indicated coordination with the three nitrogens.

Registry No. DTPA^{5-}, 14047-41-7; SrDTPA^{3-}, 69351-96-8; BaDTPA^{3-}, 69351-97-9; LaDTPA^{2-}, 69351-98-0; LuDTPA^{2-}, 69351-99-1.

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Nuclear Magnetic Resonance Relaxation in Symmetrical Cobalt(III) Complexes

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Cobalt-59 and nitrogen-14 longitudinal and transverse relaxation times have been measured in the symmetrical cobalt complex ions hexacyanocobaltate(III), tris(ethylenediamine)cobalt(III), and hexaamminecobalt(III). The ^{59}Co line width in hexacyanocobaltate(III) is narrow, 2–3 Hz, characteristic of symmetrically complexed quadrupole nuclei. The cobalt relaxation in the two N-bonded complexes, however, is complicated by a scalar interaction of the second kind from cobalt coupled to first coordination sphere nitrogen-14. Analysis of the nitrogen scalar contribution from the cobalt and nitrogen relaxation data gives the scalar coupling constants $J(^{59}\text{Co}-^{14}\text{N}) = 40.8 \pm 2.1$ and 50 ± 2.5 Hz for hexaammine and tris(ethylenediamine) complexes, respectively. In the ethylenediamine complex, cobalt coupling to the methylene and ammine protons is also observed by ^{1}H-decoupled cobalt relaxation data in H$_2$O and D$_2$O solutions. The pH dependence of the cobalt relaxation times for the N-bonded complexes clearly demonstrates the formation of the complex ion conjugate base.

Introduction

Cobalt-59 nuclear magnetic resonance has provided useful information about the structure and dynamics of cobalt(III) metal environments.[1] The ^{59}Co NMR chemical shifts are known to be very large so that even subtle differences in the second coordination sphere of complexes may be detected.[2] Although the cobalt(III) NMR spectrum is readily detected, a major difficulty arises if the symmetry at the cobalt nucleus is low because the lines become prohibitively broad through very efficient relaxation by the nuclear electric quadrupole interaction. On the other hand, symmetrical cobalt complexes are readily investigated in solution by standard techniques.[3]

When the cobalt nucleus experiences a symmetrical environment such as in a tetrahedral or octahedral ion, NMR relaxation due to the nuclear electric quadrupole interaction is expected to be inefficient. The nuclei of the central atom of symmetrical ions such as the perchlorate or permanganate ions yield readily observed NMR spectra although they possess significant quadrupole moments. In both cases the NMR quadrupole relaxation mechanism for the central nucleus is inefficient, and line widths on the order of a few hertz are reported.[4,5] In the case of cobalt(III) complexes the hexacyanocobaltate(III) ion has such a narrow spectral line, but other symmetrical complexes such as hexaamminecobalt(III) ion and nitrogen-substituted analogues have line widths on the order of 100 hertz. The present study was undertaken to examine the NMR relaxation of these symmetrical cobalt(III) complexes to determine the source of this apparent anomaly in the cobalt(III) systems. A detailed understanding of relaxation in these chemically inert cobalt(III) complexes is important because they provide very useful models for investigating the nature of nuclear electric quadrupole contributions to the NMR relaxation of ions in solution.[6]

We have found that in N-bonded cobalt(III) complexes several mechanisms contribute to the ^{59}Co NMR relaxation.

In particular measurements of both longitudinal and transverse relaxation rates for ^{59}Co and ^{14}N coupled with a series of isotopic substitution experiments have permitted resolution of the several relaxation contributions. Most notable is a large contribution from a scalar interaction between ^{59}Co and ^{14}N.

Experimental Section

Potassium hexacyanocobaltate(III), tris(ethylenediamine)cobalt(III) chloride, and hexaamminecobalt(III) chloride were synthesized and purified by standard procedures by using reagent grade chemicals.[7] Deuterium oxide (99.87 mol % D$_2$O) was purchased from Bio-Rad Laboratories. Complete deuteration of complex ammine protons, verified by the cobalt-59 resonance,[8] was accomplished by recrystallizing the cobalt complexes at least three times from D$_2$O.

