

Cobalt-59 Nuclear Magnetic Resonance Studies of Chloro-, Bromo-, and Iodo-Substituted Tris(acetylacetonato)cobalt(III) Complexes

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The cobalt-59 nuclear magnetic resonance spectra and longitudinal relaxation times have been studied for tris(acetylacetonato)cobalt(III) complexes with chloride, bromide, and iodide substitution at the methine carbon atom of the chelate ring. The cobalt-59 chemical shift is sufficiently sensitive to this remote substitution that cobalt-59 resonances are well resolved for each complex in a series of monohalo-, dihalo-, and trihalo-substituted complexes. The chemical shift is not linearly dependent on substitution. For the more electronegative halides, chlorine and bromine, static electric field gradient effects can be observed in the mixed-ligand complexes but these effects amount to less than 10% of the observed relaxation rate. Through comparison of carbon-13 and cobalt-59 relaxation times it appears that in the solvents benzene, diglyme, and acetone the cobalt-59 relaxation is a consequence of rotational reorientation but for the solvent chloroform the cobalt-59 relaxation is different. Several possible explanations for this observation are considered.

Introduction

With the advent of improved techniques for studying nuclear magnetic resonance, many nuclei are amenable to observation.¹ More than half of them have spins greater than $1/2$ and as a consequence usually relax by the quadrupolar mechanism. In this mechanism in solution, the relaxation time, and therefore the resonance line width, is dominated by the electric field gradient and its fluctuations at the nucleus. Resonances are normally very broad for complexes of reduced symmetry, but chemically important information is available if the data can be reduced to an accurate measurement of the electric field gradient. In order to investigate this possibility, it occurred to us that it would be useful to study the cobalt-59 and carbon-13 spectroscopy of several series of tris(acetylacetonato)cobalt(III) complexes in solution. Halogen substitution at the methine position of the ligand is readily achievable. Monohalo and dihalo complexes can be isolated and separated from the trihalogenated complex. In principle a static electric field gradient can be systematically varied as one substitutes halides for methine protons. Moreover, the chelate rings are fairly rigid. For partially substituted complexes, protonated methine carbon nuclei may be observed and their relaxation times measured. Since they relax by the relatively well-understood dipolar mechanism, comparisons between carbon-13 and cobalt-59 relaxation times can be useful.

With these thoughts in mind, we undertook an NMR study of the title compounds.

Experimental Section

Tris(acetylacetonato)cobalt(III), Co(acac)₃, was synthesized by a method described by Bryant and Fernelius.² The product was recrystallized twice from a benzene-heptane mixture and dried under vacuum. The halogenated complexes were prepared by a method described by Collman.³ The bromo complexes were separated by using a flash silica gel column; all other halogenated complexes were used as a mixture of mono-, di-, and trihalogenated compounds. All other chemicals were used as received with no further purification.

NMR measurements were made by using a Bruker WM-250 spectrometer operating at 62.898 and 59.36 MHz for ¹³C and ⁵⁹Co, respectively. A deuterium lock was used for all samples except those in diglyme, which were studied undocked. The measurements were made in 10-mm sample tubes at a concentration of approximately 0.1 M, if the solubility allowed, or on a saturated solution if the solubility was lower. Several samples were degassed by bubbling N₂ gas into the sample tube. No observable changes in the ⁵⁹Co or ¹³C relaxation times were detected, and so all other samples were run undegassed.

The temperature was controlled with a Bruker B-VT 1000 temperature control unit. Samples were allowed 1 h for the temperature to stabilize before measurements were made. The temperature was measured by using a 3-mm capillary of methanol⁴ inserted in the center of the 10-mm tube. A temperature calibration curve provided by Bruker Instruments was used to determine the temperature. Changes in the ⁵⁹Co

Table I. ⁵⁹Co Chemical Shifts (ppm) at 298 K and Their Temperature Dependence (ppm/K, in Parentheses)^a

complex ^b	chem shift			
	benzene- <i>d</i> ₆	chloroform- <i>d</i>	acetone- <i>d</i> ₆	diglyme
Co(acac) ₃	0 (2.03)	-104 (2.47)	64 (2.02)	26 (1.91)
mono Cl	-36 (2.11)	-132 (2.61)	9 (2.13)	-19 (1.98)
di Cl	-63 (2.19)	-158 (2.74)	-30 (2.19)	-56 (2.11)
tri Cl	-88 (2.26)	-180 (2.89)	-65 (2.28)	-89 (2.22)
mono Br	-51 (2.14)	-145 (2.60)	-15 (2.16)	-32 (2.03)
di Br	-96 (2.21)	-188 (2.72)	-58 (2.26)	-85 (2.15)
tri Br	-131 (2.34)	-218 (2.95)	-105 (2.41)	-132 (2.32)
mono I	-77 (2.06)	-162 (2.64)	-25 (2.14)	-56 (2.04)
di I	-141 (2.17)	-218 (2.82)	-97 (2.27)	-129 (2.22)
tri I	-195 (2.32)			

