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(2) The processes shown as reactions 1 and 2 differ in whether the proton is the object of catch (1) or tug-of-war (2) between the bases.

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(15) In these experiments collection efficiencies for ions of different mass have been considered by studying the $(C_5H_5N)(C_5D_5N)H^+$ ion. The corresponding peaks had an intensity ratio of 4:3 so the effect is small but can be corrected for.

(16) This assumes entropy corrections in our procedure to be negligible.

(17) For this reason the higher energy fragmenting ions formed in the course of collision-induced dissociation (CID) are less sensitive to differences in base strength. This was shown experimentally in the *sec*-butylamine/3-aminopentane case.

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Temperature Dependence of Proton Spin-Lattice Relaxation Times in Some Paramagnetic Transition Metal Acetylacetonate Complexes. The Possible Influence of the Jahn-Teller Effect on Electron Spin Relaxation

Sir:

Nuclear spin-lattice relaxation (T_1) in discrete paramagnetic transition metal complexes is dominated by electron-nuclear dipolar coupling time modulated by spin-lattice electron spin relaxation (τ_{e_1}) and molecular reorientation (τ_R); the overall correlation time (τ_c) is given by $\tau_c^{-1} = \tau_R^{-1} + \tau_{e_1}^{-1}$.[1] Electron spin relaxation is usually considered to arise by time modulation from rotational reorientation of either the anisotropic part of the g tensor (for $S = \frac{1}{2}$) and/or, for $S \geqslant 1$, the quadratic zero-field splitting. If the Redfield limit ($\tau_{e_1} > \tau_R$) holds for the electron spin relaxation, then, in general $\tau_{e_1}^{-1} = k\tau_R(1 + \omega_s^2\tau_R^2)^{-1}$, where k is a parameter and depends on the particular mechanism, and ω_s the electron resonance frequency. Usually $\omega_s\tau_R \gg 1$ and $\tau_{e_1}^{-1} = m\tau_R^{-1}$ and $\tau_c^{-1} = n\tau_R^{-1}$, where m and n are constants.[1] If the Redfield limit is not valid, τ_e is a simple fraction[2] of τ_R and the relationship $\tau_c^{-1} = n\tau_R^{-1}$ still holds. *Consequently, the temperature dependence of T_1 should always be that of τ_R*. τ_R varies with temperature as $\tau_R = \tau_0 \exp(E_R/RT)$ and because to good approximation,[3] $T_1^{-1} = K\tau_c$, we would expect a plot of ln (T_1^{-1}) vs. $1/T$ to be linear with slope E_R/R, where E_R is the activation energy for rotational reorientation. This behavior is only to be expected provided τ_R dominates τ_{e_1}.

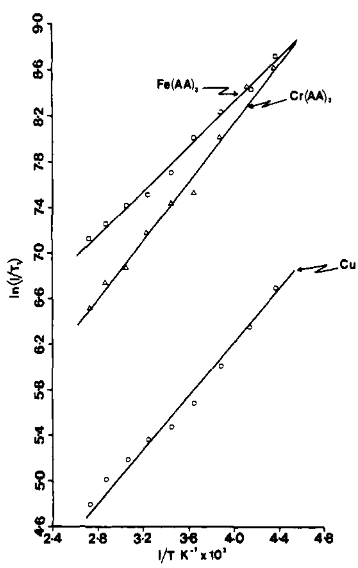

Figure 1. Plot of ln ($1/T_1$) vs $1/T$ for the CH_3 proton T_1 of $Cu(AA)_2$, $Cr(AA)_3$, and $Fe(AA)_3$.

The solvent properties of dissolved transition metal acetylacetonate $M(AA)_l$ ($l = 2, 3$) complexes should be sufficiently similar for E_R to be approximately the same for each and so the temperature dependence of τ_R should be similar for all the Tris complexes of say the first or second transition series. Room-temperature ^1H relaxation studies of the CH_3 protons have demonstrated that for some of these complexes (M = Cr, Fe, Cu), τ_R dominates T_1 whereas for others (M = V, Mn, Ru), τ_e dominates.[2,4] Consequently, variable-temperature T_1 studies on a series of these complexes will yield information on the mechanism(s) of electron spin relaxation in solution. Specifically, for paramagnetic molecules in solution, is rotational reorientation the sole process affecting τ_e?

