A study of the nuclear magnetic resonance quadrapolar relaxation of Cobalt -59 in Cobalt(III) acetylacetonates
by Scott Charles Busse

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University

Abstract:
The nuclear magnetic resonance quadrupole relaxation of 59Co in Cobalt(III) acetylacetonate was studied in the hope of determining the molecular motions responsible for the relaxation. A dual spin probe technique was used in which the 13C spin-lattice relaxation rate of the methine carbon was used to determine the rotation motion of the complex which is reported as an activation energy. The 59Co relaxation rate activation energy was compared to the 13C relaxation rate activation energy and the viscosity dependence of the 59Co and 13C relaxation rates were also compared. It was found that in the solvents d6-acetone and diglyme that the 59Co relaxation rate activation energy was the same as the relaxation rate activation energy which suggests that rotational reorientation is the predominate mechanism for the relaxation of the 59Co. In the solvents d6-benzene and d1-chloroform the 59Co and 13C relaxation rate activation energies and viscosity dependence were different which suggests that the 59Co relaxation is not due to rotational reorientation but may be due to vibrational motions. The role of the electric field gradient on the 59Co relaxation rate was examined by making a series of complexes in which one or two of the methine carbons were halogenated. This increased the electric field gradient of the complexes by a small amount. The 59Co relaxation rate activation energies and viscosity dependence of the halogenated complexes were then examined. It was determined that the magnitude of the electric field gradient had no influence on the molecular motions responsible for the 59Co relaxation.

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by

Scott Charles Busse

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APPROVAL

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Scott Charles Busse

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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To my wife Lisa Koyama and my parents George and Gloria Busse.

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TABLE OF CONTENTS

Page

Dedication. iv

Acknowledgements. v

List of Tables. vii

List of Figures viii

Abstract. xii

1. Introduction. 1

2. Statement of Objectives 10

3. Experimental. 11

Nomenclature. 11
Synthesis of Co(acac)$_3$. 11
Synthesis of Tris Cl, Tris Br, Tris I 13
Synthesis and Separation of Mono, and Bis Br. 14
Synthesis of Mono Cl, and Bis Cl. 14
Synthesis of Mono I, and Bis I. 15
Chemicals 15
NMR Measurements. 16
^{13}C T_1 Measurements 17
^{13}C Nuclear Overhauser Enhancement Factor Measurement . . 18
^{59}Co T_1 and Chemical Shift Measurements 19

4. Results and Discussion. 22

5. Summary and Conclusion. 77

6. References. 81

7. Appendix. 85

LIST OF TABLES

Page

Table 1: Activation energy ($KJmol^{-1}$) from ^{13}C relaxation rate 26

Table 2: Activation energy ($KJmol^{-1}$) from ^{59}Co relaxation rate 51

Table 3: ^{59}Co relaxation rate (s^{-1}) at 298K 61

Table 4: ^{59}Co T_1 in d_1-chloroform at 298K 63

Table 5: ^{13}C relaxation rate and rotational correlation time for $Co(acac)_3$ 64

Table 6: Slopes of plots of ^{59}Co chemical shift versus temperature 80

LIST OF FIGURES

Page

Figure 1: Co(acac)$_3$ and the three possible 3-halo complexes (x = Cl, Br, I) 12

Figure 2: Co(acac)$_3$ 24

Figure 3: ^{13}C ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_6$-benzene 27

Figure 4: ^{13}C ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_1$-chloroform 28

Figure 5: ^{13}C ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_6$-acetone 29

Figure 6: ^{13}C ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in diglyme 30

Figure 7: ^{13}C ln(1/T$_1$) versus 1/T of Mono Br in d$_6$-benzene 31

Figure 8: ^{13}C ln(1/Tl) versus 1/T of Bis Br in d$_6$-benzene 33

Figure 9: ^{59}Co ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_6$-benzene 34

Figure 10: ^{59}Co ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_1$-chloroform 36

Figure 11: ^{59}Co ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_6$-acetone 37

Figure 12: ^{59}Co ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in diglyme 38

Figure 13: ^{59}Co ln(1/T$_1$) versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in d$_6$-benzene 39

Page

Figure 14: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in d_1-chloroform 40

Figure 15: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in d_6-acetone 41

Figure 16: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in diglyme 42

Figure 17: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in d_6-benzene 43

Figure 18: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in d_1-chloroform 44

Figure 19: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in d_6-acetone 45

Figure 20: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in diglyme 46

Figure 21: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono I; b) Bis I; c) Tris I in d_6-benzene 47

Figure 22: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono I; b) Bis I in d_1-chloroform 48

Figure 23: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono I; b) Bis I in d_6-acetone 49

Figure 24: ^{59}Co $\ln(1/T_1)$ versus 1/T of a) Mono I; b) Bis I in diglyme 50

Figure 25: ^{13}C $1/T_1$ versus viscosity of $Co(acac)_3$ 54

Figure 26: ^{59}Co $1/T_1$ versus viscosity of $Co(acac)_3$ 56

Figure 27: ^{59}Co $1/T_1$ versus viscosity of a) Mono Cl; b) Bis Cl; c) Tris Cl 57

Figure 28: ^{59}Co $1/T_1$ versus viscosity of a) Mono Br; b) Bis Br; c) Tris Br 58

Figure 29: ^{59}Co $1/T_1$ versus viscosity of a) Mono I; b) Bis I 59

Page

Figure 30: ^{59}Co $1/T_1$ versus ligands with methine carbon halogenated a) Cl series; b) Br series; c) I series in d_6-benzene 68

Figure 31: ^{59}Co $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series in d_1-chloroform 69

Figure 32: ^{59}Co $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series in d_6-acetone 70

Figure 33: ^{59}Co $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series in diglyme 71

Figure 34: ^{59}Co $(\frac{\Delta}{n})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I; j) Tris I in d_6-benzene 74

Figure 35: ^{59}Co $(\frac{\Delta}{n})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I in d_1-chloroform . 75

Figure 36: ^{59}Co $(\frac{\Delta}{n})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I in d_6-acetone . . 76

Figure 37: ^{59}Co $(\frac{\Delta}{n})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I in diglyme 77

Figure 38: ^{59}Co chemical shift versus temperature of Co(acac)$_3$ in d_6-benzene 86

Figure 39: ^{59}Co chemical shift versus temperature of Co(acac)$_3$ in d_1-chloroform 87

Figure 40: ^{59}Co chemical shift versus temperature of Co(acac)$_3$ in d_6-acetone 88

Figure 41: ^{59}Co chemical shift versus temperature of Co(acac)$_3$ in diglyme 89

Page

Figure 42: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in d_6-benzene 90

Figure 43: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in d_1-chloroform 91

Figure 44: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in d_6-acetone 92

Figure 45: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in diglyme 93

Figure 46: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in d_6-benzene . 94

Figure 47: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in d_1-chloroform 95

Figure 48: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in d_6-acetone 96

Figure 49: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in diglyme 97

Figure 50: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I; 3) Tris I in d_6-benzene . . . 98

Figure 51: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I in d_1-chloroform 99

Figure 52: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I in d_6-acetone 100

Figure 53: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I in diglyme 101

ABSTRACT

The nuclear magnetic resonance quadrupole relaxation of ^{59}Co in Cobalt(III) acetylacetonate was studied in the hope of determining the molecular motions responsible for the relaxation. A dual spin probe technique was used in which the ^{13}C spin-lattice relaxation rate of the methine carbon was used to determine the rotation motion of the complex which is reported as an activation energy. The ^{59}Co relaxation rate activation energy was compared to the ^{13}C relaxation rate activation energy and the viscosity dependence of the ^{59}Co and ^{13}C relaxation rates were also compared. It was found that in the solvents d_6-acetone and diglyme that the ^{59}Co relaxation rate activation energy was the same as the ^{13}C relaxation rate activation energy which suggests that rotational reorientation is the predominate mechanism for the relaxation of the ^{59}Co. In the solvents d_6-benzene and d_1-chloroform the ^{59}Co and ^{13}C relaxation rate activation energies and viscosity dependence were different which suggests that the ^{59}Co relaxation is not due to rotational reorientation but may be due to vibrational motions. The role of the electric field gradient on the ^{59}Co relaxation rate was examined by making a series of complexes in which one or two of the methine carbons were halogenated. This increased the electric field gradient of the complexes by a small amount. The ^{59}Co relaxation rate activation energies and viscosity dependence of the halogenated complexes were then examined. It was determined that the magnitude of the electric field gradient had no influence on the molecular motions responsible for the ^{59}Co relaxation.

INTRODUCTION

In a paper describing the motions of a macroscopic nuclear magnetization vector in an externally applied magnetic field Bloch[1] first identified the time constants T_1 and T_2 for the relaxation of the magnetic vector from a perturbed state. Bloch defined the time constant T_2 as the tranverse relaxation time which describes the loss of phase coherence of the magnetic vector. T_1 was defined as the thermal or longitudinal relaxation time and described the return of the magnetic vector to its lowest energy state aligned with the external field.

Blomberg, Purcell and Pound[2] published a paper in 1948 in which they explained the process by which an excited magnetic vector would loose energy and return to its equilibrium position. Because spontaneous emission is not a viable process in NMR spectroscopy there must be a means by which the stimulated emission of an excited magnetic vector occurs. The loss of energy of the magnetic vector will occur when there is a fluctuating electromagnetic field that is of the same frequency as the larmor precession of the magnetic vector. When this occurs the magnetic vector can couple to the surroundings or lattice and the exchange of energy can occur.

