Contribution from the Central Research Department,
Monsanto Company, St. Louis, Missouri 63166, U.S.A.

Proton Magnetic Resonance Line Widths of Some Paramagnetic Octahedral Nickel(II) and Cobalt(II) Complexes

D. Forster

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The observed relatively narrow nmr linewidths of Mpy_4X_2 where M is either Ni or Co and X is a halogen or pseudohalogen are rationalized in terms of the factors leading to appropriate correlation times. For $M=Ni$, the marked dependence of the correlation time upon the nature of X is interpreted by a mechanism involving electron-spin relaxation induced by modulation of the zero-field splitting by molecular tumbling. The situation is more complex for $M=Co$, since electron-spin relaxation in this case is primarily determined by the energy separations amongst the components of the ground state manifold. The variation in these energy separations from compound to compound are poorly understood.

Introduction

Relatively sharp proton magnetic resonances have been observed for paramagnetic tetrahedral[1,2] and octahedral[3,4] nickel(II) and cobalt(II) complexes. This can be attributed[5] to a short relaxation time of the electron-spins. Numerous mechanisms for electron-spin relaxation have been postulated.[6] Of most importance in transition-metal systems are (1) interaction with low lying electronic excited states via spin-orbit coupling, (2) tumbling of a species with an anisotropic g tensor and (3) coupling of the tumbling with the zero-field splitting.

Most attempts at experimental verification of one or other of these mechanisms for a particular metal have involved determining the temperature and/or field dependence of an esr or nmr line width. This work presents a comparison of the correlation times for nuclear-electronic interaction as determined by nmr line width studies of complexes of the type M-$(pyridine)_4X_2$ where $N=Ni$ or Co and $X=Cl$, Br, I, NCS and NCO and also $Ni(dipyridyl)_3^{2+}$.

Experimental Section

The pyridine complexes were prepared according to Gill *et al.*[7] with the nickel compounds isolated as $Nipy_4X_2$ and the cobalt complexes as $Copy_2X_2$ (except for the thiocyanate which was obtained as $Copy_4(NCS)_2$). Tris-dipyridyl nickel chloride was prepared as described by Burstall and Nyholm.[8]

Pmr spectra were obtained at 60 Mc/sec with a Varian A56/60 spectrometer, equipped with a variable temperature probe.

The pyridine complexes were examined as 0.1 *M* solutions in deutero-chloroform containing 1% tetramethylsilane. Excess pyridine was also present in these solutions such that the ratio pyridine: metal was 6: 1. The dipyridyl complex was examined as a 0.05 *M* solution in nitromethane.

It was found that the line widths were not dependent upon dilution at the concentrations used.

Results and Discussion

Table I presents the nmr line width of the γ proton of coordinated pyridine in the series of complexes *trans* $Ni(pyridine)_4X_2$ where $X=Cl$, Br, I, NCS and NCO and also for $Co(pyridine)_4(NCS)_2$. Although exchange with excess ligand broadens the resonances of the pyridine complexes below room temperature,[9] the line widths are reported at a temperature high enough for this effect to be unimportant. In such a situation the resonance linewidth of nuclei on the coordinated

Table I. Line-Width Results

Compound	Conc. (mole metal per liter)	Corrected with at half height at 60° (cps)	Correlation time, τ_c (sec)
$Ni(py)_4(NCS)_2$	0.1	54	8.9×10^{-12}
$Ni(py)_4(NCO)_2$	0.1	40	6.4×10^{-12}
$Ni(py)_4Cl_2$	0.1	20	3.0×10^{-12}
$Ni(py)_4Br_2$	0.1	18	3.1×10^{-12}
$Ni(py)_4I_2$	0.1	21	3.2×10^{-12}
$Ni(dipy)_3^{2+}$	0.05	62	1.0×10^{-11}
$Co(py)_4(NCS)_2$	0.1	9	$<6\times10^{-13}$

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(2) G. N. Lamar, W. DeW. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, *41*, 2126 (1964).

(3) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, *39*, 1211 (1963).

(4) W. DeW. Horrocks, Jr., R. C. Taylor, and G. N. Lamar, *J. Am. Chem. Soc.*, *86*, 3031 (1964).

(5) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, *34*, 842 (1961).

(6) See G. N. Lamar, *J. Am. Chem. Soc.*, *87*, 3567 (1965) for leading references.

(7) N. S. Gill, R. S. Nyholm, G. A. Barkley, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, *18*, 88 (1961).

