction vessels. The reaction vessels were also fitted with a side tube through which the solid catalysts could be added.

The solvent, 1,2-dimethoxyethane, was dried over potassium sand at −78° until the ether was a dark blue. The solvent was then distilled, *in vacuo*, to the reaction vessel.

The alkyldisilanes used were prepared as described by Bolduc and Ring[6] or by Groschwitz, Ingle, and Ring.[7] These reactants

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