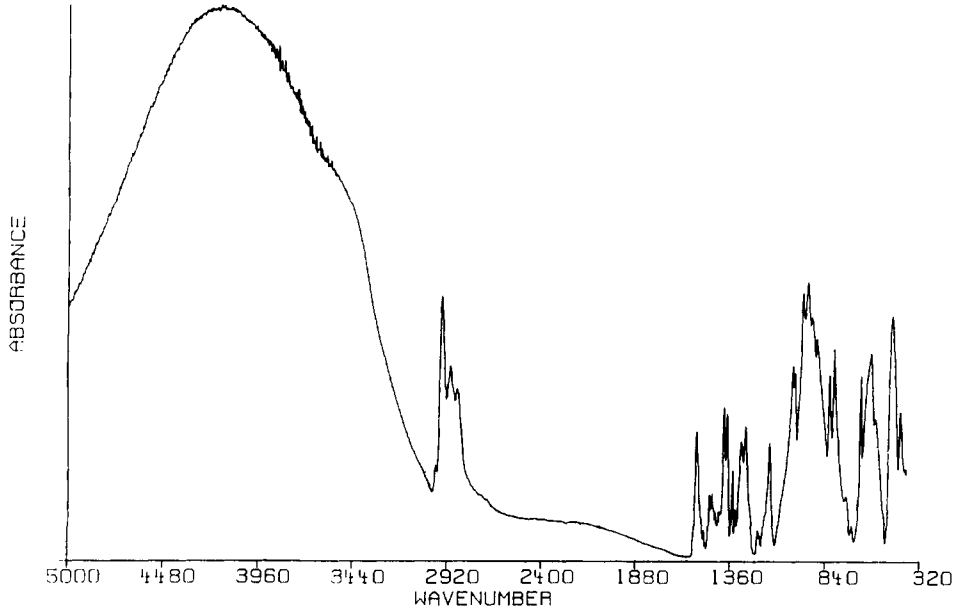

Figure 2. Infrared spectrum of Ir(1,5-COD)(3,6-DBCat)$_2$ recorded as a KBr pellet showing the normal ligand vibrational bands at low energy and an electronic transition centered at 4200 cm^{-1}. Band asymmetry is due to moisture in the KBr; a single symmetrical transition is observed for the complex in solution.

pearing as two quinone ligand-based redox couples that most closely resemble the couples of Fe(bpy)(3,6-DBSQ)(3,6-DBCat).[11] Structural features of the molecule, with the anisotropy and absence of ligand proton hyperfine coupling of the EPR spectrum, show that the electronic description is not purely that of the Ir(III) form,[2] however.

Interligand charge transfer between catecholate donor and olefin acceptor orbitals exists as a third possibility for the low-energy transition.[12] Two features of the complex may be indirectly related to this assignment. Synergistic interligand π donor-acceptor bonding would remove charge from the catecholate C-O antibonding orbital. This may contribute to the shorter C-O length for oxygen atoms bonded trans to Ir-olefin bonds and the relatively long C-C bonds for the coordinated olefin groups. Second, it was of interest to investigate the counterligand dependence of the low-energy transition. Attempts to replace the 1,5-COD ligand with CO, DIPHOS, and 2,2'-bipyridine have all failed.[13] The 1,5-COD ligand is tightly bound to the high oxidation state metal, although the Ir-C lengths to the olefin carbon atoms are not unusually short[14] and the trans Ir-O length is identical to the length at the positions cis to the olefin bonds. This is in contradistinction to the catecholate-nitrosyl bonding in Ir(NO)(PPh$_3$)(Br$_4$Cat) where cooperative trans donor-acceptor coordination resulted in shortening of both trans Ir-N and Ir-O bonds.[15] Whether or not it is responsible for the low-energy electronic transition, interligand bonding between the catecholate and olefin ligands of Ir(1,5-COD)(3,6-DBCat)$_2$ may be an important ligand stabilization effect.

Further studies on coligand bonding effects within the IrL$_2$(Cat)$_2$ series will provide more detailed information on the origin of this unusual transition.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for Ir(1,5-COD)(3,6-DBCat)$_2$ (9 pages); tables of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(11) Fe(bpy)(3,6-DBSQ)(3,6-DBCat) undergoes oxidation at -0.319 V and reduction at -0.831 V (vs Fc$^+$/Fc). Both are reversible one-electron processes that will be described in a separate publication.

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(13) In typical experiments, Ir(1,5-COD)(3,6-DBCat)$_2$ (0.05 g) was refluxed in toluene for the period of 1 day in the presence of an excess of either 2,2'-bipyridine or 1,2-bis(diphenylphosphino)ethane (DIPHOS) or with CO bubbled through the solution. Electronic spectra obtained on these solutions at the conclusion of the experiment indicated the presence of unreacted Ir(1,5-COD)(3,6-DBCat)$_2$.

