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Effect of Molecular Motion on Electron Spin Phase Memory Times for Copper(II) Complexes in Doped Solids

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Abstract. Electron spin phase memory times, T_m, as a function of temperature were measured for Cu(II) bis(diethyldithiocarbamate), $Cu(Et_2dtc)_2$; Cu(II) bis(diethyldithiophosphate), $Cu(Et_2dtp)_2$; Cu(II) bis(diphenyldithiophosphate), $Cu(Ph_2dtp)_2$; Cu(II) tetratolylporphyrin, CuTTP; vanadyl 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin, VOTTP-COOH; and Ag(II) tetratolylporphyrin, AgTTP, doped into powdered samples of closely-related diamagnetic hosts. For the three metalloporphyrins, the electron spin relaxation rate ($1/T_m$) increased monotonically with increasing temperature. However the temperature dependence of the relaxation rate was not monotonic for the three other Cu(II) complexes. For $Cu(Et_2dtc)_2$ and $Cu(Et_2dtp)_2$ the temperature dependence of $1/T_m$ between about 85 and 130 K is attributed to the effects of methyl rotation, with activation energies of 1.0 kcal/mole. Between 120 and 250 K the $1/T_m$ data for $Cu(Ph_2dtp)_2$ exhibit effects that are attributed to motion of the phenyl rings.

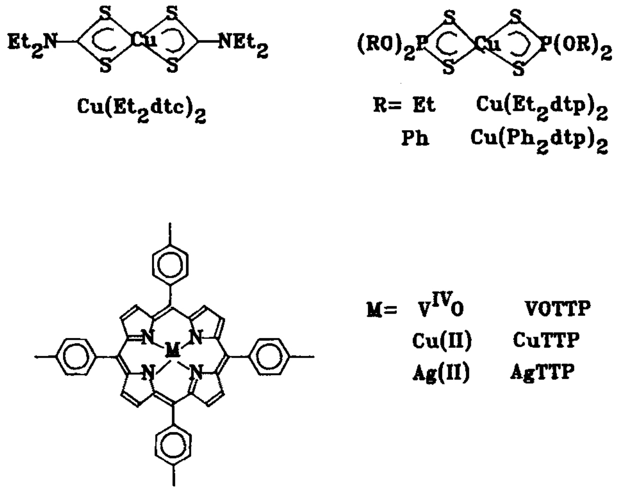
1. Introduction

In a two-pulse electron spin echo experiment, spins are flipped by the first pulse (90°) and re-focused by the second pulse (180°) to form an echo. If molecular motion changes the resonant frequency for a spin during the time between the first and second pulses, that spin is not re-focused by the second pulse. Such a process then contributes to an increased rate of de-phasing that is observed as a decrease in T_m (an increase in $1/T_m$). Examples of this effect in electron spin echoes have been documented for methyl rotation in irradiated zinc acetate [1], methyl rotation in nitroxyl radicals [2, 3], and methyl rotation in Cr(V) complexes [3]. In this paper we report dynamic effects on T_m for two Cu(II) complexes that are attributed to methyl rotation and the effects of phenyl ring motion in another Cu(II) complex.

2. Experimental

Metal complexes were prepared by literature methods: Cu(Et$_2$dtc)$_2$ and Ni(Et$_2$dtc)$_2$ [4]; Cu(Et$_2$dtp)$_2$, Ni(Et$_2$dtp)$_2$, Cu(Ph$_2$dtp)$_2$, and Ni(Ph$_2$dtp)$_2$ [5]; CuTTP [6]; ZnTTP [7]; VOTTP-COOH [8]; AgTTP [9]. The structures of Cu(Et$_2$dtc)$_2$, Cu(Et$_2$dtp)$_2$, Cu(Ph$_2$dtp)$_2$, VOTPP, CuTTP and AgTTP are shown in Scheme I.

Doped solids were prepared by co-precipitation from solutions with 1 : 500 mole ratios of the paramagnetic species to the diamagnetic host. Electron spin-echo measurements were made on the spectrometer that has been described previously [3, 10]. For measurements below 77 K an Oxford temperature controller and ESR900 liquid helium cryostat were used. Above 77 K a Varian flow-through dewar and temperature controller were used. Temperatures were calibrated by replacing the sample tube with a tube containing a thermocouple. Data were obtained with an over-coupled Varian V4531 TE$_{102}$ resonator and a $90°-\tau-180°-\tau$-echo sequence using 30 and 60 ns, 20 W pulses or 20 and 40 ns pulses attenuated from a nominal 1 kW TWT [10]. Typically 1024 data points were collected, starting at $\tau = 140$ ns, with 3 to 6 ns increments in τ. Larger τ increments were used at temperatures where T_m was longer. Values of T_m were obtained from the spin echo data by non-linear least-squares fit to a single exponential of the form $\exp(-2\tau/T_m)$. Although this expression is an incomplete representation of the echo decay in some dynamic regimes, it provides a uniform method of analysis to demonstrate the temperature-dependence of the relaxation processes.