Five mechanism[3] have been identified by which the magnetic vector can couple with the lattice they are, dipole-dipole, quadrupole, chemical shift anisotropy, scalar and spin-rotation. A mechanism of significant importance in chemistry today is the quadrupole mechanism, which is the dominant mechanism for nuclei with nuclear spins greater than one half. The relaxation is due to the interaction of the nuclear quadrupole moment with fluctuating electric field gradients at the nucleus. Many nuclei that possess quadrupole moments are important in chemistry and biological systems and NMR studies could be used to study the chemistry of the nuclei. The major obstacle in the study of quadrupolar nuclei by NMR is that the relaxation via the quadrupole mechanism is very efficient and can lead to observed linewidths that are prohibitively large. The wide lines can obscure spin-couplings to other nuclei and the overlap of the spectral lines can make resolution of separate lines impossible. To use NMR effectively to study quadrupole nuclei, the relaxation phenomenon must be used to extract information about the system, for this to occur a better understanding of the quadrupolar relaxation mechanism is needed.

NMR relaxation via the quadrupole mechanism under the extreme narrowing condition[4] is given by [5]

$$1/T_1 = 1/T_2 = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{n^2}{3}\right)\left(\frac{e^2Qq}{h}\right)^2 \tau_c \qquad (1)$$

where I is the nuclear spin quantum number, n is the asymmetric parameter, e^2Qq/h is the nuclear quadrupole coupling constant (NQCC) which consists of the nuclear quadrupole moment, eQ, and the electric field gradient (EFG), eq, and τ_c is correlation time for the reorientation of the EFG at the observed nucleus. When a quadrupolar nucleus is in an asymmetric environment in a molecule it will possess an EFG and as the molecule reorientates in an external magnetic field the EFG becomes a random function of time. This causes the fluctuating field at the nuclei that will facilitate the relaxation. However when a quadrupolar nucleus is in a symmetric environment it will not possess an EFG and the relaxation would be assumed to be via a different mechanism because the rate of relaxation calculated from equation 1 would be zero. This is not the case, experiments show that even in octahedral and tetrahedral environment quadrupole nuclei display substantial linewidths and the relaxation is via the quadrupolar mechanism.[6]

A number of theoretical studies have been undertaken to try and determine the origins and time dependence of the EFG at nuclei in symmetric environments. The explanation offered by these studies can be categorized into three groups, vibrationally induced EFG, EFG due to solvent dipoles and EFG due to distortions that fluctuate via rotational motion. The theory of vibrational induced EFG was first presented in a series of papers by Valiev[7-10] and then later in a paper by Brown and Colpa[6]. They reasoned that vibrational distortion corresponding to certain excited vibrational state will generate EFG that do not average to zero. The excited vibrational states are induced by collisions which are a random function of time so that the EFG is a random function of time and will lead to relaxation. The difference in the two studies comes in the formulation of the correlation time for the reorientation of the EFG. Valiev uses a correlation time that characterizes the damping of the vibrations. Brown and Colpa identify three correlation times, the rotational, vibrational damping and a correlation time for the dephasing of the normal vibrational coordinates. They only use the rotational and dephasing correlation times to define the overall correlation time which is defined as

$$\tau_c^{-1} = \tau_R^{-1} + \tau_2^{-1} \quad (2)$$

where τ_c is the overall correlation time, τ_R is the rotational correlation time and τ_2 is the dephasing correlation time. Brown and Colpa's overall correlation time is much shorter than the damping correlation time used by Valiev and they cite a paper by Oxtoby[11] in support of this assumption. Even though Valiev's and Brown and Colpa's correlation times are not the same both papers use the normal vibrational coordinates in the derivation of their equations for the quadrupole relaxation.

In a series of papers Hertz[12,13] identified another means by which the EFG at symmetric sites could be produced. He reasoned that solvent dipoles could produce an EFG and the random reorientation of the solvent dipole would cause the EFG to fluctuate and thereby induce relaxation. In the Hertz theory the correlation time in equation 1 would be the correlation time for the reorientation of the solvent dipoles and would be dependent on the solvent.

The third theory of quadrupole relaxation in symmetric environments is presented by Abragam[14]. In this theory the EFG are produced by small distortions from ideal symmetry. As the molecule rotates in a magnetic field the small EFG becomes a function of time this fluctuation of the EFG then induces relaxation. Because the correlation time in equation 1 will be the rotational correlation time for the molecule, the Stokes-Einstien[15] equation can be used to determine the rotational correlation time if the molecular volume and shape is known and if solvent interaction are weak. This would in principle enable one to calculate the NQCC from equation 1 using the relaxation rate and the rotational correlation time but in practice determining the rotational correlation time using the Stokes-Einstien equation can be very difficult.

A number of experimental studies have been undertaken to either prove or disprove the three different theories. Support for the vibrational theory can be found in two studies of the ^{59}Co relaxation in cobalt(III) complexes in solution. Both studies use the dual spin probe technique[16] to examine the relaxation. In the dual spin probe technique the relaxation of one nucleus in a molecule is studied by comparison of the relaxation of another nucleus that is well understood. In the majority of cases the dipole-dipole relaxation of a carbon bonded to a proton is used as the standard to which comparisons are made. The equation for the dipole-dipole relaxation of a carbon with attached protons is given by the following equation[17] in the extreme narrowing limit

$$1/T_1 = N\,\gamma_C^{\,2}\,\gamma_H^{\,2}\,\hbar^2\,(r_{CH})^{-6}\,\tau_R \qquad (3)$$

where N is the number of protons bonded to the carbon, γ_C and γ_H are the magnetogyric ratio 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 in equation 3 is assumed to be the rotational correlation time of the molecule which is determined and used in equation 1 for the quadrupole relaxation to determine if τ_C in equation 1 is a rotational correlation time or another correlation time.

The first of the ^{59}Co relaxation studies was done by Doddrell[18] who compared the ^{59}Co relaxation rates of tris(tropolonato)cobalt (III), [Co(trop)$_3$], and tris(acetylacetonate)cobalt(III), [Co(acac)$_3$]. The ^{13}C relaxation rate of the methine carbons were used to determine a rotational correlation time for each molecule which was then used along with the ^{59}Co relaxation rate to calculate the ^{59}Co NQCC for each complex. Values of 3.47 MHZ and 16.66 MHZ were found for the ^{59}Co NQCC of Co(acac)$_3$ and Co(trop)$_3$ respectively. From crystal structures of Co(acac)$_3$ and Co(trop)$_3$ Doddrell concluded that the ^{59}Co NQCC for the two complexes should be very similar and since the NQCC calculated using the rotational correlation time did not display this, the ^{59}Co relaxation is not due to rotational motion and assumed vibrational motion was responsible.

In another study of the ^{59}Co relaxation Chacko and Bryant[20] examined the ^{59}Co relaxation of $Co\,(CN)_6^{-3}$ ion using the dual spin probe technique. By comparing the temperature dependence of the ^{13}C relaxation, which is due to rotational reorientation, and the temperature dependence of the ^{59}Co relaxation they concluded that the ^{59}Co relaxation was unrelated to the rotational motion of the complex and suggested it may be due to vibrations.

The Hertz theory of solvent dipoles being responsible for the quadrupole relaxation has found its greatest utility in the study of the relaxation of solvated ions, in particular, the relaxation of alkali metals in water[13]. For larger complexes the solvent dipoles should have little effect on the EFG because of the large distance between the solvent and the quadrupole nuclei. This fact presumably limits the use of the Hertz theory to small ions.

The third theory in which rotational motion is responsible for the relaxation of quadrupole nuclei in symmetric environments has been used extensively to explain a number of experimental studies. One such study was done by Hao[21] in which he examined the relaxation of ^{47}Ti and ^{49}Ti in TiX_4 complexes where X is Cl, Br or I. Using a rotational correlation time calculated from the Gierer and Wirtz modified Stokes-Einstein equation[22] along with the ^{47}Ti and ^{49}Ti relaxation rate Hao calculated ^{47}Ti and ^{49}Ti NQCC. The NQCC were found to be of the right magnitude for a distorted tetrahedra and the ratio of the ^{47}Ti NQCC to the ^{47}Ti NQCC was equal to the ratio of the nuclear quadrupole moments. These two facts support the theory that the quadrupole relaxation of nuclei in symmetric environments is due to the fluctuations of an EFG generated by small distortions.

Another study by Dechter[23] also supports the rotational theory of quadrupole relaxation. Dechter used ^{27}Al, ^{69}Ga, ^{71}Ga, and ^{115}In acetylacetonates to examine the relaxation using the dual spin probe technique. The ^{13}C relaxation of the methine carbons were measured as a function of temperature and used to determine rotational correlation times for the complexes. The correlation time along with the quadrupole relaxation rates were used to calculate NQCC which agreed with the expected values for slightly distorted octahedals. The temperature dependence of the quadrupole relaxation also agreed with the temperature dependence of the ^{13}C relaxation which further supports the rotational theory.

Brownlee[24] also used the dual spin probe technique to examine the ^{95}Mo and ^{97}Mo quadrupole relaxation of $Mo(CO)_6$. The rotational correlation time for the complexes was determined from the chemical shift anisotropy relaxation of ^{13}C. The ^{95}Mo and ^{97}Mo relaxation rates along with the rotational correlation time were used to calculate the ^{95}Mo and ^{97}Mo NQCC. The NQCC ratio was found equal to the nuclear quadrupole moment ratio as in the Nao study and Brownlee concluded that rotational motion was responsible for the quadrupole relaxation of ^{95}Mo and ^{97}Mo.

It is clear from the experimental studies that no one theory explains the quadrupole relaxation of nuclei in symmetric environments. This is particularly evident in examining the relaxation of ^{59}Co, ^{27}Al, ^{69}Ga, ^{71}Ga and ^{115}In in acetylacetonates. ^{59}Co is said to relax via vibrational motion while ^{27}Al, ^{69}Ga, ^{71}Ga and ^{115}In are believed to relax via rotational motion. It is not obvious what could cause such a difference in the relaxation of the complexes. Because the relaxation of a quadrupolar nucleus is dependent on its nuclear quadrupole moment the answer may lie in differences in the magnitude of the nuclear quadrupole moment, this is clearly not the case because the nuclear quadrupole moment of ^{59}Co lies between that of ^{27}Al and ^{115}In and both ^{27}Al and ^{115}In relax via rotational motion. The difference may lie in the solvent or possibly on the magnitude of the EFG due to distortions so a more thorough study is needed to examine the relationship of the solvent and EFG on the type of motion responsible for the relaxation of the quadrupole nuclei.

