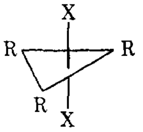
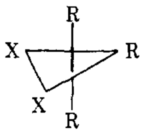
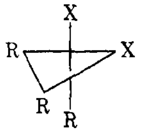
shows the same splitting[6]) to 4.22 mm sec^{-1} for $(CH_3)_3SnO_2CCF_3$. We can therefore take this range of values as being fairly typical for cases of planar trialkyltin moieties with axial O–Sn–O bridging. Thus, there is nothing unusual about a QS of ~4 mm/sec for a structure such as II.

The dependence of the QS upon geometry is worth considering in some detail, and we present here the results of a simple point-charge calculation.[9] Letting [X] denote the contribution of ligand X to the electric field gradient, the QS Δ is $\Delta \propto V_{zz}(1 + \eta^2/3)^{1/2}$, where $V_{zz} = \Sigma_X(3\cos^2\theta_X - 1)[X]$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$. We consider the three possible disubstituted trigonal-bipyramidal isomers


III


IV


V

In each case the axes were chosen to diagonalize the *efg* tensor and such that $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$. We obtain the relative values for Δ

$$\Delta_{III} = 4[X] - 3[R]$$

$$\Delta_{IV} = (7[X]^2 + 12[R]^2 - 18[X][R])^{1/2}$$

$$\Delta_{V} = (4[X]^2 + 3[R]^2 - 6[X][R])^{1/2}$$

The possible values of [R] and [X] are such that $-1 \leq [R]/[X] \leq 1$. Data for $(CH_3)_2SnF_2$ and $(CH_3)_3SnF$[9] and the point-charge result for a trans-octahedral structure[9] lead to $[CH_3] \simeq 0.26$ mm sec^{-1} ($[n\text{-}C_4H_9] \simeq 0.25$ mm sec^{-1} from data[1] for the butyltin fluorides). This value with our data[4] for $[(CH_3)_3Sn]_2SO_4$ yields $[SO_4] \cong -0.81$ mm sec^{-1}. While very tentative, these results indicate that in such compounds [R]/[X] will be fairly small and negative. For all values $-0.6 \leq [R]/[X] \leq 0$, $\Delta_{IV} \leq 0.811\Delta_{III}$, and $\Delta_V \leq 0.51\Delta_{III}$. (Even for $[R] = -[X]$, Δ_{IV} is only $0.87\Delta_{III}$.) Taking 4.0 mm sec^{-1} as a typical value of Δ_{III} as discussed above, then $\Delta_{IV} \lesssim 3.2$ mm sec^{-1} and $\Delta_V \lesssim 2.0$ mm sec^{-1}. Even severe distortions from regular geometry change Δ_{IV} and Δ_V by $\lesssim 10\%$. Thus, a compound having structure I (clearly related either to IV, V, or an intermediate between them) should show $\Delta \lesssim 3.5$ mm sec^{-1}.

We have shown that the structure discarded by Stapfer, *et al.*,[1] for $[(n\text{-}C_4H_9)_3Sn]_2SO_4$ is in fact possessed by a number of closely related compounds, that there are plausible alternatives to their interpretations of their data, and that point-charge calculations indicate the observed QS is considerably larger than that expected for structure I. While these arguments are not conclusive, we feel the weight of evidence casts reasonable doubt upon the structural assignments of Stapfer, *et al.*[1]

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Coupling with Cobalt-59 to Account for the Anomalous Proton Magnetic Resonance Spectrum of Tris(ethylenediamine)cobalt(III) Ion

Sir:

The methylene proton resonance spectrum of N-deuterated tris(ethylenediamine)cobalt(III) ion in D_2O is anomalous when compared with the spectra of the tris-ethylenediamine complexes of Pt(IV),[1] Rh(III),[1] Ir(III),[1] and Ru(II),[2] all of which have a spin-paired d^6 electron configuration. Although the appearance of these spectra varies widely, from a single sharp line for Pt (with satellites due to ^{195}Pt) to a well-resolved AA′-BB′ spectrum for Ru(II), in each case the line widths are relatively narrow. The cobalt(III) spectrum, however, consists of a single broad unresolved band. The spectrum is also peculiar in having the same line width (approximately 18 Hz) reported at both 60 and 100 MHz. Froebe and Douglas[3] recently observed the line width to be strongly temperature dependent; we have observed in contrast that the well-resolved Ru(II) spectrum has little temperature dependence.[2]

From our observations of the spectrum of the related tris(propylenediamine)cobalt(III) ion and the 220-MHz spectrum of $Co(en)_3^{3+}$ we conclude that the unusual features of the spectra of amine complexes of Co(III) are due to scalar coupling with the ^{59}Co quadrupolar nucleus ($I = {}^7/_2$). This hypothesis, which was first suggested by Powell and Sheppard,[4] can account for all of the following features of these spectra.

