suming that bullvalene is a Stokes–Einstein sphere[8] of 3-Å radius[9] embedded in a continuous medium with a viscosity of 0.05 P.[10] Clearly the molecule can reorient before it leaves the site. Since eight of the ten protons change environment with each rearrangement,[6] all the protons will sample all molecular positions frequently in the time scale of the experiment ($\sim 2 \times 10^{-3}$ sec). An equivalent picture *from the spectroscopic point of view* is that bullvalene remains in a single orientation while the proton spins are permuted rapidly over the molecule. The result of this scrambling is a single H–H coupling which is a statistically weighted average of the 12 independent couplings in the static molecule

$$\bar{B} = \frac{1}{15}\left[\sum_{k=1}^{3}\sum_{l>k}^{4} B_{kl} + \sum_{m=2}^{4}\sum_{n=2'}^{4'} B_{mn}\right] \qquad (1)$$

where

$$B_{ij} = -3\gamma_H{}^2\hbar(3\cos^2\beta_{ij} - 1)S/4\pi r_{ij}{}^3$$

γ_H is the proton gyromagnetic ratio, r_{ij} is the distance between nuclei i and j, and β_{ij} is the angle between r_{ij} and the threefold molecular symmetry axis. S is the degree of orientation of the *static* molecule.[3] The nuclear indices in eq 1 are taken from the structure shown in Figure 1. In order to obtain S from the observed splitting (*i.e.*, $3\bar{B}$), it is necessary to assume a molecular geometry. The electron[11] and X-ray diffraction results for bullvalene are in good agreement; this indicates that the molecule is undistorted by solid-state forces. Thus, it has been assumed that bullvalene retains the crystalline molecular geometry in the "loose" nematic lattice. Using fractional coordinates from the X-ray data,[9] r_{ij} and β_{ij} have been calculated for all proton pairs. A value of 0.054 is then obtained for $|S|$ from the measured splitting. On the basis of shape alone, this is a surprisingly large value,[12] since the gross-shape anisotropy in bullvalene is small.[9] Perhaps dispersion forces play a large role, since another globular solute (CH_3CCl_3) does not show an unusually high degree of orientation in this solvent. The line widths show that the rearrangement rate is not sufficiently fast to average the dipolar interactions completely and bring the spectrum to the fast exchange limit.[13] When the temperature is raised, the lines sharpen, indicating that averaging of the coupling constants is becoming more effective.

Two limiting cases are evident for the nmr spectrum of an oriented isomerizing molecule: (1) if the rate of either thermal reorientation or of site exchange is faster than the rate of isomerization, the molecule will remain oriented, and (2) only if the isomerization is faster than both of these processes will the molecule become "unoriented," and show an isotropic spectrum. Clearly, the spectrum of bullvalene reported here belongs in the first category. It seems unlikely that a stable system can be found in which the molecular reorganization rate is sufficiently greater than thermal reorientation frequencies to meet the second requirement.

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Spin Decoupling of Cobalt-59 in Proton Magnetic Resonance Studies of Cobalt(III) Complexes

Sir:

The conformations of coordinated ligands have been a subject of considerable interest to coordination chemists for many years.[1–5] Proton magnetic resonance (pmr) has made it possible in certain cases to determine the conformations of ligands,[6–8] primarily through the Karplus relationship of vicinal proton coupling constants to the dihedral angle.[9] Determination of the vicinal constants, however is possible only for pmr spectra which are sufficiently well resolved to permit accurate analysis.

Some of the best known coordination compounds, the cobalt(III) trisdiamines, have consistently exhibited pmr spectra of such low resolution as to render accurate analysis impossible.[10–15] Various authors have attributed this lack of resolution to intermediate inversion rates of the puckered five-membered chelate rings,[12] to a degree of residual paramagnetism, and to spin coupling of protons to long-lived nuclear spin states of cobalt-59 ($I = {}^7/_2$, 100% abundant).[10] Here we present the first experimental proof that the latter explanation is correct, as shown by the enhanced resolution produced by spin decoupling of cobalt-59.

Figure 1A shows the $-CH_2-CH_2-$ portion of the 100-MHz spectrum of $Co(en)_3{}^{3+}$ in aqueous solution at 36°. The half-width of the broad peak centered at 2.84 ppm *vs.* DSS is $\sim$23 Hz. Figure 1B shows the spectrum of $Co(en)_3{}^{3+}$ after N-deuteration (standing for several minutes in neutral 99.5% D_2O). The half-width of the peak has now decreased to $\sim$18 Hz because of the removal of H–N–C–H spin couplings.