Because of the questions raised by comparing the Doddrell study and the Dechter study the Co(acac)$_3$ molecule is chosen to study the quadrupole relaxation of nuclei in symmetric environments. The dual spin probe technique will be employed and the temperature dependence of both the ^{13}C and ^{59}Co relaxation will be compared, because the ^{13}C relaxation is due to rotational reorientation this will provide a means of determining if the ^{59}Co relaxation is due to rotational motion or not. Co(acac)$_3$ is soluble in a number of different solvents so that the solvent dependence of the ^{59}Co relaxation can be examined. The dependence of the motions responsible for the ^{59}Co relaxation with the EFG can be explored by varying the EFG at the cobalt through asymmetric substitution of the acetylacetonate ligands by a method described by Collman[25]. This method is used to halogenate the methine carbon of one, two or all three ligands which will allow for the systematic increase and variation of the EFG at the cobalt nucleus.

STATEMENT OF OBJECTIVES

A study of the ^{59}Co quadrupole relaxation of Co(acac)$_3$ and a series of 3-halogenated complexes is undertaken using the dual spin probe technique to determine the origins and time dependence of the EFG at the cobalt nucleus. The ^{13}C relaxation is used to examine the rotational motion of the complexes and the ^{59}Co relaxation is compared to this to determine if the vibrational, rotational or solvent dipole relaxation mode theories explain the ^{59}Co relaxation.

EXPERIMENTAL

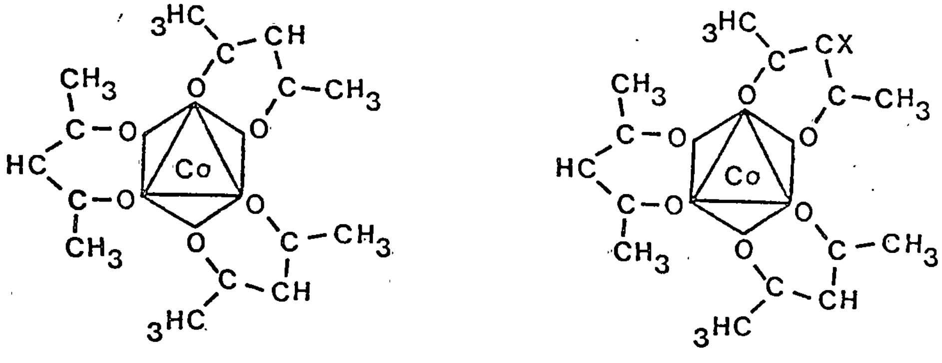
Nomenclature

The following nomenclature has been adopted for the (3-halo 2, 4 pentiediono) Cobalt(III) complexes. Figure 1 shows Co(acac)$_3$ and the three possible halogenated complexes. When X is Cl the complexes will be named Mono Cl, Bis Cl and Tris Cl, the three chloro complexes are referred to as the Cl series. The bromo and iodo complexes are named in the same manner. The term Mono complexes is used to refer to Mono Cl, Mono Br and Mono I, Bis complexes and Tris complexes similarly refer to Bis Cl, Bis Br, Bis I and Tris Cl, Tris Br, Tris I respectively.

The solvent 2-methoxyethyl ether will be referred to by it's common name of diglyme.

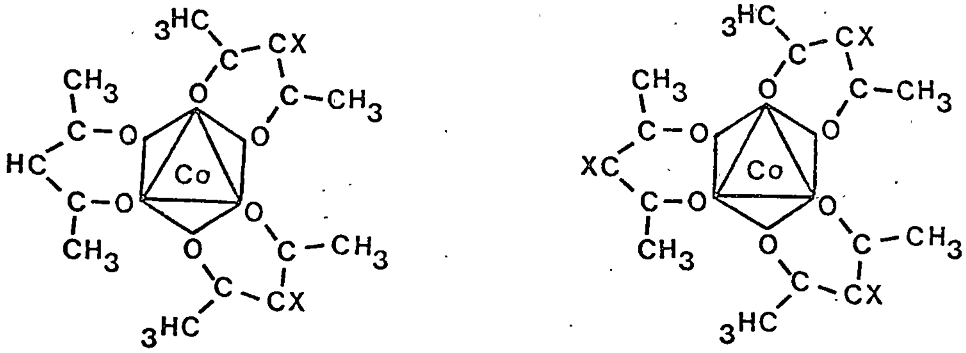
Synthesis of Co(acac)$_3$

Co(acac)$_3$ was synthesized by a method described by Bryant and Fernelius[26]. 2.5 g (0.021 mol) Cobalt(II) carbonate was added to 20 ml aetylacetonate in a erlenmeyer flask, the mixture was heated to approximately 100° C and 30 ml of 10% hydrogen peroxide was added very slowly with stirring. After the addition of all the hydrogen peroxide the mixture was allowed to stir for 30 minutes. The mixture was cooled in an ice bath and the dark green crystals were collected by filtration and dried at 110° C. The crystals were then dissolved in 25 ml benzene and 150 ml of heptane was added all at once. The crystals were again collected by filtration and recrystalized once more in a benzene-



$Co(acac)_3$

Mono X



Bis X

Tris X

Figure 1: $Co(acac)_3$ and the three possible 3-halo complexes (x = Cl, Br, I).

heptane mixture and then dried under vacuum. NMR was used to characterize the Co(acac)$_3$ and halogenated complexes. The ^{1}H NMR was acquired in $d_6{}^1$-benzene and referenced to benzene at 7.15 ppm, the ^{13}C NMR was acquired in d_6-benzene and referenced to d_6-benzene at 128 ppm and the ^{59}Co NMR was acquired in d_6-benzene and referenced to Co(acac)$_3$ at 0 ppm in d_6-benzene at 298 K^{27}.

Co(acac)$_3$: ^{1}H NMR 5.29 ppm (3-H); 1.92 ppm (18-H). ^{13}C NMR 189.23 ppm (6-Co); 97.08 ppm (3-CH); 25.77 ppm (6-CH$_3$). ^{59}Co NMR 0 ppm at 298 K.

Synthesis of Tris Cl, Tris Br and Tris I

This Cl, Tris Br and Tris I were synthesized using procedures described by Collman^{25}. Tris Cl was made by adding 0.16 g (1.2×10^{-3} mol) of N-chlorosuccinimide to a beaker containing 0.14 g (4×10^{-4} mol) of Co(acac)$_3$ in 30 ml of chloroform. This mixture was allowed to stir for 30 minutes, the solvent was then evaporated on a Brinkman rotavapor. The green solid was washed several times with distilled water and then dried under vacuum for 24 hours. Tris Br and Tris I were made in a similar way but 0.21 g (1.2×10^{-3} mol) of N-bromosuccinimide and 0.27 g (1.2×10^{-3} mol) of N-iodosuccinimide were used in place of the N-chlorosuccinimide respectively.

Tris Cl: ^{1}H NMR 2.20 ppm (18-H). ^{59}Co NMR -89 ppm at 298 K.

Tris Br: ^{1}H NMR 2.28 ppm (18-H). ^{13}C NMR 188.21 ppm (6-CO); 94.99 ppm (3-CBr); 30.02 ppm (6-CH$_3$). ^{59}Co NMR -129 ppm at 298 K.

Tris Cl: ^{1}H NMR 2.42 ppm (18-H). ^{59}Co NMR -193 ppm at 298 K.

Synthesis and separation of Mono Br and Bis Br

Mono Br and Bis Br were synthesized as a mixture of Mono Br, Bis Br and Tris Br by using 0.178 g (1.0 x 10^{-3} mol) of N-bromosuccinimide. The mixture was crudely separated on a flash silica gel column under 5 psi of nitrogen with methylene chloride as the solvent. Tris Br was the first complex off the column followed by Bis Br. Mono Br was removed from the column by changing solvents to acetone. The three fractions were then cleaned up on another silica gel column using methylene chloride as the solvent and removing the Mono Br from the column with acetone.

Mono Br: ^{1}H NMR 5.21 ppm (2-H); 2.31 ppm (6-H); 1.86 ppm (6-H); 1.81 (6-H). ^{13}C NMR 189.13 ppm (4-CO); 188.24 ppm (2-CO); 97.20 ppm (2-CH); 94.87 ppm (1-CBr); 30.02 ppm (2-CH_3); 25.77 ppm (2-CH_3); 25.64 ppm (2-CH_3). ^{59}Co NMR -48 ppm at 298 K.

Bis Br: ^{1}H NMR 5.21 ppm (1-H); 2.33 ppm (6-H); 2.30 ppm (6-H); 1.87 ppm (6-H). ^{13}C NMR 189.77 ppm (2-CO); 188.48 ppm (2-CO); 188.21 ppm (2-CO); 97.21 ppm (1-CH); 94.99 ppm (2-CBr). ^{59}Co NMR -93 ppm at 298 K.

Synthesis of Mono Cl and Bis Cl

Mono Cl and Bis Cl were synthesized by same method as the synthesis of Tris Cl but only 0.107 g (8.0 x 10^{-4} mol) of N-chlorosuccinimide was used. The mixture contained mainly Mono Cl and Bis Cl with a small amount of Tris Cl (approx. 5%). Separations were attempted with silica gel, Alumina, Magnesium oxide, Sphedex LH-20, and fractional crystalization, all attempts resulted in either no separation or the reduction of the cobalt from cobalt (III) to cobalt (II). As a result of the failed attempts at separating the Mono Cl and Bis Cl all NMR measurements were made on a mixture and limited to ^{59}Co NMR. The ^{59}Co chemical shift for Mono Cl and Bis Cl in d_6-benzene at 298 K are -33 ppm and -66 ppm respectively.