Plots of ln (T_1^{-1}) vs. $1/T$ for M = Cr, Fe, and Cu are shown in Figure 1.[5] A linear relationship is found with E_R (kJ mol^{-1}) 10.87 (Cr),[6] 9.20 (Cu), and 8.40 (Fe) demonstrating that the solution properties are approximately invariant to the metal ion.[7] Similar plots for M = V, Mn, and Ru are shown in Figure 2. The linearity of these plots is poor and for Mn and V there is a strong suggestion of curvature at the high-temperature end. If a linear least-squares fit[8] is performed E (kJ mol^{-1}) is estimated to be 2.16 (V), 1.34 (Mn), and 3.56 (Ru). We conclude that rotational reorientation is probably not the dominant time-dependent process for electron spin relaxation, the magnetic properties of the complex being modulated at a rate faster than τ_R. For Mn and V, in particular, the associated energy barrier is quite low.

There is no immediate connection between the ground states (in O_h symmetry) of those molecules Mn (^5E), V ($^3T_1$), Ru ($^2T_2$) which can account for the above behavior. All states, however, interact asymmetrically with the spatial environment and, in principle, are subject to Jahn-Teller forces.[9] It is known that Mn(III) complexes are strongly Jahn-Teller affected both in the solid and solution[10] and the ground state potential energy surfaces contain maxima and minima separated by low energy barriers. Estimates[10,11] of the barrier for $Mn(AA)_3$ from

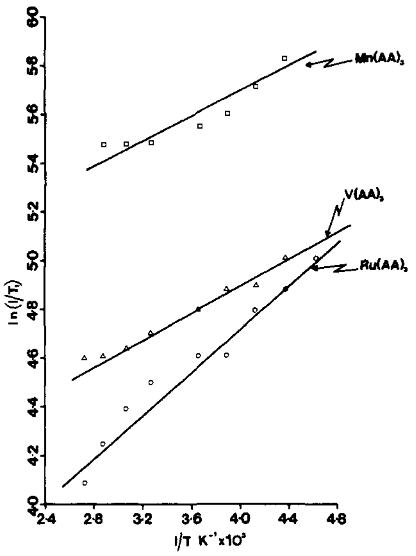

Figure 2. Plot of ln $(1/T_1)$ vs. $1/T$ for the CH_3 proton T_1 of Ru(AA)$_3$, V(AA)$_3$, and Mn(AA)$_3$.

crystal-field theory are 60 cm^{-1} (0.72 kJ mol^{-1}) and 50 cm^{-1} (0.59 kJ mol^{-1}). We propose that as this pseudorotation occurs the magnetic properties of the complex are time modulated and electron spin relaxation results. Our estimate of the barrier is somewhat higher than the theoretical although the many approximations made in the crystal-field calculations make a close comparison of the theoretical and experimental results unwarranted. This is especially so when the curvature of Figure 2 is taken into account. In fact, it may be somewhat premature to assume a simple exponential dependence of the Jahn-Teller time process on the barrier height.[8] The ground-state potential energy surface of V and Ru is likely to be quite complex although the gross effects of Jahn-Teller forces are less than for the Mn complex.[9] Our results suggest though that electron spin relaxation resulting from time modulation of the potential energy surface is probably operative for these complexes.[12]

The above analysis suggests that NMR relaxation time measurements may be a useful probe into the finer details of the ground-state potential energy surface of certain transition metal complexes. However, variable-temperature relaxation time measurements can certainly be used as demonstrated above to determine whether rotational reorientation dominates the nuclear and electron spin relaxation processes.

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(3) T_1^{-1} is given, in general, by the Solomon–Bloembergen equation $T_1^{-1} = K(\tau_{c_1} + \tau_{c_2}[1 + \omega_s^2\tau_{c_2}^2]^{-1})$. We have shown elsewhere[1] that at high magnetic field strengths term(s) associated with the spin–spin electron spin relaxation may be neglected.

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(5) Proton spin relaxation times were determined as described previously[2] at 90 MHz for a solution containing 0.05 M complex in $CDCl_3$.

