^{1}H Nuclear Magnetic Resonance and Relaxation in [Co en$(NH_3)_4$]$^{3+}$

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Summary The dynamics of ring inversion for [Co en$(NH_3)_4$]$^{3+}$ in solution are obscured by a relaxation process which dominates the CH magnetic resonance line width at low temperatures.

^{1}H NUCLEAR MAGNETIC RESONANCE spectra of cobalt(III) complexes containing ethylenediamine-type chelates usually exhibit broad NH_n and CH_n resonances, thus complicating analysis and extraction of information on the dynamics of processes such as conformational inversion. Some of the possible causes of this have been identified; for example, a line-width contribution from ^3J H–N–C–H coupling was shown by replacing the protons on nitrogen by deuterons,[1] and by proton spin decoupling.[2] Partially collapsed[3] coupling to cobalt (^3J Co–N–C–H), postulated[1] in 1959, was recently confirmed by heteronuclear decoupling.[4] Similar proton resonance broadening might be expected from ^{14}N–H and ^{14}N–C–H couplings. Intermediate rate ring-inversion has also been advanced as a cause of broad CH_2 resonances in ethylenediamine complexes.[5]

Fully protonated [Co en$(NH_3)_4$]Br_3 in D_2O/DCl showed broad NH_2, NH_3 and CH_2 resonances at room temperature (Figure, A). Irradiation of ^{14}N (7 w dissipation at transmitter coil) caused a marked sharpening of the two NH_3 resonances, a slight sharpening of the NH_2 resonance, but had no effect on the CH_2 resonance (Figure, B). Irradiation of ^{59}Co was effective in sharpening the CH_2 resonances to resolve the "quintet" caused by coupling to the four NH protons, and slightly sharpened the NH_3, NH_2 resonances (Figure, C). In D_2O–NaOD, the CH_2 resonance had a half-height width about half that in (A) and cobalt decoupling then gave a very sharp ($<1{\cdot}5$ Hz) singlet (Figure, D). Given the evidence for non-coplanarity of the CoN_2C_2 ring-atoms,[6] this result shows that there is rapid interconversion between two equivalent puckered-ring conformations, excluding the unlikely possibility of identical chemical shifts of nonequivalent CH_2 protons in a fixed puckered conformation, particularly since a sharp singlet was obtained in a variety of solvents.

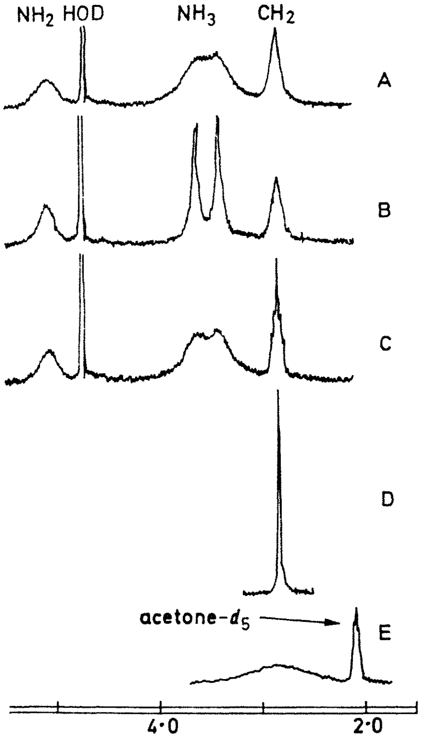

FIGURE. ^{1}H *n.m.r. spectra* (100 *MHz, chemical shifts in p.p.m. from tetramethylsilane*) *of* [Co en$(NH_3)_4$]$^{3+}$. [A] *Normal spectrum in* D_2O/DCl. [B] *Spectrum with irradiation at* ^{14}N *resonance frequency*. [C] *Spectrum with irradiation at* ^{59}Co *resonance frequency*. [D] *Spectrum in* D_2O/NaOD *with irradiation at* ^{59}Co *resonance frequency*. [E] *Spectrum in* $(CD_3)_2CO$ *at* $-72°$.

N-Deuteriated [Co en$(NH_3)_4$]$(CF_3CO_2)_3$ in perdeuterioacetone containing a little D_2O had room-temperature spectra similar to those above for the bromide (Figure, C, D). At $-20°$ the CH_2 resonance was broader than at room temperature and was unaffected by irradiation of ^{59}Co, ^{14}N, or ^{2}D. We conclude that decoupling of ^{59}Co by its own spin-lattice relaxation rate had occurred in the more viscous solution. The resonance was almost too broad to detect at −80° and no signals had reappeared by −95° as would be expected if the broadening was caused by a ring-inversion rate process. Furthermore, spectra at 60 MHz were consistently broader than those at 100 MHz at the same temperatures in the range −10° to −70°; the reverse would be expected for chemical shift averaging processes.

That the broadening is a spin relaxation phenomenon is readily corroborated. In the region where molecular rotational correlational times, τ_c, are comparable with the reciprocal Larmor frequency, ω^{-1}, all other things being equal, the 60 MHz spectrum should be broader than the 100 MHz spectrum by a factor of 1·05 for $\tau_c = 0{\cdot}4$ ns, 1·18 for $\tau_c = 1{\cdot}0$ ns, a maximum of 1·32 for $\tau_c = 2{\cdot}5$ ns, and decreasing again for larger τ_c values, if we take the intramolecular uncorrelated dipolar relaxation[7] to be dominant. This behaviour was observed for the *N*-deuteriated complex where the ratio varied between 1·07 and 1·18 for the temperature range −28° to −66°, thus suggesting that τ_c is approximately 0·5—1·0 ns, respectively. From the Debye formula, $\tau_c = \tau/3 = 4\pi\eta a^3/3kT$, using the measured viscosities of 5 and 15 centipoise at −28° and −66°, respectively, and assuming a rigid complex having a radius of about 4 Å, we obtain $\tau_c = 0{\cdot}3$ ns and 1·0 ns, respectively.

τ_c may also be estimated from n.m.r. line widths dominated by quadrupolar relaxation.[7] The ^{59}Co spectrum of [Co en$(NH_3)_4$]X_3 in the above solvents had a line width between points of maximum slope of 1 kHz, but we detected no pure quadrupole resonance for the tribromide in the region 2—16 MHz. *trans*-[Co(en)$_2$Cl$_2$]Cl,HCl,4H$_2$O on the other hand has three ^{59}Co quadrupole resonances in this region,[8] and we found a ^{59}Co line width of 10·2 kHz in aqueous acid solution. Assuming that this line width is dominated by quadrupolar relaxation and that $T_1 = T_2$ in the extreme narrowing region, we obtain $\tau_c = 0{\cdot}02$ ns, for a measured viscosity of 1·14 centipoise.

This behaviour will thus obscure conformational rate-broadening processes, particularly for the low barriers expected to obtain in ethylenediamine-type ligands. We are currently studying the dynamics of conformational processes in complexes chosen to minimise the relaxation effect.

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