Synthesis of Mono I and Bis I

Mono I and Bis I were synthesized by the before mentioned method using 0.135 g (6×10^{-4} mol) of N-iodosuccinimide. The reaction products were an almost equal amount of Mono I and Bis I. As with the Mono Cl and Bis Cl all attempts at separation failed. The ^{59}Co chemical shifts for Mono I and Bis I in d_6-benzene at 298 K are -68 ppm and -136 ppm respectively.

Chemicals

All chemicals were used as received with no further purification. The d_6-benzene was obtained from Wilmad Glass Company and had an isotopic purity of 99.5% D. The d_1-chloroform was from Stohler Isotope Chemicals and had an isotopic purity of 99.8% D. The d_6-acetone was from Norell Inc. and had an isotopic purity of 99.8% D. The acetylacetone was obtained from the Sigma Chemical Company. The N-chlorosuccinimide and N-bromosuccinimide were from Aldrich Chemical Company. The N-iodosuccinimide was obtained from Fluka AG of Switzerland. The heptane, digylme, hydrogen peroxide, acetone, silica gel, benzene and methylene chloride were from J.T. Baker Chemical Co. The cobalt(II) carbonate was from the Allied Chemical Company.

NMR Measurements

All NMR measurements were made on a Bruker WM-250 spectrometer operating at 250.132 MHZ, 62.898 MHZ and 59.36 MHZ for ^{1}H, ^{13}C and ^{59}Co respectively. A deuterium lock was used for all samples but those in diglyme, which were run unlocked. ^{1}H NMR measurements were done in a 5 mm sample tube and the temperature was uncontrolled. ^{13}C and ^{59}Co NMR measurements were done 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 in the solvent was low. A 3 mm capillary of methanol was inserted in the center of the 10 mm tube as a means of monitoring the temperature. The sample was limited to the bottom 4 cm of the 10 mm tube to keep the sample in the most homogeneous part of the magnetic and centered in the transmitter and receiver coils.

The temperature was controlled with a Bruker B-VT 1000 temperature control unit using both the heating element and the liquid nitrogen cooling unit simultaneously. The samples were allowed one hour for the temperature to stabilize before the ^{13}C or ^{59}C NMR were acquired. The temperature was measured for all samples but those in digylme by acquiring a ^{1}H spectra of the sample through the 10 mm NMR probes decoupler coils and measuring the chemical shift difference in Hz of the methyl protons and OH proton of methanol. The difference in Hz of the methyl protons and the OH proton of methanol is linearly dependent on temperature[28] and the calibration curve provided by Bruker Instruments was used to determine the temperature.

Because the proton signals in diglyme obscured the proton signals of methanol another means to measure the temperature was used. A temperature calibration curve was made for the ^{59}Co chemical shift of Co(acac)$_3$ in diglyme by the following procedure. A temperature calibration curve for Co(acac)$_3$ in d$_6$-chloroform was made using the Bruker methanol calibration curve (see appendix). This is possible because the ^{59}Co chemical shift is linear with temperature[29]. A sample of Co(acac)$_3$ in diglyme was made with a 5 mm capillary of Co(acac)$_3$ in d$_6$-chloroform inserted in the center. The ^{59}Co chemical shift of Co(acac)$_3$ in diglyme and d$_1$-chloroform was determined as a function of temperature and a temperature calibration curve for the ^{59}Co chemical shift in diglyme was made using the ^{59}Co chemical shift in d$_1$-chloroform to determine the temperature.

The ^{59}Co chemical shift was used to monitor the stability of the temperature. The ^{59}Co chemical shift of Co(acac)$_3$ in chloroform shifts 3 ppm per degree kelvin[29] so that any temperature fluctuation will show up as an unstable ^{59}Co chemical shift. It was determined that for the ^{59}Co NMR measurements which require only 4-8 seconds to acquire that the temperature stability was better than $\pm$ 0.1 K. The ^{13}C measurement required from 6-8 hours to acquire and the temperature stability was $\pm$ 0.5° K.

^{13}C T_1 Measurements

The ^{13}C T_1 of the methine carbon at 97 ppm was determined as a function of temperature from 280 K to 310 K for Co(acac)$_3$ in d$_6$-benzene d$_1$-chloroform, d$_6$-acetone, diglyme; and for Mono Br and Bis Br in

d_6-benzene. The T_1 was measured by the modified fast inversion-recovery technique[30] which employs the following pulse sequence

$$[180^\circ, \tau, 90^\circ, (\Delta - \tau)] \quad (4)$$

where τ is the variable delay, and Δ is determined to be 2.5 T_B (where T_B is the upper limit of an interval of time known to contain T_1; $T_A < T_1 < T_B$). The 180° and 90° pulses were determined before each experiment and the spectral window was centered on the methine carbons at 97 ppm to reduce error due to frequency offset. Between 6-12 τ values were used for each experiment and between 400-800 transient were collected for each τ value.

The T_1 values were obtained using the following equation[31]

$$\ln(A_\infty - A_\tau) = \ln 2A_\infty - \tau/T_1 \quad (5)$$

where A_∞ is the signal intensity for a very long (>5 T_1) and A is the signal intensity for a given τ value. T_1 is determined from the slope of a plot of $\ln(A_\infty - A_\tau)$ versus τ which is equal to $1/T_1$. The experimental data was fit to a straight line using the linear regression program of a Texas Instruments SR-51-II calculator. All plots were linear with a correlation coefficient between .99-.98 with the majority falling in the .99 region.

^{13}C Nuclear Overhauser Enhancement Factor Measurement

The ^{13}C Nuclear Overhauser Enhancement (NOE) factor was measured for the methine carbon of $Co(acac)_3$ in d_1-chloroform at room temperature. A method described by Freeman[32] was used to determine the NOE factor.

The technique involves acquiring two ^{13}C NMR spectra of the resonance understudy, one is acquired with the protons broadband decoupled and the other with the protons decoupled but with the NOE suppressed.

To minimize the heating due to broadband proton decoupling an experiment was set up to acquire both the broadband proton decoupled spectra and the ^{13}C spectra with NOE suppressed alternately. By acquiring only ten transients of the broadband decoupled spectra at a time then acquiring ten transients of the NOE suppressed spectra and continuing to alternate the temperature was maintained at room temperature.

The NOE factor was determined from the average of five separate measurements and the error was assigned as ± one standard deviation of the average.

^{59}Co T_1 and Chemical Shift Measurements

The ^{59}Co T_1 and chemical shift were measured as a function of temperature from 280 K to 310 K for $Co(acac)_3$ and the halogenated complexes in d_6-benzene, d_1-chloroform, d_6-acetone and diglyme. For $Co(acac)_3$ the measurements were made on either a .1 M solution or a saturated solution depending on the solubility in the solvent. The measurements of the halogenated complexes were made on mixtures of the Cl series, the Br series or the I series. The mixtures were either saturated or approximately .1 M overall depending on the solubility. Between 10-80 transients were collected depending on the solubility.

The ^{59}Co chemical shift was measured using the Bruker peak pick routine and an internal reference set so that the ^{59}Co chemical shift of Co(acac)$_3$ in d_6-benzene at 298 K is 0 ppm. The resultant plots of ^{59}Co chemical shift versus temperature for Co(acac)$_3$ and the halogenated complexes in d_6-benzene, d_1-chloroform, d_6-acetone and diglyme can be found in the appendix.

The ^{59}Co T_1 was determined from the width at half height of the spectral line for a complex. This is possible because of the following equation[33]

$$1/T_2 = \Delta_{1/2} \quad (6)$$

where $\Delta_{1/2}$ is the width at half height, and

$$1/T_1 = 1/T_2 \quad (7)$$

under the extreme narrowing condition. Because the solvents are nonviscous and the Co(acac)$_3$ and halogenated complexes are fairly small molecules, the extreme narrowing condition will hold and the ^{59}Co relaxation rate will be given by

$$1/T_1 = \Delta_{1/2} \quad (8).$$

Equation (8) was experimentally tested by measuring the ^{59}Co T_1 for Co(acac)$_3$ by the inverse-recovery technique and comparing it to the T_1 measured from the linewidth. In all cases the T_1 measured from the linewidth was in good agreement (approx. 5%) with the T_1 determined by the inversion-recovery technique.

The ^{59}Co T_1 reported for a complex in a given solvent and at a given temperature is the average of five separate linewidth determinations. The linewidths were determined by hand from scaled plots of the ^{59}Co spectra because the Bruker linefit program was found to give erroneous linewidth. The error was assigned as ± one standard of the average. Most errors were within 5% of the average.

RESULTS AND DISCUSSION

As stated earlier the purpose of this study is to determine the origins and time dependence of the EFG at the cobalt nucleus in $Co(acac)_3$, and related halogenated complexes. The three theories of the origin and fluctuation of the EFG in symmetric environments, rotational, vibrational and solvent reorientation, differ mainly in the interpretation of the correlation time in the equation for quadrupole relaxation,

$$1/T_1 = \frac{3\pi^2}{10} \frac{2I+3}{(2I-1)} (1 + \frac{n^2}{3})(\frac{e^2Qq}{h})^2 \tau_c. \quad (1)$$

Since τ_c is the only temperature dependent term in equation 1 and because the correlation times for the three different theories should have different termperature dependence, a temperature study of the ^{59}Co relaxation, could in principle be used to determine if the motion described by τ_c are rotational, vibrational or due to the solvent.

