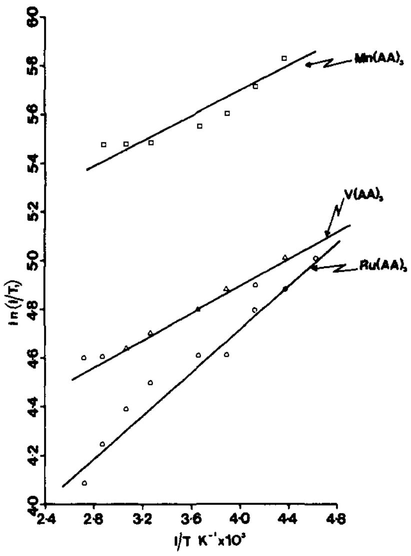

Figure 2. Plot of ln $(1/T_1)$ vs. $1/T$ for the CH_3 proton T_1 of $Ru(AA)_3$, $V(AA)_3$, and $Mn(AA)_3$.

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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(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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(12) A referee has suggested that the anomalous temperature dependence of T_1 in the Mn, V, and Ru complexes may arise from depopulation of low-lying Kramers multiplets. Although this possibility cannot be excluded for $Ru(AA)_3$ for which the CH_3 protons exhibit a non-Curie law dependence of their isotropic shift, it can be dismissed as a possibility for $V(AA)_3$ and $Mn(AA)_3$ because the methyl proton isotropic shift follows a T^{-1} dependence. This result is particularly significant for $Mn(AA)_3$ where the T^{-1} dependence of the isotropic shift is almost exact whereas the departures from linear behavior in the relaxation time are greatest.

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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-

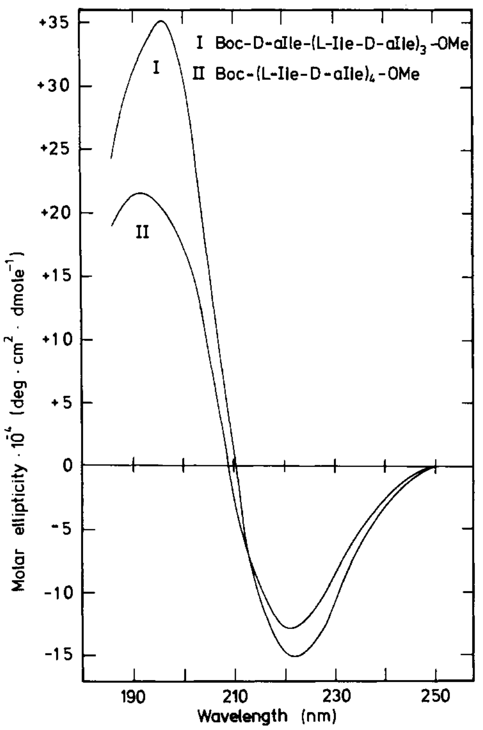

Figure 1. CD spectra of indicated cooligopeptides in cyclohexane solution: concn, 0.2 mg/ml; T, 25 °C. Values for the molar ellipticity of each oligomer are recorded.

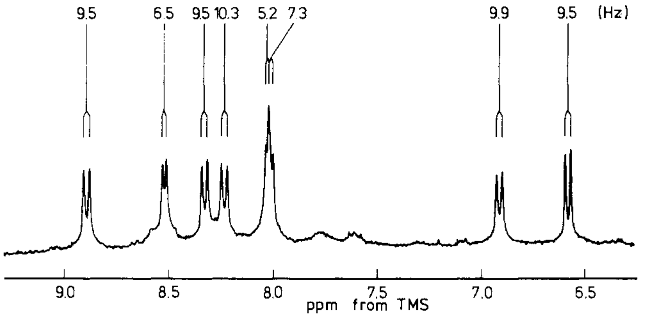

Figure 2. Peptide proton resonances in the 360-MHz FT ^{1}H NMR spectrum of II in cyclohexane-d_{12} (concn, 20 mg/ml; T, 25 °C). The assignment is based on the integrated spectrum and on NMR spectra of other oligopeptides.[5,11] The digital resolution is 0.488 Hz/point.

trations from 1 to 10 mg/10 ml and that vapor pressure osmometry measurements (at 37 °C) yield apparent molecular weights only 1.9 times the formula weights at concentrations as high as 200 mg/10 ml. In the case of I, for which measurements at different concentrations down to 50 mg/10 ml were carried out, the data extrapolate to the formula weight of the cooligopeptide at infinite dilution. Although the possibility of an association to dimer at high concentrations cannot be ruled out, these data suggest that I and II are monomeric in the conditions of our spectroscopic measurements. NMR spectra (360 MHz) of cyclohexane solutions of I and II show well-resolved peptide proton resonances with several vicinal coupling constants larger than 8.6 Hz. Figure 2 illustrates this for II. Using the refined relationship given by Bystrov et al.[7] such large coupling constants can be assigned with large confidence to dihedral angles θ between the H-N-C$^\alpha$ and the N-C$^\alpha$-H planes which are in the range of 150° to 180°. These correspond to conventional [8]dihedral angles ϕ about the N-C$^\alpha$ bond in the range of $-90°$ to $-150°$ for L-residues and of $+90°$ to $+150°$ for D-residues. Values of ϕ in these ranges characterize β-helices.[2,3] On these grounds we conclude that helical conformations of this type exist for I and II in cyclohexane. A regular β-helix, which would have a number of nonbonded NH protons at its two extremities, is not consistent with the results of IR-absorption measurements, which reveal only a very weak band at the frequencies expected (~3440 cm^{-1}) for nonbonded NH protons. The amide A region shows a band with a maximum (3310 cm^{-1}) in the range of frequencies typical[9] of the strong hydrogen bonds of L-oligopeptides in the β-sheet structure, implying there are hydrogen bonds of comparable strength in I and II in cyclohexane solution. This band has a shoulder on the high frequency side, suggesting that some of the hydrogen bonds may be weaker. It seems therefore that the NH protons, which are not involved in the strong interturn bonding, form less strong intramolecular bonds, possibly of the C$_7$ type.[10] These bonds and a distortion of the helix could account for the several coupling constants observed (Figure 2).

The similarity of the two curves of Figure 1 may evidence an identity of the sense of twist. For infinitely long chains of alternating diastereomeric L- and D-residues, the difference in energy of the two senses of twist of a β-helix is determined solely by the configuration of the side groups. For short chains such as those of I and II, the sequence number of the two different residues in the chain may play an important role in stabilizing or destabilizing one sense of twist with respect to the other. Further study is projected to establish the relative influence of the chiral side groups of identical configuration on the conformation of I and II.

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Solvolysis of Secondary Substrates by a Limiting Mechanism. The Cyclooctyl System

Sir:

The solvolysis reactions of secondary substrates have recently been described in terms of competitive neighboring-group (k_Δ) and nucleophilic solvent (k_s) assisted processes, eq 1,

$$k_t = k_\Delta + k_s \tag{1}$$

with these processes approaching a limiting or unassisted k_c process as assistance becomes weak.[1-4] There has been much debate concerning the importance of the k_c pathway for the