(8) F. A. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(9) D. Forster, unpublished observations.

ligand can be derived readily from the observed linewidth by a knowledge of the stoichiometry of the system (which in these experiments was always 2 uncoordinated and 4 coordinated pyridines). However for the corresponding cobalt complexes, the only line width which can be reported with any certainty is that of Co(py)$_4$(NCS)$_2$. In the other cases exchange broadening complicates the interpretation below 0°; while above this temperature, the equilibrium[10] between octahedral Co(py)$_4$X$_2$ and tetrahedral Co(py)$_2$X$_2$ interferes. Therefore, in order to obtain a comparison amongst the cobalt complexes, it was necessary to observe the broadening of an inert internal reference signal at a temperature low enough to ensure that all of the cobalt was in the octahedral form. The results are reported in Table II.

Table II. Relative linewidths of TMS internal reference in solutions containing octahedral cobalt complexes

Compound [a]	TMS linewidth at −50° (cps)
Copy$_4$(NCS)$_2$	2.3
Copy$_4$Cl$_2$	11
Copy$_4$Br$_2$	3.0
Copy$_4$I$_2$	4.3

[a] All compounds were examined as 0.1 *M* solutions in CDCl$_3$ containing 1% TMS which was also 0.2 *M* with respect to pyridine.

This series of compounds is particularly suitable for a study of this type since crystallographic studies[11] show that the metal-nitrogen distance (and hence metal-γ-proton distance) does not vary much.[12] Further, the position of the excited states has recently been determined[13,14,15] for the nickel complexes. The line widths reported in Table I can be used to calculate a correlation time, τ_c, for the interaction between the nuclear and electronic spins, using the equations for the longitudinal and transverse relaxation rates of Solomon[16] and Bloembergen,[17] which under the conditions prevailing in these experiments reduce to

$$\frac{1}{T_{1M}} = \frac{1}{T_{2M}} = \frac{4}{3}\frac{\mu_{eff}{}^2\gamma_I{}^2\beta^2}{r^6}\tau_c + \frac{2}{3}\frac{S(S+1)A^2}{\hbar^2}\tau_e$$

where τ_e is the correlation time for the hyperfine interaction. The other symbols have their conventional meaning.

The first term in the above equation is due to dipole-dipole interaction between electrons and nuclei and the second term is due to hyperfine interaction. The hyperfine interaction with the γ-proton for the pyridine complexes is relatively small[3,9] and the second term in the above equation does not significantly contribute to the line width

Nickel Complexes. The correlation times obtained are so short that they can be identified[5] with the electron-spin relaxation time. The correlation time for the other mechanism which could have determined τ_c, the tumbling of the complex, can be estimated by use of the Debye equation, $\tau = \dfrac{4\pi\eta r^3}{3kT}$ where η is the viscosity of the solvent and r is the effective radius of the particle. This gives a tumbling time of $\sim 10^{-10}$ sec for a value of r = 5.9Å. However, this value may be too small, since it has been shown[18] that transition-metal halide complexes, related to the complexes used here, form hydrogen bonds with chloroform. This would increase the effective radius of the species and thus the rotational correlation time.

Now the g-tensor anisotropy of all octahedral nickel compounds so far determined by esr[19] has been found to be less than 10 per cent and thus relaxation by coupling of the anisotropy to the tumbling[20] is not able to explain the very fast relaxation times. Further there are no low-lying excited states in these molecules[13] (*i.e.* < 1000 cm^{-1}) and thus relaxation via interaction with electronic excited states is not expected to be very efficient. The mechanism which can explain the order of magnitude of the electron-spin relaxation time is that of modulation of the zero-field splitting by the tumbling in solution.

This mechanism also appears to be able to explain, at least qualitatively, the ordering of the line widths in solution. The zero-field splitting of the $^3A_{2g}$ ground state of an octahedral nickel(II) complex with a small tetragonal distortion is dictated[21] primarily by the splitting of the first triplet excited state $^3T_{2g}$ (which in a tetragonal field gives rise to a ^3E_g and a $^3B_{2g}$ level). For a small distortion, the zero-field splitting $2D = 8\lambda^2\left(\dfrac{1}{E_1} - \dfrac{1}{E_2}\right)$ where λ is the spin-orbit coupling constant, E$_1$ is the separation between the $^3B_{1g}$ ground state and the ^3E_g level and E$_2$ is the $^3B_{1g}$—$^3B_{2g}$ separation. Now in the complexes Nipy$_4$Cl$_2$, Nipy$_4$Br$_2$, and Nipy$_4$I$_2$, the excited $^3T_{2g}$ level is split[13,14] by a considerable amount (2-4000 cm^{-1}). Thus large zero-field splittings are expected for these compounds. However, the $^3T_{2g}$ level in both Nipy$_4$(NCS)$_2$ and Nipy$_4$(NCO)$_2$ gave[15] no evidence for a large distortion, although the room-temperature measurement of the electronic spectrum probably would not detect a splitting less than ~ 500 cm^{-1}. Thus the zero-field splitting for the pseudohalide complexes is expected to be appreciably smaller than those of the halide complexes. The interpretation[21,22,23] of the electronic spectrum of Ni(dipy)$_3^{2+}$ has been the subject of some controversy, because the $^3T_{2g}$ and ^1E_g levels fall close together. Suffice it to say that no gross splitting

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(10) H. C. A. King, E. Körös and S. M. Nelson, *J. Chem. Soc.*, 5444 (1963).