The ^{13}C relaxation of ligand carbons with hydrogens directly bonded to them can be used as a standard for the rotational motion of $Co(acac)_3$. The equation for the dipole-dipole relaxation of carbons with hydrogens bonded to them is given by equation (3)

$$1/T_1 = \gamma_c{}^2\gamma_H{}^2h^2(r_{cH})^{-6}\,\tau_R. \quad (3)$$

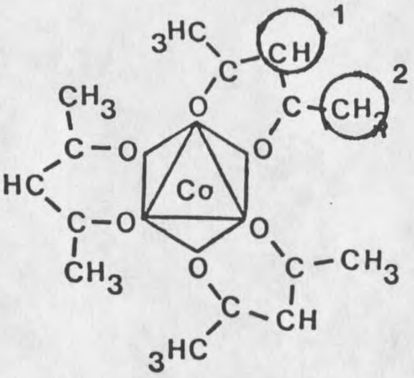
If τ_R, the rotational correlation time of the C-H vector, is the same as the rotational correlation time for the entire $Co(acac)_3$ molecule equation 3 gives a means by which the rotational motion of the $Co(acac)_3$ molecule can be studied directly.

Before the ^{13}C relaxation data can be used to study directly the rotational motion of the $Co(acac)_3$ molecule a number of questions must be answered. The first is if the rotation of the $Co(acac)_3$ molecule is isotropic and the rotational motion can be described by only one correlation time. Two studies by Yamatera[33,34] found that the rotational motion of tris(ethylenediamine)cobalt(III), tris(1,10-phenanthroline)cobalt(III) and tris(2-2'-bipyridine)cobalt(III) are nearly isotropic, and can therefore be described by one correlation time. Because $Co(acac)_3$ is also a tris bidentate complex its rotational motion is assumed to be isotropic.

Another question to address is if any of the carbon atoms with hydrogens bonded to them in the actetylacetonate liqand will have correlation times for the reorientation of their C-H vector that are the same as the rotational correlation time for the $Co(acac)_3$ molecule. In Figure 2 it can be seen that $Co(acac)_3$ has two different carbons with hydrogens directly bonded to them, these are the methine carbons (1) and the methyl carbons (2). The methyl carbons can be eliminated as a probe to the rotational motion of the $Co(acac)_3$ molecule, because the C-H vectors can reorienate by rotation about the carbon-carbon bond, as well as by rotation of the molecule, the ^{13}C relaxation is described by two correlation times and equation 3 can not be used to directly study the rotation of the $Co(acac)_3$ molecule.

The methine carbon on the other hand is ideal for a study of the rotational motion of the $Co(acac)_3$ molecule. Because the acetylacetonate liqand possesses a significant amount of π electron delocalization it is in a ridged planar arrangement. This fact means that the motions of the methine carbon and its associated hydrogen are limited, and consist mainly of the rotational reorientation of the $Co(acac)_3$ molecule. Therefore equation (3) can be used directly to study the rotation motion of the $Co(acac)_3$ molecule.

Figure 2. $Co(acac)_3$



The last question to answer is if the methine carbon relaxation due only to the dipole-dipole mechanism or are other mechanisms contributing to the relaxation. In other words is the ^{13}C relaxation of the methine carbon given by

$$1/T_1 = 1/T_{1d-d} + 1/T_{1i} \quad (8)$$

where $1/T_{1d-d}$ is the relaxation due to the dipole-dipole relaxation, and $1/T_{1i}$ is the relaxation due to other mechanisms.

By measuring the nuclear overhauser enhancement (NOE) of the ^{13}C nucleous while irradiating the protron directly bonded to it the percentage[35] of dipole-dipole relaxation can be determined. The following equation is used to determine the NOE factor

$$S_\infty/S_0 = \eta + 1 \quad (9)$$

where S_∞ is the ^{13}C signal intensity while irradiating the protrons, S_0 is the ^{13}C signal intensity with no irradiation, and η is the NOE factor. Grant[36] showed that if the relaxation of a carbon bonded to a proton is 100% dipole-dipole that the ^{13}C NOE factor is equal to 1.988. If the NOE factor is less than 1.988 the ^{13}C relaxation is not 100% dipole-dipole. The percentage of dipole-dipole is given by the following equation

$$\frac{\eta\ \text{experimental}}{1.988} \times 100 = \text{percent dipole-dipole.} \quad (10)$$

The NOE factor for the methine carbon of $Co(acac)_3$ in d_1-chloroform was determined to be 1.87 ±.2. The ^{13}C relaxation of the methine carbon can be considered to be 100% dipole-dipole because the NOE factor is within experimental uncertainty of 1.988. Even if the NOE factor was actually 1.87 the contribution of other mechanism would only be 6% so that the contribution of the other mechanism could be safely ignored.

Now that it has been determined that the ^{13}C relaxation can be used as a direct probe of the rotational motion of the $Co(acac)_3$ molecule a means by which the temperature dependence of the ^{13}C relaxation can be compared to the temperature dependence of the ^{59}Co

relaxation is needed. It has been determined that the temperature dependence of the correlation time is given by [37]

$$\tau_C = \tau_0 \, e^{(E_a/RT)} \qquad (11)$$

where τ_C is the correlation time, τ_0 is a preexponential term, T is the temperature in Kelvin, R is the gas constant and E_a is the activation energy. Since $\tau_C \propto 1/T_1$ equation 11 can be rewritten as

$$1/T_1 = A_0 \, e^{(E_a/RT)} \qquad (12).$$

Equation 12 now resembles the Arrhenius equation and a plot of $\ln(1/T_1)$ versus 1/T should yield a straight line with a slope of E_a/R.

Figures 3-7 are plots of $\ln(1/T_1)$ versus 1/T for the ^{13}C relaxation of the methine carbon of $Co(acac)_3$ in d_6-benzene, d_1-chloroform, d_6-acetone and diglyme respectively. The plot are indeed linear and activation energies are listed in Table 1. The activation energies are viscosity dependent with the least viscous solvent d_6-acetone displaying the lowest activation energy and the most viscous solvent diglyme displaying the highest activation energy.

Table 1. Activation energy ($KJmol^{-1}$) from ^{13}C relaxation rate.

	solvent			
complex	d_6-benzene	d_1-chloroform	d_6-Acetone	Diglyme
$Co(acac)_3$	12	11	7	13
Mono Br	16	--	--	--
Bis Br	11	--	--	--

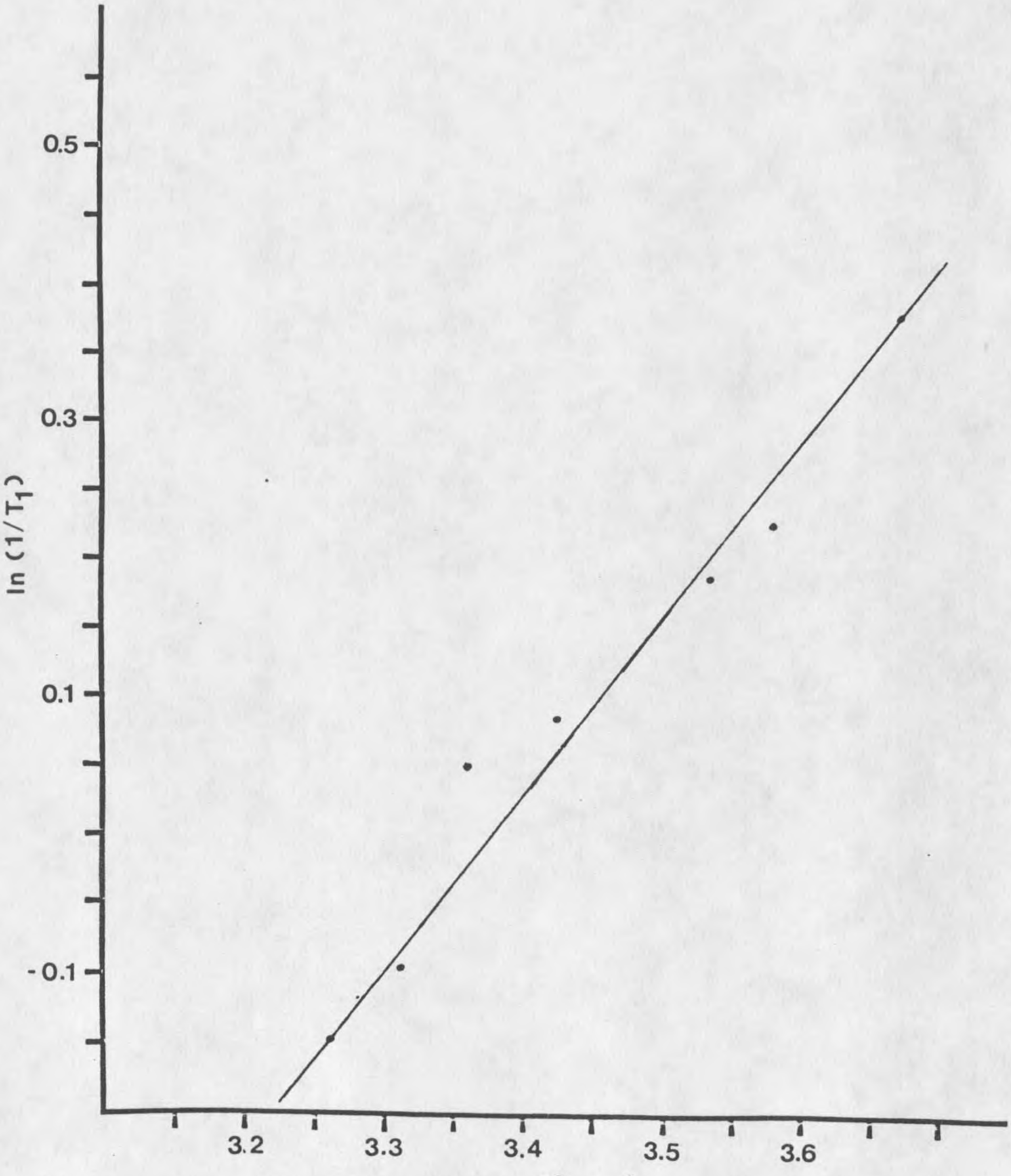


Figure 3: ^{13}C ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_6$-benzene.