The NMR relaxation measurements on cobalt-59 and nitrogen-14 were performed in a 1.4-T field by using a spectrometer assembled in this laboratory.[9] Cobalt-59 longitudinal relaxation times, T_1, were measured by inversion recovery with phase alternation. Transverse relaxation times, T_2, for K$_3$Co(CN)$_6$ were measured by the Carr–Purcell–Meiboom–Gill sequence[10] since in this complex the measured line width is controlled by magnetic field inhomogeneity. A representative Carr–Purcell–Meiboom–Gill spin echo experiment on cobalt-59 in 1.25 M K$_3$Co(CN)$_6$ is shown in Figure 1. Line widths from the Fourier transform spectra were used as a measure of T_2 for all other samples. Estimated error for these measurements is 5%. Nitrogen-14 T_1 measurements were made at 4.3 MHz without phase alternation of the 90° pulses in order to minimize the pulse widths. Estimated error for the nitrogen measurements is 10%. The phase-modulated broad-band proton decoupling used in these experiments was calibrated by observing the proton-decoupled oxygen-17 resonance in enriched water at neutral pH. Probe temperature was 32 ± 1 °C.

Results and Discussion

The ^{59}Co NMR spectra for hexacyanocobaltate(III) ion, hexaamminecobalt(III) ion, and tris(ethylenediamine)cobalt(III) ion are shown in Figure 2. The chemical shift differences are characteristically large, and satellite lines are clear in the hexacyanocobaltate(III) spectrum. The satellite lines account for 6% of the cobalt signal which is consistent

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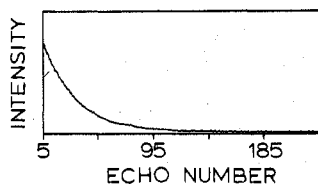
Figure 1. ^{59}Co transverse relaxation time measurement using a Meiboom–Gill modification of the Carr–Purcell pulse sequence for a 1.25 M solution of $K_3Co(CN)_6$. The curve shown represents signal to noise after 10 repetitions of the experiment are averaged. The 180° pulse transients have been suppressed by use of a sample and hold circuit. T_2 for this sample is 107 ms. Full scale is 0.9 s.
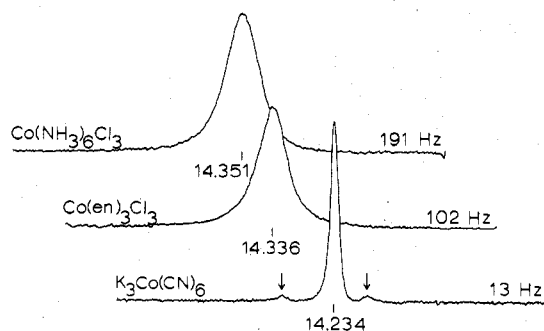
Figure 2. ^{59}Co NMR spectra of $Co(NH_3)_6Cl_3$, $Co(en)_3Cl_3$, and $K_3Co(CN)_6$ saturated in water. Resonance frequencies are measured in megahertz and are not corrected for magnetic susceptibility. The full line widths measured at half-height are listed at the right of each spectrum.

Table I. ^{59}Co and ^{14}N Longitudinal and Transverse NMR Relaxation Rates in Symmetrical Co(III) Complexes

		^{59}Co relaxn rates			^{14}N relaxn rates
		^{1}H coupled	^{1}H decoupled		
		$1/T_2$, s^{-1}	$1/T_2$, s^{-1}	$1/T_1$, s^{-1}	$1/T_1$, s^{-1}
0.10 M	H_2O	7.5		7.2	3000
$K_3Co(CN)_6$	D_2O	8.2		8.3	
1.0 M	H_2O	280	254	132	3120
$Co(en)_3Cl_3$	D_2O	280	261	152	3120
0.25 M	H_2O	553	545	20	500
$Co(NH_3)_6Cl_3$	D_2O	509	503	23	556

the complexes should be in an ion pair with potassium.