^aChemical shifts are referenced to Co(acac)₃ in benzene-*d*₆ at 298 K. ^bMono, di, and tri indicate the degree of substitution.

chemical shift were used to monitor the stability of the temperature. Typically ⁵⁹Co has a ~2 ppm/K chemical shift temperature dependence in these compounds so that temperature fluctuations were easy to monitor. Measurements were made after the chemical shift was constant. Data were discarded if the chemical shifts differed by more than 10 Hz before and after an accumulation.

The T₁ relaxation times of the ⁵⁹Co and ¹³C measurements for the methine carbon were determined as a function of temperature from 280 to 310 K by using the modified fast inversion-recovery technique of Freeman et al.⁵ This offers significant savings in time without a loss of accuracy. The technique involves a 180°-τ-90° pulse sequence, where τ is a variable delay. Between 6 and 12 values of τ were used in each experiment. Between 400 and 800 transients were collected for each τ value for the ¹³C experiments, and 10-80 transients were collected for each τ value for the ⁵⁹Co experiments. The T₁ values were determined from linear plots of ln(A_∞ - A) vs time, where A_∞ is the peak height for τ > 5T₁ and A is the peak height at a given value of τ. All plots were linear with correlation coefficients between 0.99 and 0.98. Several measurements of T₁ were made by using the conventional inversion-recovery method, and the results agreed within experimental error with those done by fast inversion recovery. The errors in the T₁ measurements are all better than ±1% as determined from the standard deviation in the slope of ln(A_∞ - A) vs τ or the standard deviation of five line-width measurements.

In some cases the ⁵⁹Co T₁ value was determined from the resonance line width at half-height. These measurements agree with those obtained by using the modified fast inversion-recovery technique.

Results

Cobalt-59 Chemical Shifts and Temperature Dependence. The chemical shift of cobalt-59 and its temperature dependence were

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Table II. ^{59}Co Relaxation Rates (s^{-1}) at 298 K

complex ^a	relaxation rate			
	benzene- d_6	chloroform- d	acetone- d_6	diglyme
Co(acac) ₃	375	274	214	605
mono Cl	620	493	446	978
di Cl	804	636	561	1212
tri Cl	907	767	605	1287
mono Br	608	505	431	1007
di Br	893	724	570	1346
tri Br	1153	871	682	1572
mono I	750	584	469	1022
di I	1097	921	677	1510
tri I	1473			

^a Mono, di, and tri indicate the degree of substitution.

Table III. ^{13}C Relaxation Rates and Rotational Correlation Times for Co(acac)₃

	benzene- d_6	chloroform- d	acetone- d_6	diglyme
$1/T_1, \text{s}^{-1}$	1.06	0.97	0.53	1.45
$10^{11}\tau_R, \text{s}$	5.2	4.8	2.6	7.1

measured in each of the complexes. In the case of the bromine-substituted compounds, the mono-, di-, and tribromo complexes were separated and structures assigned by comparison of the methine to methyl ratio in the proton spectrum. The chloro complexes and the iodo complexes were not separated but rather were studied as mixtures of mono-, di-, and trisubstituted complexes. Assignments were made by comparison of integrals of the cobalt-59 resonances in reaction mixtures where 1, 2, and 3 equiv of halogenating reagent had been added to the integral of the initial, unsubstituted Co(acac)₃. The results appear in Table I. Cobalt-59 resonance line widths were observed to vary from approximately 90 Hz up to 700 Hz in these compounds.