Scheme I.

3. Results

Representative data showing the temperature dependence of the electron spin echo data for $Cu(Et_2dtc)_2$ and $Cu(Et_2dtp)_2$ in the doped solids are shown in Figs. 1 and 2. Relaxation rates as a function of temperature are shown in Fig. 3 for the six complexes that were studied. There is an overall increase in relaxation rate with increasing temperature. Within the series of metalloporphyrins, the temperature dependence increases in the order VOTTP < CuTTP < AgTTP. The $g_{\parallel}$ and $g_{\perp}$ values for these complexes are VOTTP, 1.984, 1.964; CuTTP, 2.203, 2.049; and AgTTP, 2.108, 2.040. Thus the temperature dependence of T_m does not correlate with g anisotropy or deviation from $g = 2.0023$. It also does not correlate with the magnitude of the metal nuclear hyperfine splitting, which is larger for Cu(II) than for Ag(II). ENDOR studies have shown that the extent of delocalization of unpaired electron spin density into the porphyrin ring increases in the order CuTTP < AgTTP [11]. The magnitude of the nitrogen hyperfine splitting (A_N) in the fluid solution EPR spectra of MTPP also is an indica-

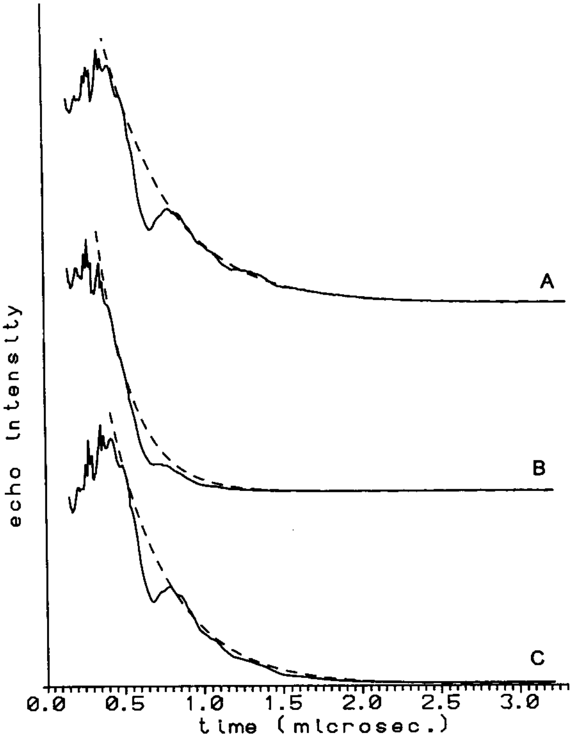


Fig. 1. Two-pulse electron spin echo data for $Cu(Et_2dtc)_2$ doped into $Ni(Et_2dtc)_2$ at the magnetic field that corresponds to the maximum intensity for the perpendicular lines, recorded at A) 150 K, B) 98 K, and C) 85 K. The dotted lines are fits to a single exponential decay with time constant, T_m = A) 0.91 μs, B) 0.36 μs, and C) 0.78 μs.

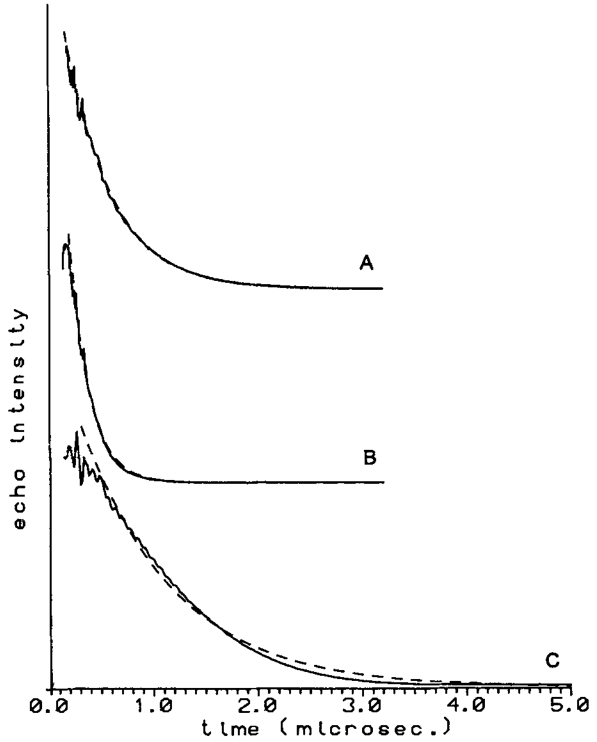


Fig. 2. Two-pulse electron spin echo data for $Cu(Et_2dtp)_2$ doped into $Ni(Et_2dtp)_2$ at the magnetic field that corresponds to the maximum intensity for the perpendicular lines, recorded at A) 160 K, B) 109 K, and C) 77 K. The dotted lines are fits to a single exponential decay with time constant, T_m = A) 0.88 μs, B) 0.37 μs, and C) 1.73 μs.

tion of the extent of delocalization of the metal unpaired electron. The values of A_N increase in the order vanadyl (2 to 3 G) < Cu^{2+} (~16 G) < Ag^{2+} (~22 G) [12]. More extensive delocalization results in stronger electron-nuclear hyperfine interaction with protons on the periphery of the porphyrin ring. It is proposed that modulation of these interactions is a major contribution to the differences in the temperature dependence of T_m for the three metalloporphyrins.