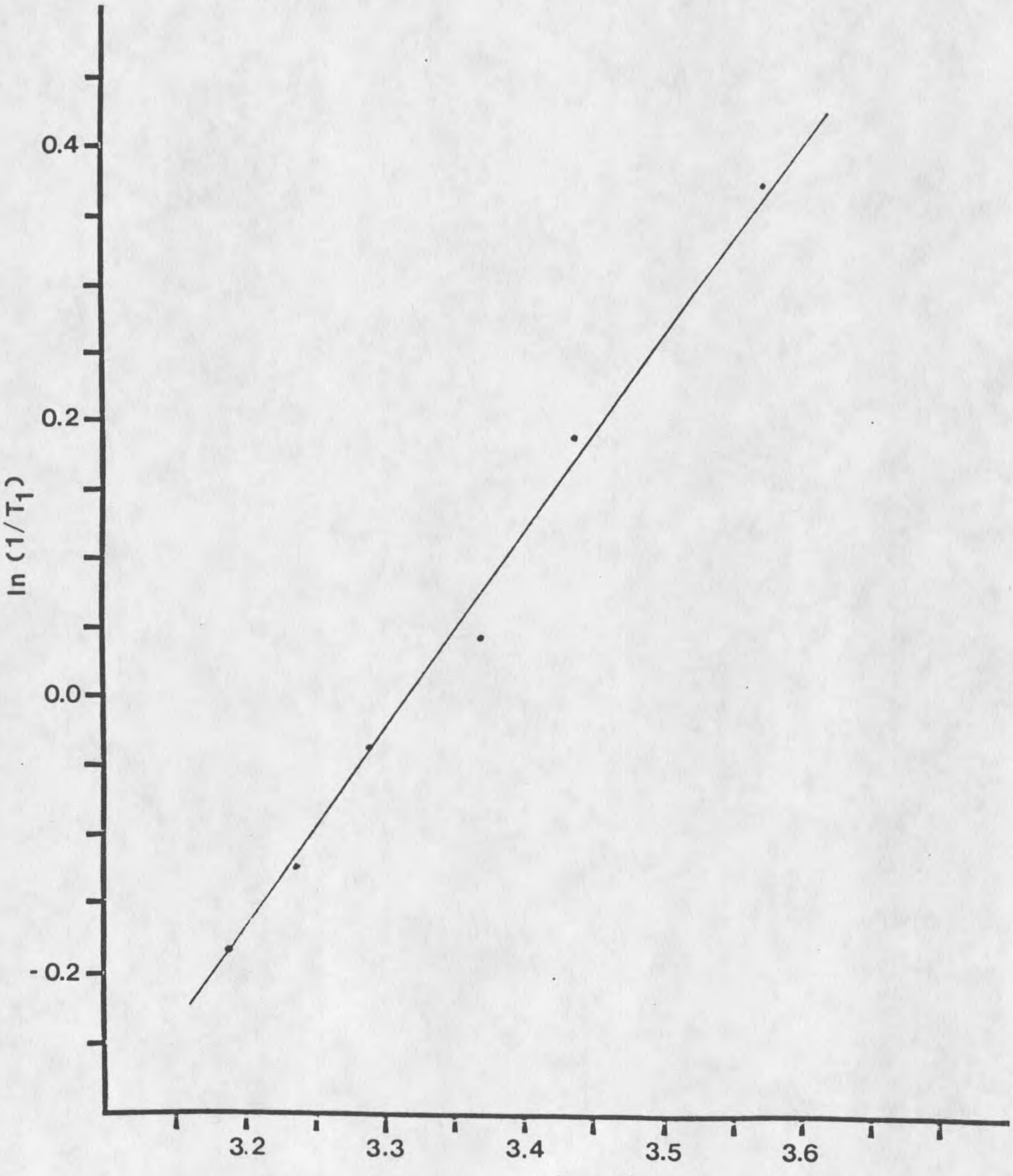


Figure 4: ^{13}C ln(1/T_1) versus 1/T of $Co(acac)_3$ in d_1-chloroform.

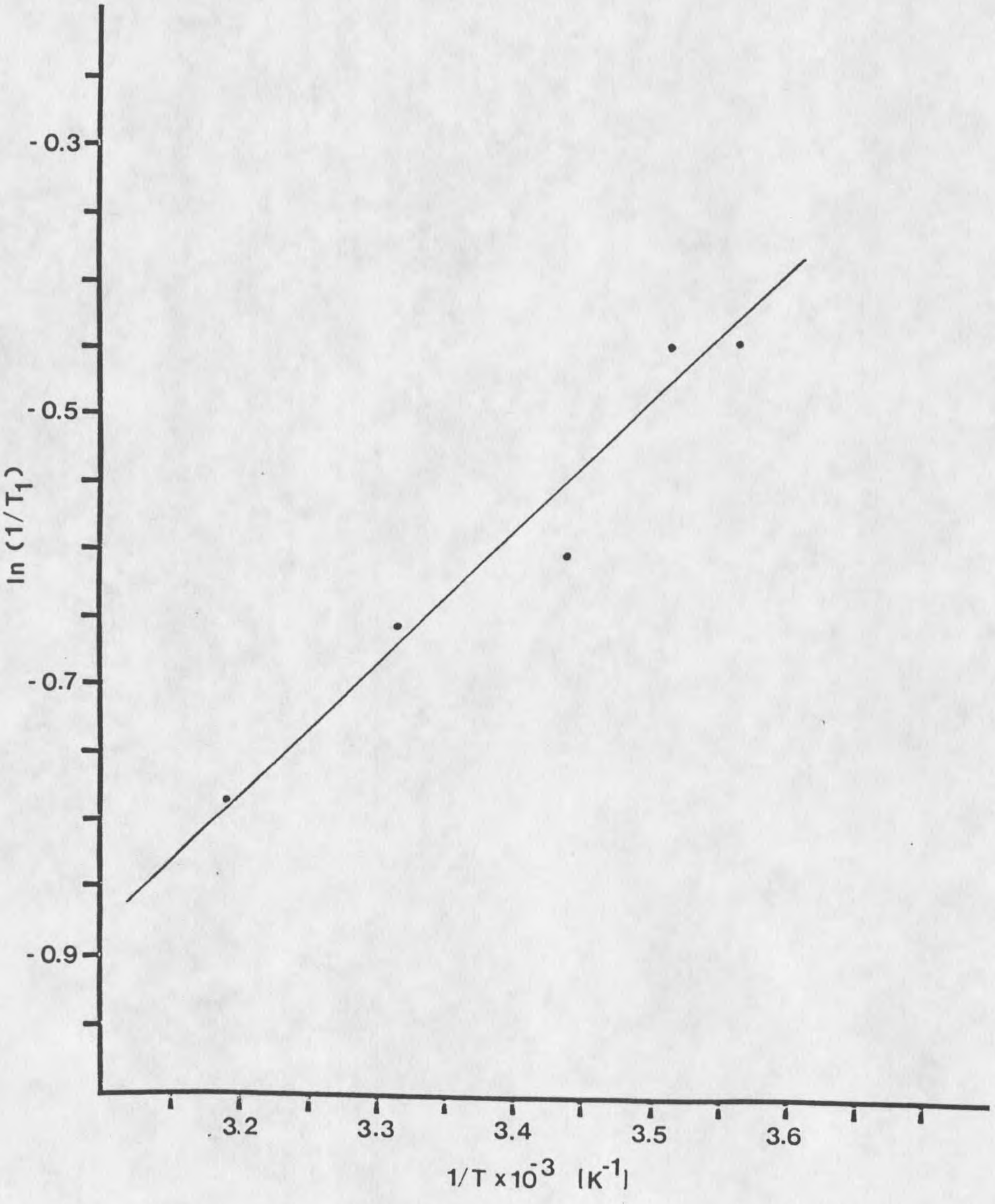


Figure 5: ^{13}C $\ln(1/T_1)$ versus 1/T of $Co(acac)_3$ in d_6-acetone.