Cobalt-59 Relaxation Rates. The cobalt-59 longitudinal relaxation rates for each complex were measured at several temperatures. It was assumed that the extreme narrowing condition holds and $T_1 = T_2$ for these compounds. This hypothesis was tested by studying the bromo-substituted compounds both by inversion-recovery measurement of T_1 and line-width measurement. Since the ^{79}Br resonance frequency is close to that of cobalt-59, it is possible that these compounds could display an additional relaxation pathway through scalar relaxation of the second kind. However, it was observed that inversion-recovery measurements were identical with line-width measurements within experimental error, and so it was assumed that the same is true for chloro and iodo derivatives. Since the chemical shift is strongly temperature dependent and since line widths were determined from spectra resulting from multiple scans, particular care was taken to be sure that no temperature fluctuations occurred during an accumulation. Data are reported only for cases where the observed cobalt-59 chemical shifts were within 10 Hz of one another before and after a given accumulation. The results are presented in Table II.

Carbon-13 Relaxation Rates. Carbon-13 longitudinal relaxation rates and the resulting rotational correlation times for the ^{13}C - ^1H vector were determined for the protonated methine carbon atoms of some of the complexes in the four solvents. The data appear in Table III. It was established that the relaxation mechanism is dipolar for each of these carbon nuclei through measurement of the nuclear Overhauser enhancement⁶ for ^{13}C . Irradiating the methine proton results in an enhancement factor of 1.9 ± 0.1 for the methine carbon resonance. Therefore, relaxation is via the dipole-dipole mechanism.

Discussion

Cobalt-59 Chemical Shift Effects. A conspicuous feature of the chemical shift dependence on halide substitution is its non-

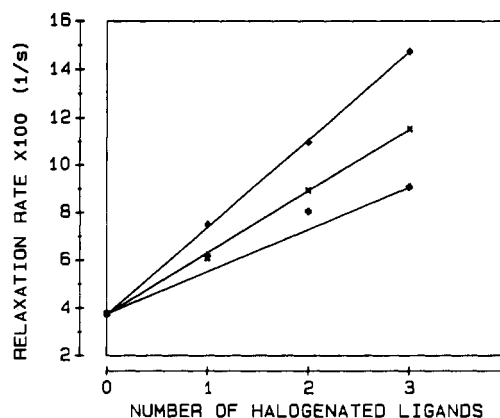


Figure 1. Relaxation rate (in benzene- d_6) of ^{59}Co versus the number of halogenated ligands in Co(acac)₃: (+) Cl series; (x) Br series; (♦) I series.

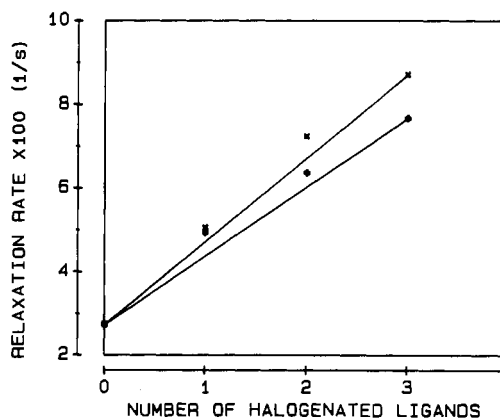


Figure 2. Relaxation rate (in chloroform- d) of ^{59}Co versus the number of halogenated ligands in Co(acac)₃: (+) Cl series; (x) Br series. Similar plots in acetone- d_6 and in diglyme are qualitatively similar with values for mono- and dihalo complexes falling significantly above the line.

linearity. The nonadditivity of chemical shifts upon substitution is expected. However, the deviation from additivity for other Co^{3+} complexes has been in the direction of higher fields⁶ while the Co(acac)₃ system deviates from additivity in the direction of lower field.

Electric Field Gradient Effects beyond the First Coordination Sphere. The relaxation rate of a quadrupolar nucleus like cobalt-59 in a complex depends directly on the magnitude of the electric field gradient (EFG) at the nucleus and inversely on the rate by which the EFG is modulated by the tumbling of the complex. Russell and Bryant⁸ investigated the relaxation properties of cobalt-59 in the trication tris(ethylenediamine)cobalt(III) with various anions. In the presence of phosphate ion they showed that the cobalt-59 relaxation was significantly accelerated; however, comparisons to carbon-13 relaxation times in the ethylenediamine rings showed that the effect was largely or entirely due to slower tumbling of the complex as a consequence of ion pairing rather than an increase in electric field gradient (EFG) due to ion-pair formation. Chelate ring deformation motions made a precise estimation of EFG effects impossible at low phosphate ion concentrations. The acetylacetonate compounds we have studied present an opportunity for additional study of these effects because of their relatively rigid chelate rings due to the π bonding among the atoms of the ring and because of the relatively precise placement of substituents. While these considerations indicate that ring motions are reduced, they are certainly not eliminated altogether and could conceivably play a role in the relaxation phenomena. In a series of complexes beginning with tris(acetylacetonato)cobalt(III) through the monohalo- and dihalo-substituted species and on to the trihalo complex, tumbling motions