(12) A. S. Antsishkinn and M. A. Porai-Koshits, *Kristallografiya*, 3, 684 and 694 (1958).

(12) This is probably not the case for species of the type M(py)$_6^{2+}$ where the crystal-structure of the only example so far obtained in the solid-state, Fe(py)$_6^{2+}$ [see R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, *88*, 4847 (1966)] shows an anomalously long Fe-N distance, presumably for steric reasons.

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of the $^3T_{2g}$ level is apparent in the single-crystal polarised spectrum[23] and thus the zero-field splitting is expected to be considerably smaller for $Ni(dipy)_3^{2+}$ than for the halo-pyridine complexes.

Now since the mechanism for electron-spin relaxation involving coupling of the zero-field splitting to the tumbling in solution requires that the relaxation rate be inversely proportional to the square of D,[24] the afore-mentioned facts require that the electronic relaxation time of the halo-pyridine complexes be substantially shorter than those of $Nipy_4(NCS)_2$, $Nipy_4(NCO)_2$, and $Ni(dipy)_3^{2+}$. The difference is indeed reflected in the correlation times and line widths listed in Table I.

Cobalt(II) Complexes. The correlation time calculated for $Copy_4(NCS)_2$ can be equated with the electronic relaxation time, as in the case of the nickel complexes. The relaxation time is approximately an order of magnitude shorter for the cobalt complex than for the nickel complexes. In fact the value of 6×10^{-13} sec represents an upper limit since $Copy_4(NCS)_2$ displays[9] considerable magnetic anisotropy in which case the equation developed by Sternlicht[25] for calculation of correlation times in magnetically anisotropic systems should be used. However since the magnitude of the anisotropy is not known, it was not possible to apply this equation. Use of the equation[16] for magnetically isotropic systems leads to an upper limit since use of Sternlicht's equation with values of $g_\parallel$ and $g_\perp$ estimated the literature[19] leads to smaller correlation times (often by a factor of 3 or 4).

It is apparent that the relaxation times of the cobalt-pyridine complexes as judged by the linewidths of the reference resonance (see Table II) follow a different order from that found for the nickel complexes.[25a] In particular it is observed that the TMS line width in the presence of $Copy_4Cl_2$ is substantially greater than in the presence of the other cobalt complexes. This difference is also apparent in the pyridine resonances however additional broadening due to exchange prevents a quantitative evaluation of the various correlation times.

The ground electronic state of a cobalt(II) ion in O_h symmetry is $^4T_{1g}$. Under the combined action of a tetragonal perturbation and spin-orbit coupling, the degeneracy is lifted giving six Kramers doublets. In only one case to date has complete information been obtained on the ordering of the ground state manifold. This is Co^{2+} in MgF_2 where fluorescence spectra[26] show that the six Kramers doublets all fall within 1500 cm^{-1}, with the separation between the lowest pair being only 152 cm^{-1}. Interaction with the low-lying excited states will limit the lifetime of a spin state.[27] The relaxation times for the various cobalt complexes will depend upon the energy separations in the ground-state manifold which in turn depend upon the axial distortion and spin-orbit coupling constant for a particular case. McClure[28] has developed an emperical M.O. theory of the splittings of degenerate levels by low symmetry fields in which level splittings are related to the difference in σ and π-antibonding energies experienced by the d-orbitals of the central metal ion. Application of McClure's theory to the $^4T_{1g}$ ground state of an octahedral Co^{II} complex predicts that the splitting of this level by tetragonal perturbation will depend only upon the π-antibonding difference between the axial and equational ligands. Although there have been few experimental applications of the McClure theory it can be said from the available results[13,29] that the splitting of the $^4T_{1g}$ state is expected to be small. In fact the splittings will probably be of the same order of magnitude as the spin-orbit coupling. This suggests that all cobalt(II) complexes should have very efficient spin relaxation and a rationale of the observed τ_c values will probably have to await establishment of accurate positions for the levels derived from the $^4T_{1g}$ state.

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(25a) Support for this indirect method is obtained from consideration of the TMS linewidths in solutions containing the nickel complexes. The TMS linewidths in 0.05 *M* solutions of the complexes in $CDCl_3$ at +40° (containing excess pyridine) are as follows $Nipy_4Cl_2$, 3 cps; $Nipy_4Br_2$, 3 cps; $Nipy_4I_2$, 3 cps; $Nipy_4(NCO)_2$, 8 cps; $Nipy_4(NCS)_2$, 8 cps. Thus the same general order observed for the proton resonances on the ligands is followed by the internal reference.

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