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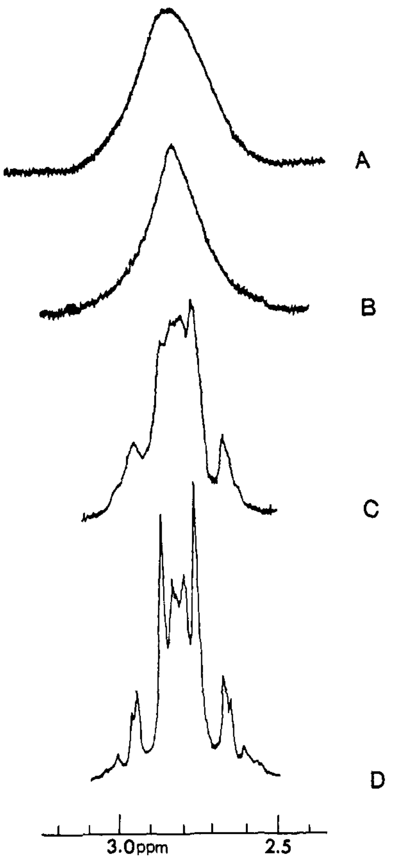


Figure 1. Pmr spectra of D-[Co(en)$_3$]Cl$_3$ at 100 MHz: A, in H_2O; B, in D_2O; C, in D_2O solution of 0.5 *M* K_3PO_4; D, in D_2O solution of potassium phosphate with Co-59 decoupling.

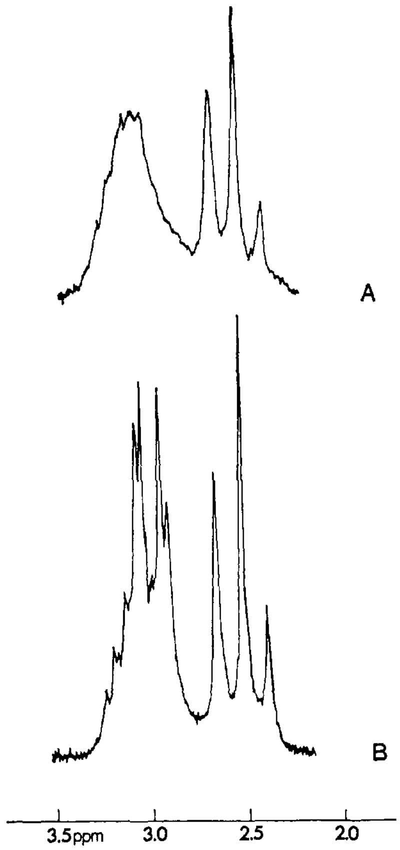


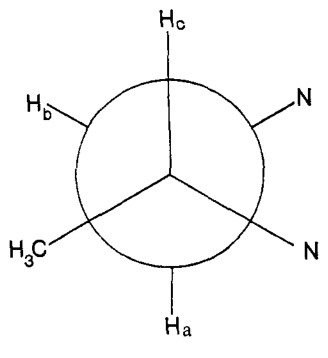
Figure 2. Pmr spectrum of L-[Co((−)pn)$_3$]Cl$_3$ at 100 MHz in D_2O solution of 0.5 *M* K_3PO_4: A, before; B, after Co-59 decoupling.

Figure 1C shows the spectrum of the N-deuterated complex at 36° after addition of 0.5 *M* K_3PO_4. The increased resolution is attributed to partial decoupling of cobalt-59 through the increased rotational correlation times, τ_c, caused by phosphate complexing.[3] That is, greater τ_c produces smaller T_1 for cobalt-59 through quadrupole relaxation.[16]

Figure 1D shows the effect of irradiating[17] cobalt-59 of the N-deuterated complex. The symmetrical AA′BB′ pattern indicates the presence of only two types of protons on a time average, which can be called "axial" and "equatorial." The rate of interconversion of the δ and λ puckered forms of each diamine ring is presumed to be rapid at room temperature. Determination of the exact position of the δ–λ conformational equilibrium is possible by exact analysis of the AA′BB′ pattern, preferably at higher spectrometer frequencies. Such a study, as a function of temperature and phosphate concentration, is now underway in this laboratory.

In a previous study of Ru(en)$_3^{2+}$,[5] the $-CH_2-CH_2-$ region of the pmr spectrum exhibited a similar highly resolved AA′BB′ pattern. This result was attributed to virtually 100% abundance of the most stable conformer (*i.e.*, the $\delta\delta\delta$ form of the Λ configuration). We believe, however, that these authors did not give adequate consideration to the case of a labile conformational equilibrium in which significant amounts of less stable conformers are present, *e.g.*, the $\delta\delta\lambda$ form. The implication that a rapid interchange of equal amounts of the $\delta\delta\delta$ and $\delta\delta\lambda$ forms would collapse the AB chemical shift difference is false.[18]

Figures 2A and 2B show the partial spectra of N-deuterated L-[Co((−)pn)$_3$]$^{3+}$ [19,20] without and with decoupling of cobalt-59, respectively. In this complex, all three propylenediamine rings are in equivalent magnetic environments, with all rings having their methyl groups in the "equatorial" position, as shown in I. The



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methyl resonance (not shown) is a doublet at 1.37 ppm *vs.* DSS and has a spacing of 6.0 Hz. Of the three protons remaining on the propylenediamine backbone, it appears that H_a produces the triplet-like resonance at highest field, and that H_b and H_c are almost coincident at lowest field. The triplet-like resonance of H_a results from spin coupling to H_b and H_c with nearly equal magnitudes ($J_{ab} \approx -12.5$ and $J_{ac} \approx 11.0$ Hz).[6,7] Simultaneous irradiation of cobalt-59 and the methyl doublet leads to changes in the low-field portion of Figure 2**B** which are consistent with the assignment of H_c. The approximate chemical shifts are $\delta_a \sim 2.48$, $\delta_b \sim 2.93$, and $\delta_c \sim 3.05$ ppm *vs.* DSS. Use of solvent shifts and a higher spectrometer frequency spreads out the spectrum sufficiently for a complete analysis, now in progress.