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of the complexes should slow progressively because of the increased mass of the complexes. This is supported by the observation of a progressively reduced ^{13}C T_1 value as the molecular mass of the complex is increased. Owing to the reduction of symmetry, only the monohalo and dihalo complexes should have a static contribution to the EFG due to halide substitution.

This can be illustrated by plotting the ^{59}Co relaxation rate against the degree of substitution by a given halide. Figures 1 and 2 show that if this is done for chloro complexes and if one uses a straight line to connect the point for the unsubstituted complex with the point for the trisubstituted complex, then the points for the monosubstituted and disubstituted complexes lie above the line. The line represents the relaxation rate for the complex if the only factor affecting relaxation rate were reduced rate of tumbling due to increased molecular mass and if the rate of tumbling were reduced linearly by increased mass. In our interpretation, the deviation of mono- and disubstituted complexes from the line is due to a contribution to relaxation via the static EFG in these complexes and to changes in the asymmetry parameter.

Figure 1 contains data for the series of complexes with iodine substitution in the one case where the triiodo complex was sufficiently soluble for study. The electronegativity of iodine is nearly the same as for carbon. Consequently there should be little change in EFG when iodine replaces hydrogen at the methine position of these complexes. All points fall on the straight line. From these data, it appears that about 10% of the relaxation rate observed for mono- and disubstituted chloro complexes is due to EFG effects but changes in ligand bite size or solvation effects could also lead to more rapid relaxation. In any event, EFG effects beyond the first coordination sphere are clearly small.

Cobalt-59 Relaxation Mechanisms for $\text{Co}(\text{acac})_3$ Complexes.

The nuclear magnetic relaxation of nuclei with nuclear spin greater than $1/2$ is generally dominated by relaxation via the quadrupolar mechanism. In this mechanism the relaxation is brought about by interactions of the nuclear electric quadrupole moment with fluctuations of the electric field gradient at the observed nucleus. In systems where the quadrupolar nuclei are in symmetric environments it is not clear how the fluctuations of the electric field gradient occur; however, the process must be dynamic. Theoretical explanations fall into three categories, EFG induced by molecular vibrations,⁹⁻¹³ EFG due to solvent dipoles,^{14,15} and EFG due to small distortions from ideal symmetry due to collisions that fluctuate via rotational motion.¹⁶

The experimental evidence to date does not conclusively support any one of the theories and in some cases is quite confusing. An example of the confusion is evident in two studies of similar complexes, metal tris(acetylacetonates). In one study by Doddrell et al.¹⁷ the relaxation of ^{59}Co in $\text{Co}(\text{acac})_3$ with chloroform as the solvent was reported. A dual-spin-probe technique was used in which the rotational motion of the complex was determined by comparing the ^{13}C relaxation of the methine carbon to the relaxation rate observed for ^{59}Co . Doddrell concluded that the relaxation of ^{59}Co was not due to rotational motion but rather vibrational motion.

In a similar study by Dechter et al.¹⁸ the dual-spin-probe technique was also used to study the quadrupolar relaxation of $\text{Al}(\text{acac})_3$, $\text{Ga}(\text{acac})_3$, and $\text{In}(\text{acac})_3$ in toluene- d_6 . In this study

Table IV. Activation Energies for ^{13}C Relaxation (kJ/mol)^a

complex ^b	E_a			
	benzene- d_6	chloroform- d	acetone- d_6	diglyme
$\text{Co}(\text{acac})_3$	12	11	7	13
mono Br	16			
di Br	11			

^aThe error in these measurements is estimated to be ± 2 kJ/mol. ^bMono and di indicate the degree of substitution.