(6) The relaxation behavior of the CH_3 protons in Cr(AA)$_3$ is complicated by the overlapping of the CH_3 and CH resonances. This may introduce a substantial error in E_R. E_R for the analogous Tris complex of 3-methylacetylacetonate is 8.4 kJ mol^{-1}.

(7) E_R for the diamagnetic Pd(AA)$_2$ and Co(AA)$_3$ complexes as determined from ^1H T_1 measurements are 10.79 and 10.39 kJ mol^{-1}, respectively.

(8) A nonlinear curve fitting of the T vs. T_1 data to the expression $T_1 = k_1 \exp(-k_2/T) - k_3T$ yielded for Mn(AA)$_3$, $k_1 = 0.055$ (4), $k_2 = 274$ (1), $k_3 = 6.0$ (5) $\times 10^{-5}$, and $E = k_2R = 2.3$ kJ mol^{-1}. We have noted as well, anomalous temperature dependence of CH_3 proton T_1 in tris(diethyldithiocarbamato)manganese(III) and estimate from a linear least-squares analysis a barrier height of 6.1 kJ mol^{-1} or $k_1 = 0.042$ (2), $k_2 = 3.37$ (2), $k_3 = 3.2$ (3) $\times 10^{-5}$, and $E = 2.8$ kJ mol^{-1}. Although we have been unable at present to justify theoretically an expression of the above form, electron spin relaxation in paramagnetic solids resulting from Jahn–Teller forces is known (R. Englman, "The Jahn–Teller Effect in Molecules and Crystals", Wiley-Interscience, New York, N.Y., 1972, Chapter 6, p 190) to exhibit a complex temperature dependence, an exponential function at low temperatures tending to a linear dependence at high temperatures. This theoretical approach has been developed, however, by assuming that the crystals are strained by intermolecular interactions. Such a theoretical model cannot be applied directly in solution because of the different nature of the forces acting. Nevertheless, the solid-state results tend to support a functional dependence of T_1 vs. T of the form introduced above.

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Cyclohexane-Soluble, Helical Cooligopeptides with Alternating L-Isoleucine and D-Alloisoleucine Residues

Sir:

Specific helical conformations variously called β-, π_{LD}-, or LD-helices have been proposed[1-3] for chains of alternating L- and D-amino acid residues. However, experimental evidence for these helices is rather limited. We are investigating a series of Boc-protected L,D-alternating cooligopeptide methyl esters derived from the diastereomeric amino acids L-isoleucine (H-L-Ile-OH) and D-alloisoleucine (H-D-aIle-OH) with -D-aIle- as the C-terminal residue. The highest members of this series that we have synthesized, Boc-D-aIle-(L-Ile-D-aIle)$_3$-OMe (I) and Boc-(L-Ile-D-aIle)$_4$-OMe (II), are soluble in cyclohexane. Our data suggest that in this solvent these two cooligopeptides assume helical conformations of the β-type, with the same prevailing sense of twist.

Analytically pure I and II were prepared from commercial amino acids of very high optical purity using conventional racemization-free methods. We checked the optical purities and found that L-isoleucine was practically 100% pure, and D-alloisoleucine contained less than 3% of combined enantiomeric and diastereomeric impurities.

The CD spectra of I and II in cyclohexane between 185 and 250 nm (Figure 1) have very high molar ellipticity maxima, indicating that these cooligopeptides are predominantly in either one or a small number of similar conformation(s). The profiles are similar to that observed[4,5] for poly(L-Ala-D-Val) in trifluoroethanol, which has been assigned to a β-helix, but the intensity of the dichroic bands is much higher (molar ellipticity per residue at the extrema: I, −21 500, +50 000; II, −16 000, +27 000; poly(L-Ala-D-Val), −3300, +6000. The poly (L-Ala-D-Val) values have been approximated from Figure 3 of ref 5). Although the curves of Figure 1 also resemble those[6] of L-oligopeptides in the β-sheet structure, they cannot be attributed to any multimolecular aggregate. Our evidence for this is that spectroscopic measurements at 25-30 °C reveal no appreciable concentration dependence for the properties of I and II in cyclohexane in the range of concen-