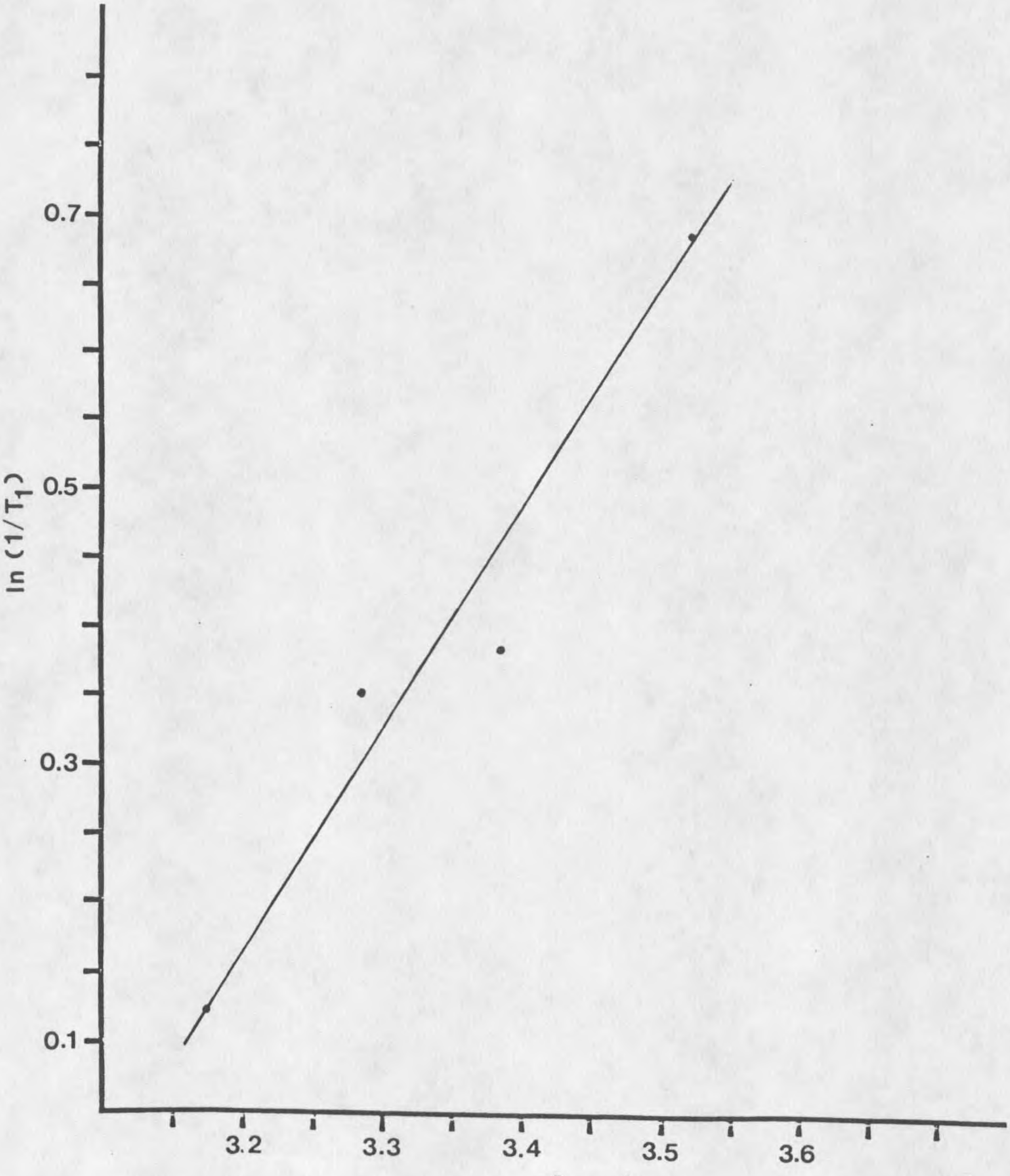


Figure 6: ^{13}C ln(1/T_1) versus 1/T of Co(acac)$_3$ in diglyme.

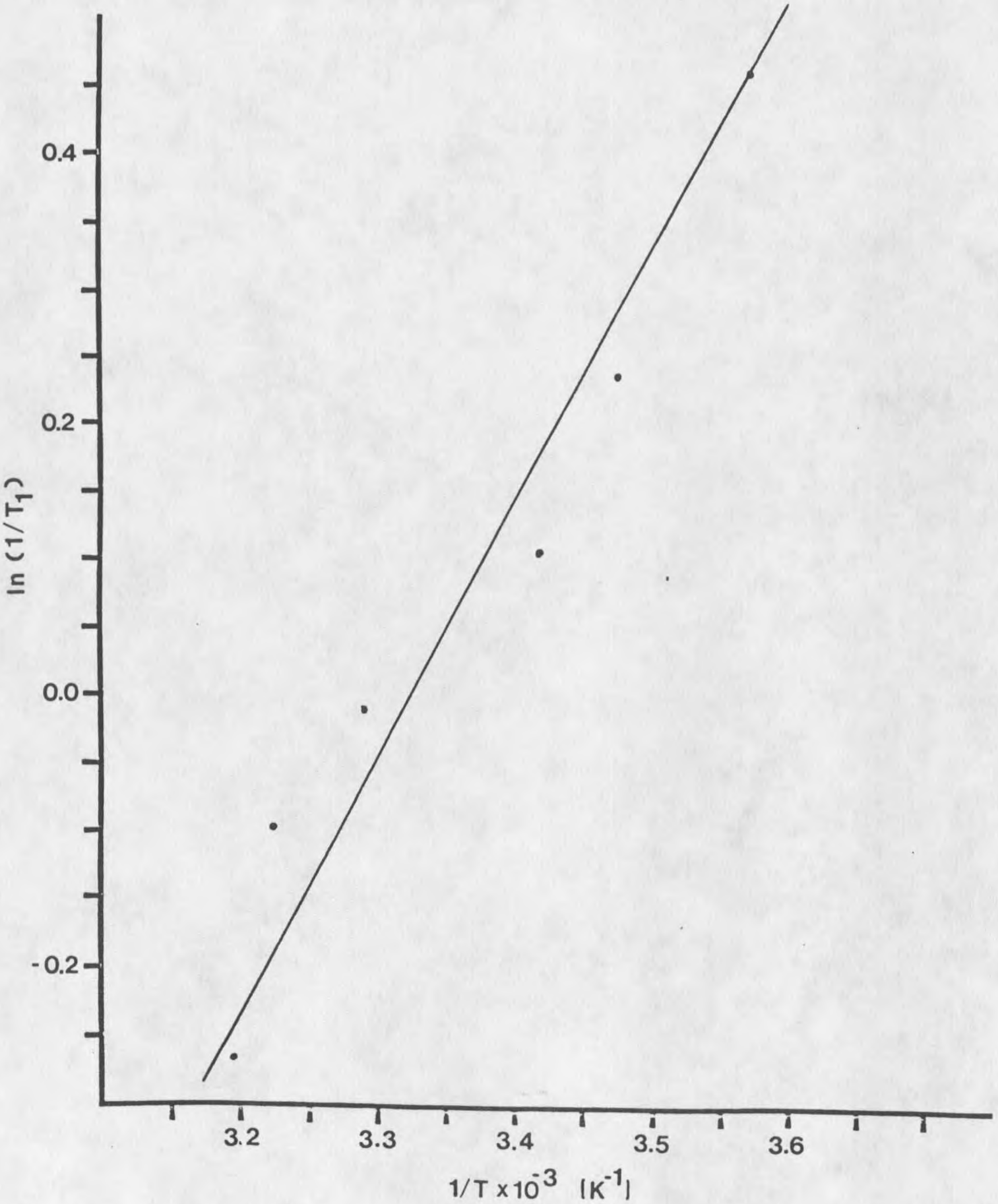


Figure 7: ^{13}C ln(1/T_1) versus 1/T of Mono Br in d_6-benzene.

Figure 8 and 9 are plots of $\ln(1/T_1)$ versus $1/T$ for Mono Br and Bis Br in d_6-benzene respectively. It is interesting even though the rotational motion of these complexes is not isotropic the plots are still linear. The activation energies determined for Mono Br and Bis Br are listed in Table 1. The activation energies for Mono Br and Bis Br will reflect the temperature dependence of a correlation time that is given by [38]

$$\tau_C^{-1} = \sum_i \tau_p^{-1} \qquad (13)$$

where τ_p is the rotational correlation time for rotation about each of the principal rotation axes, and τ_C is the reduced correlation time. The reduced correlation time for Mono Br and Bis Br in d_6-benzene has about the same temperature dependence as the correlation time for $Co(acac)_3$ in d_6-benzene. Mono Br has a slightly higher energy and Bis Br has a slightly lower activation than $Co(acac)_3$, this suggests that size does not influence the rotational activation energy to a very large extent.

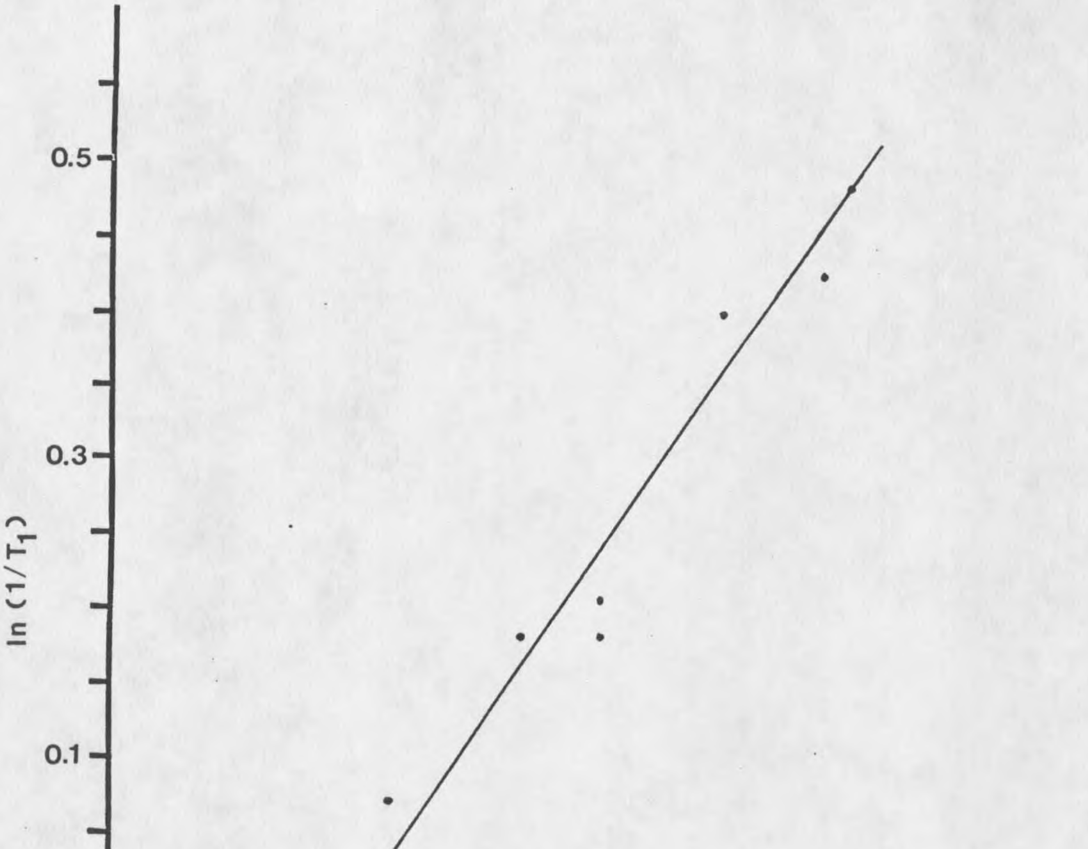


Figure 8: ^{13}C $\ln(1/T_1)$ versus 1/T of Bis Br in d_6-benzene.