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A Solid-State ^{2}H NMR Relaxation Study of a 12 Base Pair RNA Duplex

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In a recent attempt to determine the solution-state structure of a 12 base pair DNA-RNA-DNA chimera ([d(CGCG)r(AAUU)d(CGCG)]$_2$), Wang et al.[1] found that the nonselective ^{1}H T_1 relaxation times of the RNA were significantly longer than

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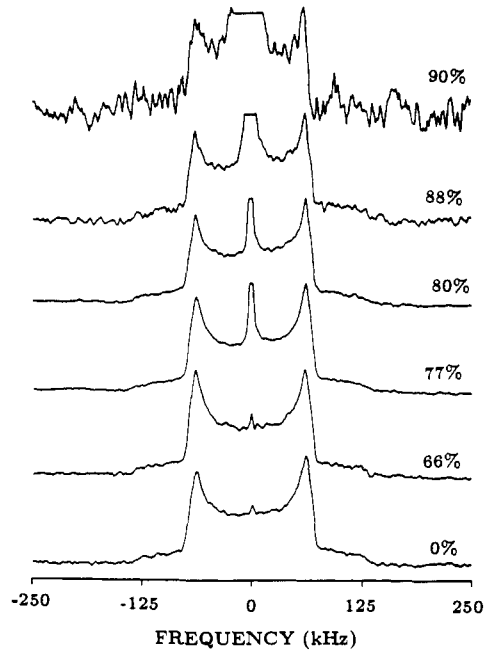

Figure 1. ^{2}H NMR (76.75 MHz) quadrupole echo line shapes of [r-(CG*CG*A*A*UUCG*CG*)]$_2$ at 0%, 66%, 77%, 80%, 88%, and 90% relative humidity. The 90° pulse width was between 2.2 and 3.0 μs, and the pulse spacing was 50 μs. The $QCC_{effective}$ is 166 ± 2 kHz and the OCC_{static} is 179 ± 2 kHz.[3,4] To all experimental spectra, 2500 Hz of line broadening was applied to the FID prior to Fourier transformation. The * indicates the replacement of the purine H8 by dueterium. Notice that as the hydration level increases the signal-to-noise (S/N) ratio of the anisotropic component decreases while that of the mobile component increases. Several reasons can account for this. First, as the hydration level is increased, the fraction of isotropically reorienting RNA molecules increases due to sample heterogeneity.[5] Second, back-exchange of the purine D8 with H_2O would yield isotropically reorienting HDO at the expense of S/N of the anisotropic component. Third, the natural abundance of deuterium in normal water contributes to the isotropic line in the center of the spectra[6-9] in an amount proportional to the hydration level.

those of the DNA. However, they were unable to determine whether the ^{1}H T_1 difference was due to dynamic or structural differences due the presence of proton–proton spin diffusion and global motions. However, knowledge of the internal motion differences between DNA and RNA is important for solution-state structural investigations of RNA:DNA hybrids and RNA–DNA chimeras. Specifically, quantification of NOESY cross-peak intensities used to determine interproton distances may harbor errors if RNA/DNA dynamic differences are not taken into account. In light of the many important biological roles of RNA, the observation that the solution ^{1}H T_1 values of RNA are longer than those of DNA motivated us to investigate the origin of the ^{1}H T_1 difference, i.e., whether the difference is due to structural or dynamic differences. A solid-state NMR investigation provides a simplified system where differences in internal motion can be probed selectively since complex global motions are minimized. Furthermore, spin diffusion can be neglected when analyzing deuterium quadrupole relaxation.

Tsang et al.[2] have reported on the solid-state ^{2}H NMR relaxation of purines in heterogeneous 150 base pair RNA duplexes. We report the first solid-state ^{2}H NMR investigation of an RNA dodecamer with a *defined* sequence, [r-(CG*CG*A*A*UUCG*CG*)]$_2$ (* indicates deuteration at the purine C8 position). Quadrupole echo line shapes (Figure 1) and spin-lattice relaxation times were obtained at 0%, 66%, 77%, 80%, 88%, and 90% relative humidity (RH). The ^{2}H T_1 values which were collected at 76.75 MHz decrease from 4.8 ± 0.1 s at 0% RH to 0.1 ± 0.6 s at 90% RH. The short ^{2}H T_1 values at all hydration levels indicate the presence of motion (internal and/or global), and the decrease in ^{2}H T_1 values as a function of hydration indicates that the motion (amplitude and/or rate) changes. At 0% RH, the internal motion is in the fast regime based on a measured field-independent ^{2}H T_1 at 76.7 and 61.4 MHz. Since at 0% RH the global motion is minimized, the field-independent ^{2}H T_1 value is largely due to the fast *internal* motion of the H8 deuteriated purines. The line shape at 0% RH resembles a static Pake powder pattern, which precludes any large amplitude (>25°) motion. This component exists at all humidities between 0% and 90% RH in addition to an isotropic component that grows with increasing hydration. The anisotropic component's effective