Table V. Activation Energies for ^{59}Co Relaxation (kJ/mol)^a

complex ^b	E_a			
	benzene- d_6	chloroform- d	acetone- d_6	diglyme
$\text{Co}(\text{acac})_3$	10	6	7	12
mono Cl	8	5	6	10
di Cl	8	7	7	11
tri Cl	8	6	6	11
mono Br	8	6	5	11
di Br	10	6	6	11
tri Br	11	5	4	8
mono I	6	6	3	11
di I	8	6	8	12
tri I	8			

^aThe error in these measurements is estimated to be ± 0.2 kJ/mol; however, numbers were rounded to the nearest integral value. ^bMono, di, and tri indicate the degree of substitution.

it was determined that relaxation of the quadrupolar nuclei is linked to the rotational motion of the complexes.

The relaxation rate of the methine carbon in $\text{Co}(\text{acac})_3$ was determined to be via the dipole-dipole mechanism through NOE measurement. The relaxation rate is given by eq 1, in the extreme

$$1/T_1 = N\gamma_C^2\gamma_H^2h^2r_{\text{CH}}^{-6}\tau_R \quad (1)$$

narrowing limit,¹⁹ where N is the number of protons bonded to the carbon, γ_C and γ_H are the magnetogyric ratios for carbon and hydrogen, respectively, r_{CH} is the carbon-hydrogen internuclear distance, and τ_R is the correlation time for the reorientation of the CH vector. The correlation time is assumed to be the rotational correlation time of the molecule because of the limited motion of the methine carbon.

If we assume that the internuclear distance is not temperature dependent, then the only temperature-dependent term in eq 1 is τ_R . By determining the temperature dependence of the relaxation rate, we are also determining the temperature dependence of the rotational motion of $\text{Co}(\text{acac})_3$. This can then be used to examine the relaxation of the cobalt via the dual-spin-probe technique.

If the relaxation of the cobalt in $\text{Co}(\text{acac})_3$ is via the quadrupolar mechanism, it is given by eq 2 in the extreme narrowing limit,²⁰ where e^2Qq/h is the nuclear quadrupole coupling constant, which consists of the nuclear quadrupole moment (eQ), the z component of the EFG tensor (eq), and η the asymmetry parameter, which is related to the difference in the x and y components of the EFG in the principal axis system, and τ_c is the correlation time for the reorientation of the EFG of the observed nucleus. As in eq 1 the only temperature-dependent term is τ_c ,

$$1/T_1 = (4.08 \times 10^{-2})\pi^2 \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2Qq}{h}\right)^2 \tau_c \quad (2)$$

the correlation time. By comparing the temperature dependence of the correlation time for the quadrupolar relaxation of the cobalt with the temperature dependence of the rotational motion of the complex (determined for the relaxation rate of the methine carbon), one can at least determine whether rotational motion is responsible for the relaxation of the cobalt.

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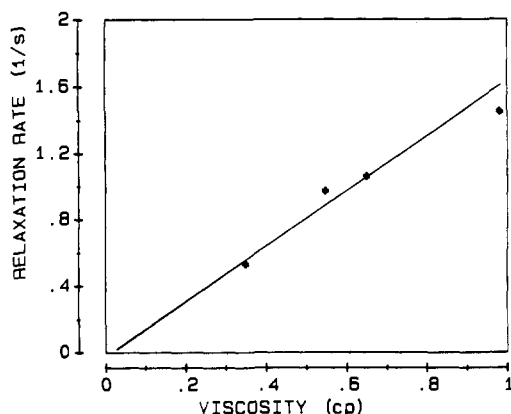


Figure 3. ^{13}C relaxation rate of the methine carbon in $\text{Co}(\text{acac})_3$ versus viscosity in acetone- d_6 , chloroform- d , benzene- d_6 , and diglyme. Viscosities are macroscopic viscosities for the bulk solvents.

The comparison can be done by calculating the activation energy²¹ for the relaxation of ^{13}C and ^{59}Co , from the equation

$$1/T_1 = A_0 e^{-(E_a/RT)} \quad (3)$$

The activation energies for the relaxation of the methine carbon and the cobalt in $\text{Co}(\text{acac})_3$ in chloroform- d , benzene- d_6 , acetone- d_6 , and diglyme are listed in Tables IV and V.

In Tables IV and V the temperature dependences for the relaxation rate at the methine carbon and the cobalt are the same within experimental error in each of the solvents benzene- d_6 , acetone- d_6 , and diglyme, but in chloroform- d the value for the activation energy of the cobalt is significantly higher than that of the methine carbon. This suggests that the relaxation of the cobalt may be due to rotational modulation (reorientation) of the EFG in benzene- d_6 , acetone- d_6 , and diglyme but is not due to rotational reorientation in chloroform- d .