The ^{14}N relaxation is dominated by the nuclear electric quadrupole interaction. If extreme narrowing conditions are assumed, the longitudinal relaxation rate will be given to a good approximation by eq 1, where the nuclear spin I is unity

$$\frac{1}{T_1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 \tau_c \qquad (1)$$

and τ_c represents the correlation time for reorientation of the field gradient, eq, at the observed nucleus with quadrupole moment, eQ.[17] The asymmetry parameter has been neglected. Equation 1 implies that knowledge of the nuclear quadrupole coupling constant, e^2qQ/h, and the nitrogen relaxation rate, T_1^{-1}, provide an estimate for the rotational correlation time of the complex. The average quadrupole coupling constant for the nitrogen nucleus is reported to be 3.68 MHz in the crystalline potassium salt.[18] Though the potassium hexacyanocobaltate(III) crystal demonstrates polytypism of the crystal structure,[19,20] the nitrogen quadrupole coupling constant is not strongly affected by changes in crystal morphology[18] and is consistent with values observed in electronically similar MCN systems.[21] If we assume that this value approximates the solution coupling constant, the reorientational correlation time, and consequently the cobalt complex, calculated from eq 1 is 15 ps. This approximate value suggests that the hexacyanocobaltate ion rotates significantly faster in water than do those cobalt complexes with ligands that may favorably hydrogen bond with the solvent.[22] The estimate of the rotational correlation time for the complex permits a calculation of the effective cobalt nuclear quadrupole coupling constant provided that the rotational motion of the complex appropriately describes the electric field gradient fluctuations at the cobalt nucleus. With this caution, eq 1 modified for the $I = {}^7/_2$ cobalt-59 spin yields a quadrupole coupling constant of 1.1 MHz for the cobalt nucleus. This result is significantly smaller than the value of 7.3 MHz reported for the crystalline potassium salt[23] and suggests either that distortions of the cyanide ligand system in the crystal decrease the symmetry at the cobalt nucleus[20] or that the correlation time for the quadrupole interaction at cobalt is not rotation of the complex.

$Co(NH_3)_6^{3+}$ **and** $Co(en)_3^{3+}$. The ^{59}Co longitudinal relaxation rates for these two complex cations differ significantly from the transverse relaxation rates. The longitudinal relaxation rate for the hexaammine complex is greater than that of the hexacyanocobaltate ion by more than a factor of 2.5 but is less than that of the tris(ethylenediamine) complex by more than a factor of 6. An increased longitudinal relaxation rate for the ethylenediamine complex is anticipated because distortion of the bond angles from perfect O_h symmetry of the bonded N atoms is required by the five-membered chelate ring. In addition, the large size of the chelate complex should cause it to reorient more slowly than either monodentate complex. Differences in the longitudinal relaxation rate may arise from

with a scalar coupling of the ^{59}Co nucleus to naturally abundant ^{13}C in the complex. The coupling constant deduced from the ^{13}Co splitting is 126 ± 1 Hz which is consistent with measurements of the eight-line ^{13}C spectrum obtained on the sample.[11] This value is also consistent with an earlier report.[12] The downfield shift attending the isotopic substitution of ^{13}C for ^{12}C is in agreement with a more detailed study of cobalt chemical shifts[13] and may be qualitatively accounted for by a ligand field argument.

Each of the three complexes is classically octahedral with respect to coordinated atoms; however, only the hexacyanocobaltate(III) ion provides the narrow line expected for the octahedral symmetry at the central atoms. Measurements of longitudinal and transverse relaxation rates for ^{59}Co and ^{14}N in H_2O and D_2O in the presence and absence of ^{1}H decoupling are summarized in Table I.