The sharpness of the H_a lines compared to the H_b lines tends to indicate that the Co–N–C–H coupling constant is greater for equatorial protons than for axial protons. A similar result is evident for $Co(en)_3{}^{3+}$ in Figure 1C.[21] This finding, in addition to the fact that $\delta_b > \delta_a$ in L-$[Co((-)pn)_3]^{3+}$ supports the assignment of $\delta_{axial} \sim 2.75$ ppm and $\delta_{equatorial} \sim 2.93$ ppm in $Co(en)_3{}^{3+}$.

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The Chemistry of Trifluoramine Oxide. VI. Formation of Trifluoramine Oxide in the Fluorine–Nitric Oxide Flame[1]

Sir:

Recent interest in the spontaneous, exothermic reaction of fluorine and nitric oxide as an energy source for chemical lasers[2] prompts us to describe an unexpected and chemically useful observation in the course of our own studies of the fluorine–nitric oxide flame.

Earlier workers had shown that the fluorination of nitric oxide proceeds according to the equation[3]

$$2NO + F_2 \longrightarrow 2FNO \qquad (1)$$

Through studies of the dilute diffusion flame and its emission spectrum, others measured the kinetics of the reaction and proposed the following mechanism[4,5]

$$F_2 + NO \longrightarrow FNO + F\cdot \text{ (rate determining)} \qquad (2)$$

$$F\cdot + NO \longrightarrow FNO^* \longrightarrow FNO + h\nu \text{ (6000 Å)} \qquad (3)$$

$$FNO^* \xrightarrow{(M)} FNO$$

In this mechanism, the FNO* is essentially a metastable triplet-state molecule. The 6000-Å chemiluminescence is ascribed to the small fraction of FNO* which undergoes the spin-forbidden transition to the ground state, with the remainder of the FNO molecules simply undergoing collisional deactivation (M).

In our examination of this system, however, we observed that the effluent from the nitric oxide–fluorine flame contained traces of trifluoramine oxide, F_3NO, suggesting that the very exothermic initial reaction provided the energy necessary for further fluorination of nitrosyl fluoride. Rapidly quenching the energy-rich gas mixture in the flame (by impinging on a cold surface) increased the yield of F_3NO, and further enhancement resulted when fluorine in excess of that required for FNO formation was used. These observations led to the development of a convenient, continuous-flow process for F_3NO synthesis in yields up to 20% using the empirically optimized reactor geometry, reactant ratio, gas flow rates, and quench temperature described below.

Materials. Nitric oxide (Matheson Co.) was freed of traces of NO_2 and N_2O by passage through a −78° trap packed with silica gel. Fluorine (Allied Chemical Corp.) was passed over NaF pellets to remove traces of HF.

Apparatus and Procedure. Figure 1 is a schematic representation of the "jet"-type reactor used. The entire assembly, constructed of nickel, was immersed in a stirred coolant bath which could be maintained at any desired temperature over the range −125 to 25°. A pump was used to circulate coolant through the $^3/_8$-in. o.d. cold-finger insert. Flows of gaseous fluorine and nitric oxide at atmospheric pressure were metered into the reactor through calibrated Fisher–Porter rotameters. The nitric oxide nozzle and cold finger were movable so that the volume and geometry of the flame zone could be altered as needed. Products leaving the reactor were led at ambient temperature through an infrared cell to permit continuous on-stream monitoring of F_3NO concentration. The yields of F_3NO estimated by infrared analysis were periodically confirmed by collection of the condensable reactor effluent and recovery of the F_3NO (bp −87.5°) by distillation in an all-nickel low-temperature still.

In the course of around 80 runs it was established that the optimum yield of F_3NO (15% at production rate 37.5 ml/min) for the reactor shown was reproducibly obtained in continuous operation with the NO nozzle positioned 0.5 in. above the quenching section, the cold finger 0.5 in. below the flame zone, a coolant temperature of −125°, total ($NO + F_2$) flow rate of 1000 ml/min, and reactant ratio $NO:F_2 = 1.0$.

Better yields of F_3NO (∼20%) and higher production rates were obtained by modifying the reactor of Figure 1 as follows. The modified reactor incorporated a nitric oxide inlet with a 0.0135-in. orifice positioned 0.5 in. above a larger cold finger (0.5-in. o.d.), the latter fitting closely in the quenching section of the outer tube (0.516-in. i.d.). With this configuration, the annular space for product flow around the cold finger was only 0.008 in. wide, thus providing high-velocity flow in the quenching section. In addition, the cold-finger insert was squared off at the top, as was the shoulder of the flame zone, and the top of the cold finger was po-

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