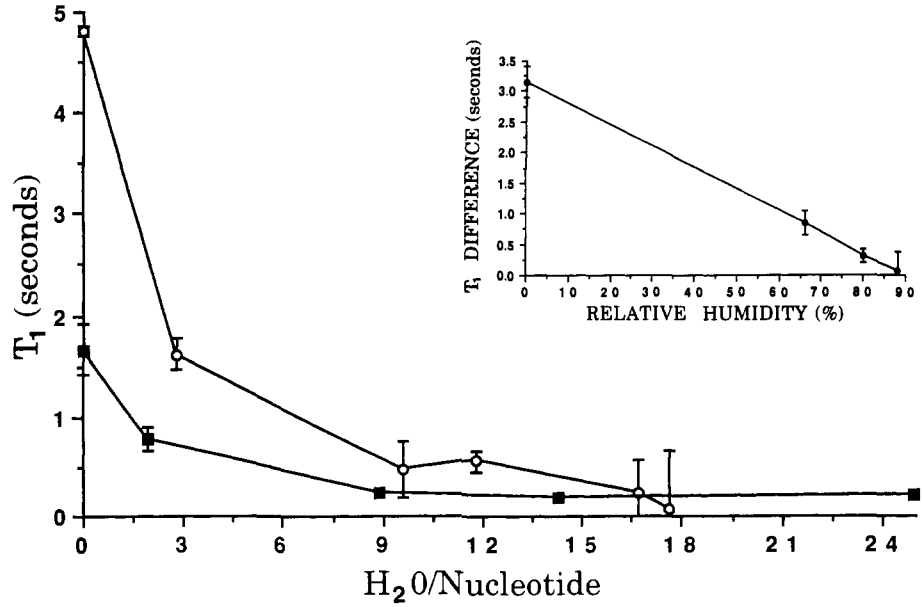

Figure 2. ^{2}H (76.75 MHz) T_1 values of [r(CG*CG*A*A*UUCG*CG*)]$_2$ (○) and [d(CG*CG*A*A*TTCG*CG*)]$_2$ (■) plotted as a function of H_2O molecules per nucleotide. The T_1 data were collected using the progressive saturation experiment and fit using a nonlinear least-squares routine.[10] The error bars for the RNA T_1 data were determined[11] to be ±0.05 s at 0.0 H_2O/nucleotide (0% RH), ±0.16 s at 2.8 H_2O/nucleotide (66% RH), ±0.29 s at 9.6 H_2O/nucleotide (77% RH), ±0.10 s at 11.8 H_2O/nucleotide (80% RH), ±0.32 s at 16.7 H_2O/nucleotide (88% RH), and ±0.59 s at 17.6 H_2O/nucleotide (90% RH). The error bars for the DNA T_1 values are ±15% for 0%, 66%, 80%, and 88% RH and ±20% for 92% RH (Kintanar, personal communication). In other words, the uncertainties for the DNA T_1 values are ±0.26 s at 0.0 H_2O/nucleotide (0% RH), ±0.12 s at 1.9 H_2O/nucleotide (66% RH), ±0.04 s at 8.9 H_2O/nucleotide (80% RH), ±0.03 s at 14.3 H_2O/nucleotide (88% RH), and ±0.04 s at 24.9 H_2O/nucleotide (92% RH). The inset is a plot of the T_1 difference between the DNA and RNA at all comparable hydration levels (0%, 66%, 80%, and 88% RH). The error bars for the difference values were determined from standard error propagation protocols.[11] The * indicates the replacement of the purine H8 by deuterium. Note that the average difference between DNA and RNA purine proton H8 T_1 values in solution was found to be 1.31 ± 0.29 s.[1]

quadrupole coupling constant (QCC_{eff}) of 166 ± 2 kHz is constant between RH levels 0%–90%, indicating that there is no significant change in the amplitude of the motion.

The RNA results were compared to those of the analogous DNA dodecamer ([d(CG*CG*A*A*TTCG*CG*)]$_2$).[3,4] First, the ^{2}H T_1 values of RNA and DNA which are significantly different at the low hydration levels converge with increasing hydration (Figure 2). Second, the horn-to-horn splittings and line shapes of RNA are similar to those of DNA at all hydration levels up to 88% RH, indicating that their amplitudes of internal motions are similar. The differences in ^{2}H T_1 values between DNA and RNA at 0%, 66%, and 80% RH, given the similar line shapes, are consistent with a difference in rates despite the uncertainty in amplitudes (12.5 ± 2.0° assuming a two-site jump[12]). The percent differences in rates are calculated to be 200 ± 61% at 0% RH, 120 ± 65% at 66% RH, and 151 ± 94% at 80% RH. It is important to note that as the hydration level increases the internal rate decreases, assuming the motion is in the fast regime. The ^{2}H T_1 values, correspondingly, becomes less sensitive to changes in rate. Therefore, at higher hydration levels (88% and 90% RH), although the DNA and RNA line shapes are still similar, the uncertainty in the ^{2}H T_1 values precludes any knowledge of rate convergence or divergence.