To examine the quadrupolar relaxation of the cobalt further, we studied the viscosity dependence of the relaxation rates for the methine carbon and the cobalt. The viscosity dependence of the rotational correlation time if it is assumed that there is no anisotropy, is given by²²

$$\tau_R = Vn/KT \quad (4)$$

where V is the molecular volume and n is the viscosity. Plotting $1/T_1$ versus viscosity, one expects a straight line if the correlation time is the rotational correlation time. Figure 3 gives a plot of $1/T_1$ versus viscosity for the methine carbons in $\text{Co}(\text{acac})_3$. The data show the linear dependence of the relaxation on viscosity, as expected for dipolar relaxation. In Figure 4 a similar plot for the cobalt relaxation shows a straight line connecting the acetone- d_6 , benzene- d_6 , and diglyme points; however, the point for chloroform- d falls significantly below the line. For the chloro-substituted complexes similar results are observed, as shown in Figure 5, thus supporting the assumption that the complexes have little or no anisotropy. Bromo- and iodo-substituted complexes behave similarly. This tends to corroborate the temperature dependence data, which showed that the ^{59}Co relaxation rate is consistent with rotational reorientation in acetone- d_6 , benzene- d_6 , and diglyme but not in chloroform- d .

It appears that the relaxation rate for cobalt in ostensibly symmetrical complexes like $\text{Co}(\text{acac})_3$ can be explained by small dynamic distortions from ideal symmetry that fluctuate due to rotational reorientation in solvents other than chloroform.

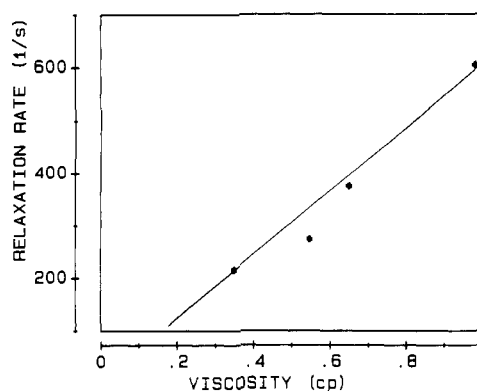


Figure 4. ^{59}Co relaxation rate for $\text{Co}(\text{acac})_3$ versus viscosity in acetone- d_6 , chloroform- d , benzene- d_6 , and diglyme. Viscosities are macroscopic viscosities for the bulk solvents.

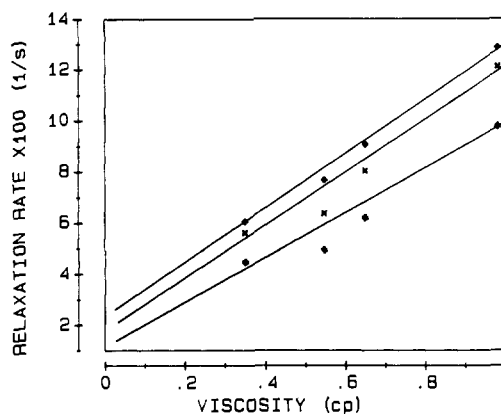


Figure 5. ^{59}Co relaxation rate for halogenated $\text{Co}(\text{acac})_3$ versus viscosity in acetone- d_6 , chloroform- d , benzene- d_6 , and diglyme of (+) monochloro complex; (x) dichloro complex; (♦) trichloro complex. Viscosities are macroscopic viscosities for the bulk solvents.

However, in chloroform the situation appears more complex and rotational reorientation does not account for the relaxation. The imposition of a small, static EFG onto a complex might be expected to alter the motional properties responsible for fluctuation of the EFG. However, this is not the case in the systems we have studied. Complexes with monohalo and dihalo substitution at the methine carbons have measurable static EFG's, but as shown in Figure 5, the ^{59}Co relaxation rate is anomalously slow in chloroform. Similar results were observed in bromo- and iodo-substituted complexes. The questions as to what motions are responsible for the fluctuation of the EFG, where the EFG of $\text{Co}(\text{acac})_3$ in chloroform originates, and why chloroform is so different from the other solvents are left for further study. The answer may lie in the reported formation of an outer-sphere complex between $\text{Co}(\text{acac})_3$ and CDCl_3 .²³ The correlation time for the modulation of the EFG would then be a combination of the rotational correlation time as well as a correlation time for the formation of the outer-sphere complex.

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