1. The spectrum of $Co(pn)_3^{3+}$ has been analyzed[5] and the protons are assigned as shown in Figure 1. The important feature for the present discussion is that the equatorial methylene proton, H^2, appears as a single broad band rather than the predicted four-line multiplet. The other spectral lines are not appreciably broadened. Coupling with the ^{59}Co nucleus might plausibly be larger for proton H^2 than for either of the axial protons, due to the dihedral angles made with the Co–N bond as shown in Figure 1. The methyl protons are an additional bond removed from the cobalt and are apparently not affected. The equatorial proton H^2 is the only one which is strongly coupled to the cobalt nucleus and is thereby broadened. Similar differences in

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(1) T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, **9**, 1299 (1970).
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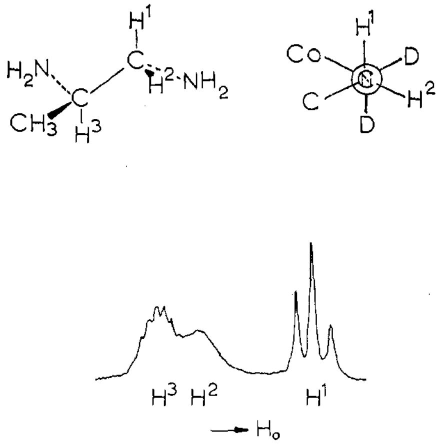

Figure 1.—Assignment of the methylene and methine proton magnetic resonance spectrum of Co(pn)$_3$$^{3+}$.

coupling constants between the metal ion and axial and equatorial protons have been observed in other complexes.[6]

2. A broad line for H^2 is not observed in the spectrum of Co(CN)$_4$pn$^-$; instead, the expected four-line multiplet is found.[7] In this complex the cobalt nucleus is in a strongly asymmetric electronic environment which causes the nuclear quadrupole to relax rapidly, effectively decoupling the ^{59}Co from the proton. In Co(pn)$_3$$^{3+}$ the electric field about the metal is more symmetric and the quadrupolar relaxation apparently does not decouple the scalar ^{59}Co–^{1}H interaction.

3. The 220-MHz spectrum of Co(en)$_3$$^{3+}$ is shown in Figure 2. In the absence of coupling with the cobalt nucleus an AA′BB′ spectrum would be expected with a line width determined primarily by the effective chemical shift difference between nonequivalent protons. This effective chemical shift difference is the result of the intrinsic chemical shift difference between an axial and an equatorial proton in one conformation and the effects of conformational averaging. In all of the spectra which have been analyzed the equatorial protons are observed to occur at a lower field strength than the axial protons.[2,5,7] The equatorial protons are also more strongly coupled to the cobalt nucleus. Consequently, the low-field half of the Co(en)$_3$$^{3+}$ spectrum is broadened substantially more than the high-field half, leading to the observed asymmetry.

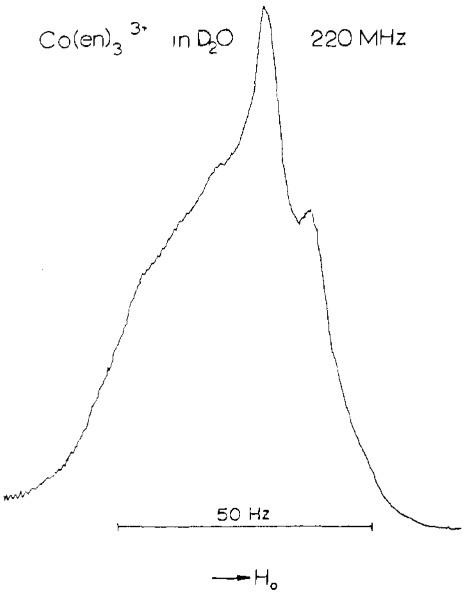

Figure 2.—The 220-MHz spectrum of N-deuterated Co(en)$_3$$^{3+}$.

4. A similar asymmetry was observed by Froebe and Douglas[3] in the spectrum of Co(en)$_3$$^{3+}$ at 60 MHz and 82°. On lowering the temperature the line width is reduced to a nearly symmetric band of 7-Hz width at 4°. We interpret this effect of temperature on the spectrum as a consequence of the temperature dependence of the ^{59}Co quadrupole relaxation frequency. At higher temperatures quadrupolar relaxation is ineffective in decoupling the cobalt nucleus from the protons and a broadened asymmetric spectrum is observed. At lower temperatures the frequency of the quadrupolar relaxation effectively decouples the cobalt nucleus from the protons and a narrow line results. A similar temperature dependence has been observed for coupling between ^{14}N and protons in various amines.[8]

5. Decoupling of the cobalt nucleus can occur through creation of an asymmetric environment about the cobalt as in the formation of ion pairs. Such an effect has been observed with the phosphate anion by Froebe and Douglas,[3] who found that addition of 0.1 *M* PO$_4$$^{3-}$ led to a reduction of the line width from 17 to 8 Hz and that in 0.5 *M* PO$_4$$^{3-}$ the spectra of Co(en)$_3$$^{3+}$ and Rh(en)$_3$$^{3+}$ were identical. Phosphate is believed to form stereospecific ion pairs with M(en)$_3$ complexes. Presumably in the latter spectra the line widths are determined by conformational effects alone with the ^{59}Co–^{1}H spin–spin splitting effectively decoupled. Similar effects have been observed in our laboratory on solutions of Co(en)$_3$$^{3+}$ dissolved as the tetraphenylborate salt in various nonaqueous solvents such as acetone and nitromethane. In these low dielectric constant solvents ion pairing and other contributions to an asymmetric environment can alter the ^{59}Co relaxation time, eliminate the cobalt–proton coupling, and consequently reduce the proton line width.