For $Cu(Et_2dtc)_2$ and $Cu(Et_2dtp)_2$ the phase memory times, T_m, were shorter and the relaxation rates, $1/T_m$, were faster between about 85 and 130 K than at either lower or higher temperatures. This behavior is characteristic of a temperature interval in which the rate of a dynamic process (ω_c^{-1}) that averages different magnetic environments is of the same order of magnitude as the time between the first and second pulses of the two-pulse echo sequence. Equations have been published that relate ω_c^{-1} to T_m for the limiting cases of ω_c^{-1} greater than or less than the hyperfine splitting that is collapsed by the motion ($\Delta\omega$) [1, 2]. In accordance with these equations,

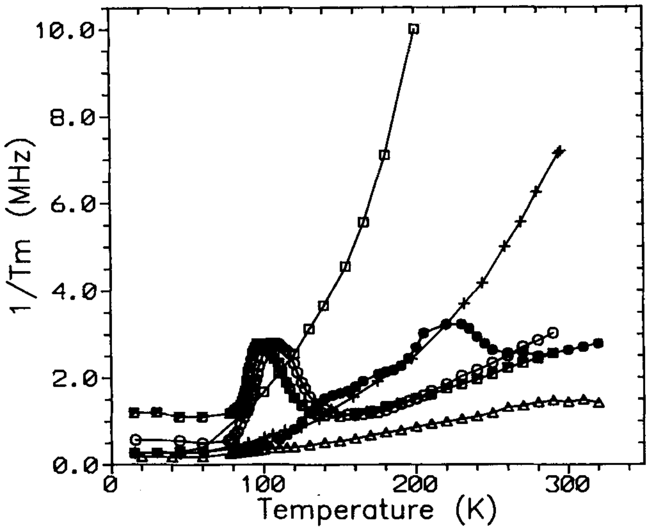


Fig. 3. Temperature dependence of $1/T_m$ for the perpendicular lines in the spectra of VOTTP doped into ZnTTP (△), CuTTP doped into ZnTTP (+), AgTTP doped into H_2TTP (□), $Cu(Et_2dtc)_2$ doped into $Ni(Et_2dtc)_2$ (◪), $Cu(Et_2dtp)_2$ doped into $Ni(Et_2dtp)_2$ (O), and $Cu(Ph_2dtp)_2$ doped into $Ni(Ph_2dtp)_2$ (●).

ln(T_m^{-1}) was plotted vs. $1/T$ for $Cu(Et_2dtp)_2$ between 85 and 105 K and for $Cu(Et_2dtc)_2$ between 85 and 96 K. Values of ln(T_m) were plotted vs. T for $Cu(Et_2dtp)_2$ between 115 and 130 K and for $Cu(Et_2dtc)_2$ between 112 and 130 K. The slopes of these plots gave $E_a = 1.0 \pm 0.1$ kcal/mole. The small temperature intervals over which data were obtained limits the accuracy of the value of E_a. However, it should be noted that a 15 K interval at about 100 K corresponds to three times as large a change in $1/T$ as a 15 K interval at 300 K.

Between 120 and 240 K the values of T_m for $Cu(Et_2dtp)_2$ in the doped solids were shorter than for $Cu(Et_2dtc)_2$. This increase in relaxation rate is attributed to torsional motion of the phenyl rings.

Values of T_m also were measured for $Cu(Et_2dtc)_2$ and CuTTP in frozen toluene : chloroform solution (2 : 1 by volume). In the frozen glass, the relaxation rates above about 70 K increased more rapidly with increasing temperature than in the doped solids. This increase in relaxation rate is attributed to molecular motions that occur to a greater extent in the glass than in the solid. This overall increase made it more difficult to detect the effects of the methyl rotation on T_m in frozen solution than in the doped solids.

Barriers to rotation for aliphatic methyl groups that have been measured previously for other compounds by a variety of techniques are in the range of 1.0 to 3.0 kcal/mole [1–3, 13, 14]. The higher values typically are for more sterically encumbered environments including the gem-dimethyls of nitroxyl radicals [2, 3] and a steroid methyl [13].

4. Conclusion

The effects of methyl group rotation on T_m for $Cu(Et_2dtc)_2$ and $Cu(Et_2dtp)_2$ can be observed in doped solids between 85 and 130 K. The activation energy for the rotation is 1.0 kcal/mole, which is consistent with values obtained for other aliphatic methyl groups. These results provide an example of the utility of electron spin echo techniques in probing molecular dynamics in $S = 1/2$ transition metal complexes.

Acknowledgements

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