Given the rates and amplitudes of motion in DNA and RNA from solid-state data, we can attempt to explain the ^{1}H T_1 differences observed in solution. The experimental RNA/DNA nonselective ^{1}H T_1 ratio equals 1.7 ± 0.2[1] for the purine H8 nuclei. The calculated ^{1}H T_1 ratio based on proton density using idealized coordinates[13,14] for A-form RNA and B-form DNA tumbling in solution[15,16] without internal motion is 1.2–1.3 and therefore falls short of the experimental range. The calculated ^{1}H T_1 ratio including internal motion parameters obtained at 80% RH (two-site jump: amplitude = 12.5 ± 2.0°, $^{RNA}\tau_c$ = 14 ± 3 ps, $^{DNA}\tau_c$ = 33 ± 7 ps) is 1.5–1.6 and is within the experimental bounds, implying that motion is required to account for the RNA/DNA ^{1}H T_1 ratio. However, calculated ^{1}H T_1 values fail to successfully reproduce the experimental values, e.g., $^{calcd}T_1$(DNA) = 3.24 ± 0.04 s and $^{expt}T_1$(DNA) = 1.9 ± 0.3 s → %Δ(DNA) = 68% (%Δ(RNA) = 56%). There are several possible contributions to the ^{1}H T_1 value that were ignored. For example, differential $J_0(0)$ contamination of the nonselective proton H8 T_1 values between DNA and RNA could not be quantitated and could either raise or lower the calculated ^{1}H T_1 ratio. This exercise highlights the difficulty of extracting accurate dynamic information from high-resolution ^{1}H T_1 data of biological macromolecules. In spite of the inability to account for the nonselective ^{1}H T_1 differences in solution, solid-state experiments allow us to successfully extract dynamical information and to rigorously conclude that the amplitudes of DNA and RNA purines are similar at 0%, 66%, 80%, and 88% RH and that their internal rates of motion are different at 0%, 66%, and 80% RH.

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Registry No. r(CGCGAAUUCGCG), 118681-51-9; d(CGCGAATTCGCG), 77889-82-8.

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Deuterium Quadrupole Echo NMR Spectra and Spin–Lattice Relaxation of Synthetic Polyribonucleotides

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The nuclear spin relaxation behavior and internal motion of solid DNA fibers, films, and powders have been the subject of several studies in recent years.[1-8] So far similar NMR studies of solid polyribonucleotides have not been performed, although Bendel et al.[9] reported limited T_1 data for solid poly(I) and poly(I)·poly(C). In addition, Drobny et al.[10] have recently conducted deuterium relaxation studies of an *oligo*ribonucleotide. Here we report the results of deuterium T_1 measurements on synthetic polyribonucleotides deuterated in the purine 8-position. A partial account of these results was presented elsewhere.[11]

Sodium salts of the single-stranded polyribonucleotides pA, pI, pG, pU, and pC were obtained from Pharmacia P-L Biochemicals. Deuteration of the 8-position of pA, pI, and pG was achieved by heating the polyribonucleotides to 65 °C for about a week at pH 4–6 in a D_2O solution containing NaCl (0.05 M), Tris (0.01 M), Na_4EDTA (0.005 M), and the appropriate amount of DCl, followed by re-exchange of ND and OD by repeated lyophilization and redissolution in H_2O. The integrity of the single-stranded material was checked by polyacrylamide gel (7%) electrophoresis, and the concentration was determined by UV spectroscopy. Equivalent amounts of complementary single-stranded material were then added to allow formation of the duplexes poly(A)·poly(U), poly(I)·poly(C), and poly(G)·poly(C), henceforth referred to simply as AU, IC, and GC. It is particularly important to use accurate equivalents for poly(A) and poly(U), which are known to form triple-stranded UAU readily.[12] Duplex formation was verified by observation of the known hypochromic shifts in the UV spectrum, after which the duplex solutions were dialyzed for 8–24 h against distilled water and lyophilized to give fluffy, white powders. Polyacrylamide gel electrophoresis was used to determine the size distribution of the RNA samples; the average length was found to be 100 base pairs, with some material present in the range ~30–200 base pairs. A ca. 10% (w/w) extra sodium ion content was established from atomic absorption spectrophotometry.

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