$Co(CN)_6^{3-}$. In alkaline solutions the ^{59}Co longitudinal and transverse NMR relaxation rates are equal to within the experimental error of the present measurements. The small values of the relaxation rates are expected because the nuclear electric quadrupole interaction should vanish to first order. The origin of the ^{59}Co line width in hexacyanocobaltate ion or similar species is not quantitatively understood;[15] however, several contributions may be eliminated. Proton decoupling does not affect the cobalt(III) line width for this complex and substitution of deuterium for hydrogen in the solvent does not change the cobalt relaxation times by an amount greater than that expected from changes in solution viscosity. Therefore, dipolar interactions involving protons do not make important contributions to the cobalt relaxation in this complex. Since the chemical shifts of the cobalt compounds are large, fluctuations in the geometry of the cobalt complex should provide a significant time dependence of the chemical shielding tensor that may contribute to relaxation in some cases. We have no evidence to support this mechanism in the present case. It is also interesting to note that the association constant between potassium ion and the complex anion is significant.[16] With the conditions of the present measurements, at least 75% of

Table II. Cobalt-59 Line Widths in Symmetrical Cobalt(III) Complexes at Two Temperatures

complex		line width at 32 °C, Hz	line width at 65 °C, Hz
1.25 M	$K_3Co(CN)_6$	2.9	2.4
1.0 M	$Co(en)_3Cl_3$	89	139
0.25 M	$Co(NH_3)_6Cl_3$	176	208

Table III. $J(^{59}Co-^{14}N)$ for the Symmetrical Complexes Hexaamminecobalt(III) Chloride and Tris(ethylenediamine)cobalt(III) Chloride in Aqueous Solutions at 32 °C

complex	solvent	$J(^{59}Co-^{14}N)$, Hz
0.25 M $Co(NH_3)_6Cl_3$	H_2O	41 ± 2.1
	D_2O	41 ± 2.1
1.0 M $Co(en)_3Cl_3$	H_2O	49.8 ± 2.5
	D_2O	48.6 ± 2.5

either changes in the electrical symmetry about the cobalt or the motion of the complex. A difference in the electrical symmetry might originate in different interactions of the two oppositely charged ions with the counterions present in the solution, but these effects are expected to be small.[6,24] We can envision two obvious sources for motional differences: (1) There may be differences in the interaction of the complex with the counterions that change the effective size of the rotational unit. (2) There may be differences in the capacity of the complexes to hydrogen bond with the solvent thus changing the rotational correlation time for the complex. Since a detailed model for quadrupole relaxation of such symmetrical complexes is not at hand, it is also possible that the relaxation in these two types of complexes is different in some fundamental way not presently apparent. Nevertheless, the possibility that the motional properties of the two monodentate ions are significantly different is suggested by the earlier discussion.

The transverse and longitudinal relaxation rates are equal in the hexacyanocobaltate complex anion; however, this is far from the case in either of the two cations studied. The difference must arise from slow modulation of the spin interactions that contribute to transverse but not longitudinal relaxation. Since such a slow process does not contribute to the quadrupole relaxation, we may take the longitudinal relaxation rates as a measure of the basic relaxation rate contribution from the nuclear electric quadrupole interaction. Other contributions may be resolved on the basis of this justifiable assumption. There are two major differences magnetically between the hexacyanocobaltate complex and the two cations studied: (1) In the ammine complexes a nitrogen rather than a carbon atom is bonded directly to the cobalt. (2) The ammine complexes have covalently incorporated protons that may couple to the cobalt nucleus. Proton–cobalt coupling in these complexes has been reported on the basis of proton spectrum at high fields.[25,26] We might also anticipate a significant cobalt–nitrogen coupling constant based on the observation of a significant cobalt–carbon coupling constant.