6. The approximately constant line width of 18 Hz for Co(en)$_3$$^{3+}$ at both 60[3] and 100[9] MHz in D$_2$O at ambient temperatures is not what would be expected if the spectrum were that of an AA′BB′ system or overlapping AA′BB′ systems. In these cases the effective chemical shift difference between axial and equatorial protons would be field dependent and the line width would increase at higher field strengths. On the other hand, if the line width were determined primarily by the ^{59}Co–^{1}H coupling constants and the quadrupolar relaxation time, the spectrum would be independent of the applied field, as is observed. At 220 MHz the effective

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chemical shift difference is sufficiently large to contribute to the line width.

All of these features of the nmr spectra of cobalt(III)–diamine complexes can be explained if it is assumed that substantial spin–spin coupling occurs between ^{59}Co and the equatorial protons of the ligands and that this coupling can effectively be removed by the quadrupolar relaxation of the cobalt nucleus. A direct test of this hypothesis is to decouple the cobalt nuclear spin in a heteronuclear double-resonance experiment. We predict that the spectrum of proton H^2 in $Co(pn)_3^{2+}$ will be sharpened to a four-line multiplet and that the line width of the $Co(en)_3^{3+}$ spectrum will be substantially reduced.[10]

With this explanation of the anomalous $Co(en)_3^{3+}$ spectra all of the spectra of the $M(en)_3$ complexes can be understood with a single model. The ethylenediamine chelate rings undergo rapid inversion between δ and λ conformers with small free energy differences among the various configurations.[11] An effective chemical shift difference between axial and equatorial protons is the result of the incomplete averaging by conformational inversion of the intrinsic chemical shift difference between an axial and equatorial protons held in a fixed conformation. The intrinsic chemical shift difference varies greatly with the metal ion[5] and with the exception of Co(III) is primarily responsible for the variety of spectra observed for $M(en)_3$ complexes.

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The Kinetics and Mechanism of the Dissociation of Di-μ-hydroxo-octaaquodiiron(III)[1]

Sir:

There is considerable interest in the properties of hydroxy- and oxy-bridged binuclear complexes. Although many transition metal ions form such complexes,[2-7] in recent years attention has been focused on the properties of iron(III) dimers.[8-13] This report is concerned with the dimer which is present in iron(III) solutions of low acidity[11] and which is also formed in the oxidation of iron(II) by 2-equiv oxidizing agents.[12] Magnetic measurements indicate that this dimer has a dihydroxy-bridged structure.[10] Equations 1 and 2 describe the equilibria obtaining between the dimer and monomeric iron(III) in dilute perchloric acid solution. The values of K_a and K_b

$$\mathrm{Fe(OH)_2Fe^{4+}} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} 2\mathrm{FeOH^{2+}} \quad K_a \tag{1}$$

$$\mathrm{Fe(OH)_2Fe^{4+}} + \mathrm{H^+} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} \mathrm{Fe^{3+}} + \mathrm{FeOH^{2+}} + \mathrm{H_2O} \quad K_b \tag{2}$$

are $(1.4 \pm 0.3) \times 10^{-3}$ M and 0.87 ± 0.42, respectively, at 25° and 1.0 M ionic strength.[14] This study is, in part, an extension of our earlier work on the kinetics of the dissociation of the dimer. We have previously shown that the dimer dissociates by parallel acid-independent and acid-dependent paths (eq 3).[12] This

$$k_{\mathrm{obsd}} = k_a + k_b[\mathrm{H^+}] \tag{3}$$

rate law has been confirmed in two recent studies of the dimer dissociation.[15,16] However the values of the activation energy for the acid-dependent dissociation of the dimer reported in these studies differ by about 5 kcal mol^{-1}. Because of this discrepancy and in view of the current interest in this system we are prompted to report some additional results which we have obtained on the dimer dissociation.

Iron(III) perchlorate was purified by recrystallization from perchloric acid and a stock solution of iron(III) in perchloric acid was prepared and standardized as previously described.[17] Solutions containing the dimer in 0.010, 0.025, or 0.050 M perchloric acid were prepared by adding aliquots of the iron(III) stock solution to a solution containing the appropriate amount of perchloric acid and sufficient sodium perchlorate to adjust the ionic strength to 3.0 M. These solutions were mixed with solutions containing varying amounts of perchloric acid and sodium perchlorate (ionic strength 3.0 M) on the stopped-flow apparatus,[18] and the disappearance of the dimer was followed at 340 nm.

The values of k_{obsd} at 25° are plotted against the perchloric acid concentration in Figure 1. Each rate

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