The contributions to the cobalt(III) relaxation from the protons may be directly detected by measurement of the cobalt relaxation rates in the presence of proton decoupling. Additionally, the contributions of the CH protons may be de-

termined independently of the NH protons in the chelate complexes by studying the ^{59}Co relaxation in D_2O as well as H_2O since the nitrogen protons are readily exchanged for deuterons.[27]

Direct confirmation of the cobalt–nitrogen coupling could be achieved by observation of the ^{14}N-decoupled ^{59}Co spectrum. The effectiveness of the nitrogen coupling to the cobalt relaxation may be determined directly also by taking advantage of the well-known inverse-temperature and viscosity dependence for the line width of a nucleus that is relaxed by a scalar interaction of the second kind.[17] The data in Table II show that the cobalt relaxation rate for the N-bonded cobalt complexes increases with increasing temperature even though the viscosity of the solution and therefore the correlation time in eq 1 decreases. The temperature dependence observed is anticipated in the event that the cobalt nucleus is relaxed by scalar coupling to a rapidly relaxing ^{14}N. If we assume that the scalar contribution to the total ^{59}Co NMR relaxation is additive, the contribution is

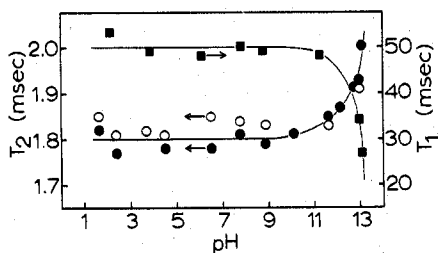$$\left(\frac{1}{T_2}\right)_{sc} = \left(\frac{8\pi^2}{3}\right)[J(Co-N)]^2 T_{1N} \qquad (2)$$

where $J(Co-N)$ is the cobalt–nitrogen coupling constant measured in hertz and T_{1N} is the ^{14}N longitudinal relaxation time.[17] The nitrogen data are summarized in Table I. Two independent calculations may be made since data are available for both D_2O and H_2O solutions. The coupling constants calculated from eq 2 and ^{14}N relaxation data are summarized in Table III. The errors appropriate to these results are appreciable since they depend on two measured relaxation rates and the assumption of the constancy of other relaxation contributions. We have not confirmed their magnitudes based on observation of the ^{15}N spectrum nor have we resolved the ^{15}N splitting in the cobalt spectrum. Nevertheless, these values do not appear to be very far from expectations since they are on the order of the carbon coupling shown in Figure 2.

The contributions of the several relaxation mechanisms to the ^{59}Co NMR relaxation rates at pH 5.9 are summarized in Table IV. The contributions from the NH protons in the hexaammine complex are on the order of the experimental error so that no entry is listed; however, the NH protons make a measurable but small contribution to the ^{59}Co relaxation in the ethylenediamine complex. The contributions of the CH protons in the ethylenediamine complex are approximately four times greater than the NH protons even though they are further away from the cobalt nucleus. This result supports the suggestion that the NH protons are partly decoupled due to either proton exchange with solvent or a relaxation rate difference caused by proton coupling to the rapidly relaxing nitrogen nucleus. Work is continuing in this area.

The entries in Table IV listed under T_{1Q}^{-1} include all mechanisms that contribute to the longitudinal relaxation rate. As argued earlier, the quadrupole interactions are expected to dominate this term. However, the chemical shift known for cobalt is large. It is possible that chemical shift anisotropy is large enough to contribute to the observed relaxation. The difference in the symmetry at the cobalt atom between the hexaammine and the chelate complex is reflected in the large difference in the longitudinal relaxation rates. The relaxation rate differences (of about 15%) between the H_2O and D_2O

Table IV. Contributions to ^{59}Co Relaxation at pH 5.9

complexes		T_{1Q}^{-1}, s^{-1}	T_{2SC-N}^{-1}, s^{-1}	T_{2HC}^{-1}, s^{-1}	T_{2HN}^{-1}, s^{-1}
0.25 M $Co(NH_3)_6Cl_3$	H_2O	20	530	0	
	D_2O	23	480	0	
1.0 M $Co(en)_3Cl_3$	H_2O	130	120		
	D_2O	150	110	25	6

Figure 3. ^{59}Co NMR relaxation times as a function of pH for a 0.10 M solution of the hexaamminecobalt(III) chloride. The open circles are for proton-decoupled ^{59}Co T_2 values.
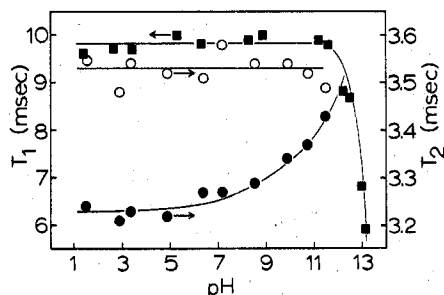
Figure 4. ^{59}Co NMR relaxation times as a function of pH for a 0.10 M solution of tris(ethylenediamine)cobalt(III) chloride. The open circles are for proton-decoupled ^{59}Co T_2 values.

solutions are expected based on the differences in the solution viscosity.

The scalar contribution clearly dominates the hexaammine spectrum apparently because the symmetry is high at both ^{59}Co and the ^{14}N. The long ^{14}N T_1 provides a very efficient relaxation path for the cobalt in hexaammine, but the shorter ^{14}N T_1 in the chelate attenuates the efficiency of this contribution even though the cobalt–nitrogen coupling constants are similar.

An interesting feature of the ^{59}Co NMR relaxation in these complexes is shown in Figures 3 and 4 in which both longitudinal and transverse ^{59}Co NMR relaxation rates are plotted as a function of pH. The longitudinal relaxation time for both complexes decreases with increasingly high pH while the transverse relaxation time increases. For the ethylenediamine complex the transverse relaxation rate is a function of proton decoupling as expected. The contribution to T_1 at high pH must arise from a change in either the motional properties of the complexes or from changes in the effective field gradient at the metal atom. We are unaware of any change with pH that would produce a significant alteration in the correlation times for these complexes. However, the possibility of the loss of a proton from the coordinated nitrogen atom is well-known as an explanation for the increased substitution rates of these complexes at higher pH values.[28] The formation of the complex ion conjugate base would very significantly alter the electrical symmetry of the cobalt environment and produce an increase in the effective field gradient at the cobalt nucleus. If we assume a mechanism involving the formation of conjugate base, the relaxation equation becomes

$$\frac{1}{T_1} = \frac{1}{T_{1HB}} + \frac{1}{K_a + [H^+]}\left\{K_a\left(\frac{1}{T_{1B}} - \frac{1}{T_{1HB}}\right)\right\} \quad (3)$$

where HB refers to the metal complex, B to its conjugate base, and K_a to the acid dissociation constant for the metal complex. If the hydrogen ion concentration is large compared with K_a, the change in relaxation rate is a linear function of the reciprocal of the hydrogen ion concentration and only the product

in brackets may be extracted from the data. Unfortunately, in the ethylenediamine case, the required plot is indeed linear up to pH values of 13.2. This result suggests that K_a is small compared with 6×10^{-14} in the ethylenediamine complex, which is consistent with earlier reports.[29,30] It is important to note that at high pH values substitution chemistry may alter the complex; however, these substitution rates are sufficiently slow that the present measurements were made without difficulty. If significant concentrations of other complexes, the hydroxo-substituted complex, for example, did develop, the inertness of the first coordination sphere, the sensitivity of the cobalt line width to radical changes in the ligand system, and the large chemical shifts between cobalt complexes would eliminate any contribution to the symmetrical cobalt complex signals from the less symmetrical substitution products.

We note finally that longitudinal and transverse relaxation rates for the hexacyanocobaltate ion are equal at pH values greater than 11. At lower pH values, however, a difference between these measurements develops approximately linearly with pH so that by pH 1, T_2 is 20% shorter than T_1. This difference exists in both H_2O and D_2O. We have not pursued this observation further.

In summary, there are three dynamic contributions to the cobalt transverse relaxation rate which change with pH: (1) the contribution, both directly and indirectly, through ^{14}N of the N-bonded protons which may be decoupled by exchange, (2) the contribution of the carbon bonded protons, which may be decoupled by a pH-dependent ring-inversion rate, and (3) direct alterations in the equilibrium concentration of the conjugate base form of the complex with pH. Substantially more precise data would be required to attempt a quantitative analysis of these several contributions.

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