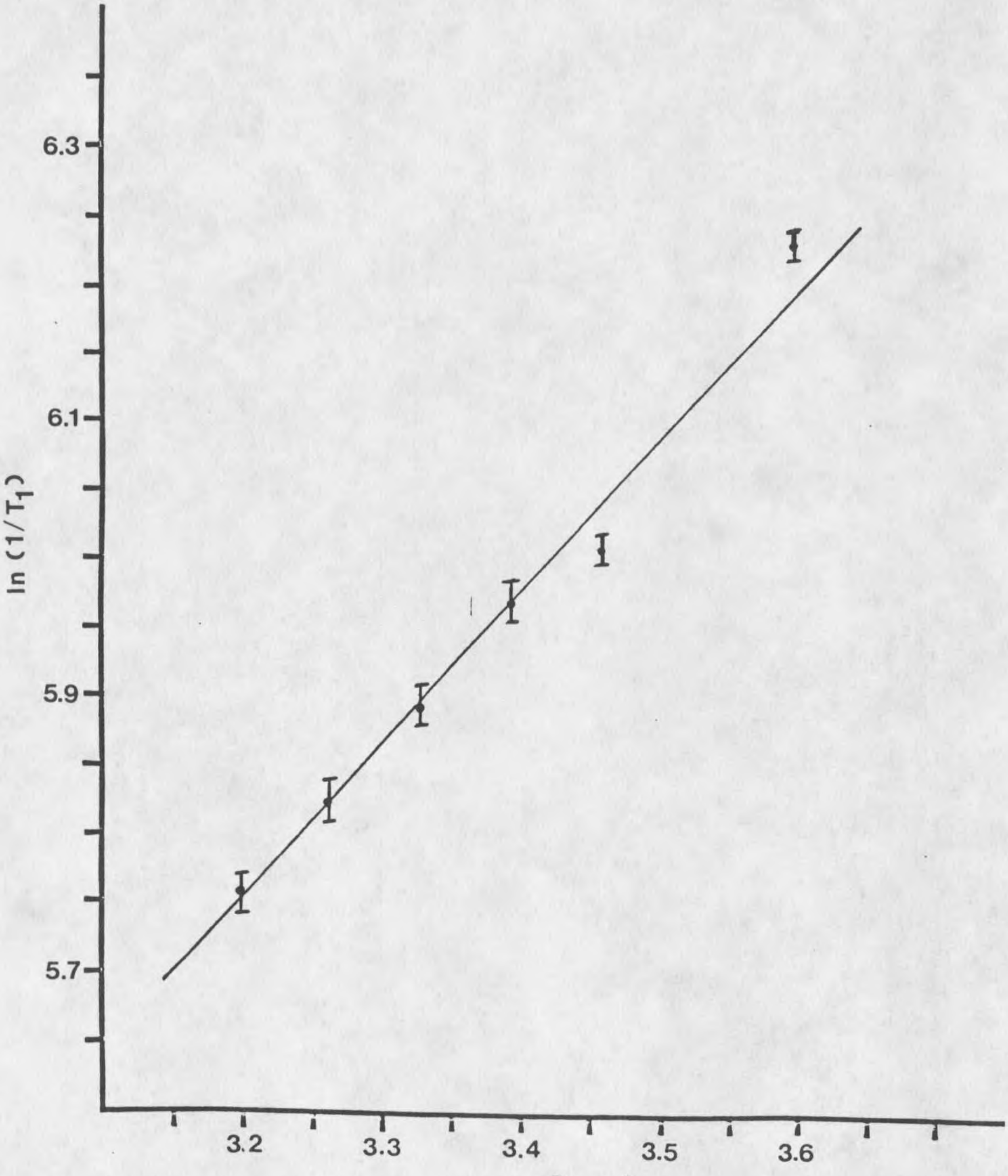


Figure 9: ^{59}Co ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in d$_6$-benzene.

Figures 10-12 show plots of ln(1/T) versus 1/T for the ^{59}Co relaxation of Co(acac)$_3$ in d_6-benzene, d_1-chloroform, d_6-acetone and diglyme respectively. The plots are linear and the activation energies derived from the plots are listed in Table 2. The activation energies for ^{59}Co relaxation no longer follows the temperature dependence displayed by the ^{13}C relaxation. The ^{59}Co activation energy in d_1-chloroform is the smallest it is 45% less than the ^{13}C activation energy. The ^{59}C activation energy is also smaller than the ^{13}C activation energy in d_6-benzene but the drop is only 17%. In d_6-acetone and diglyme the activation energies of the ^{59}Co and ^{13}C relaxation are the same.

Figures 13-24 are the plots of ln(1/T_1) vs 1/T for the Cl series, the Br series, and the I series in d_6-benzene, d_1-chloroform, d_6-acetone and diglyme. As in the previous cases plots are linear and activation energies were determined for each plot and listed in Table 2. The trends displayed by the ^{59}Co activation energy of Co(acac)$_3$ are evident for the halogenated complexes also with one exception. Activation energy in d_6-benzene is lower than that of Co(acac)$_3$ by an average of about 18%. However the difference between the ^{13}C activation energy and ^{59}Co activation energy is still the largest in d_1-chloroform.

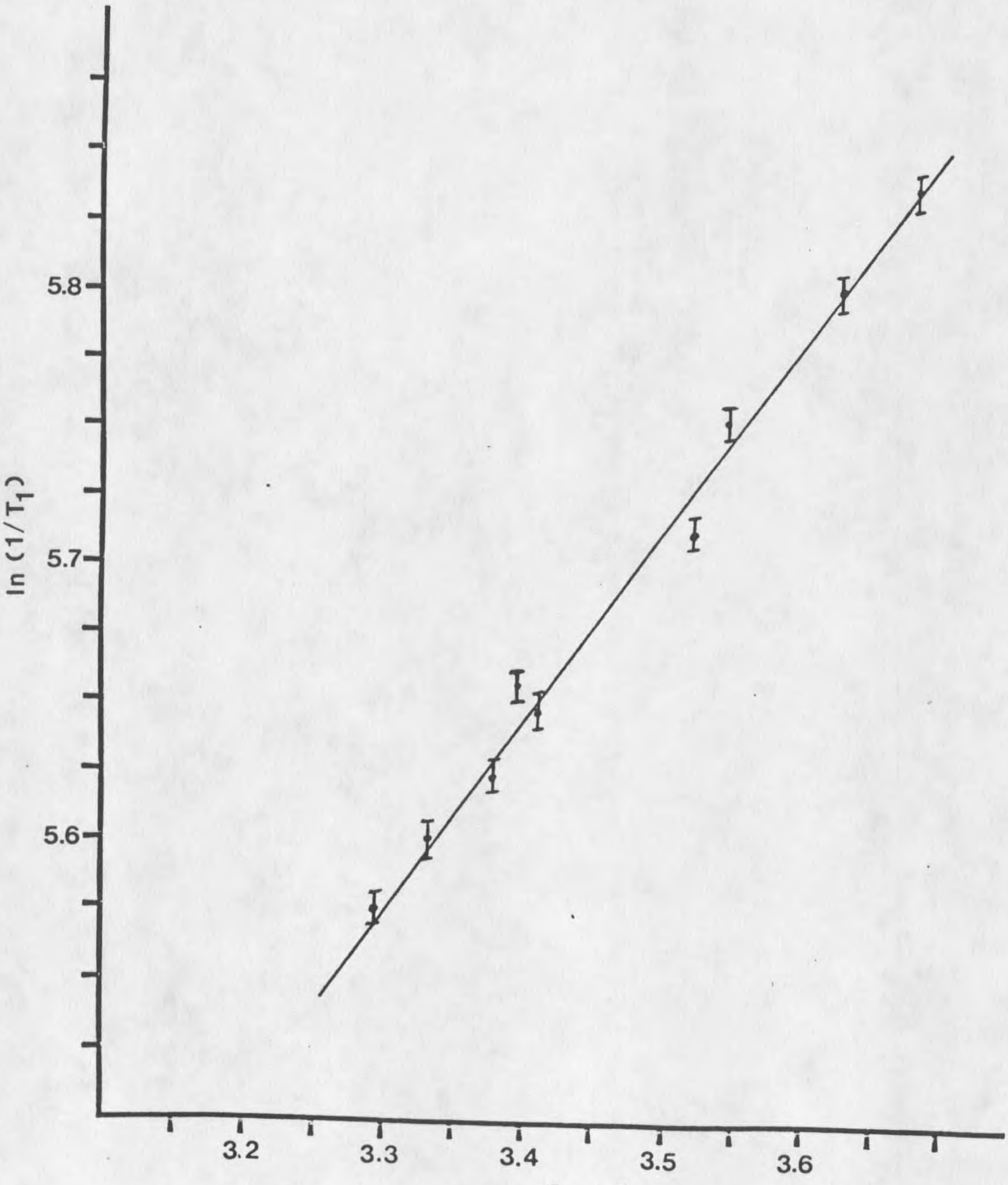


Figure 10: ^{59}Co ln(1/T_1) versus 1/T of Co(acac)$_3$ in d_1-chloroform.

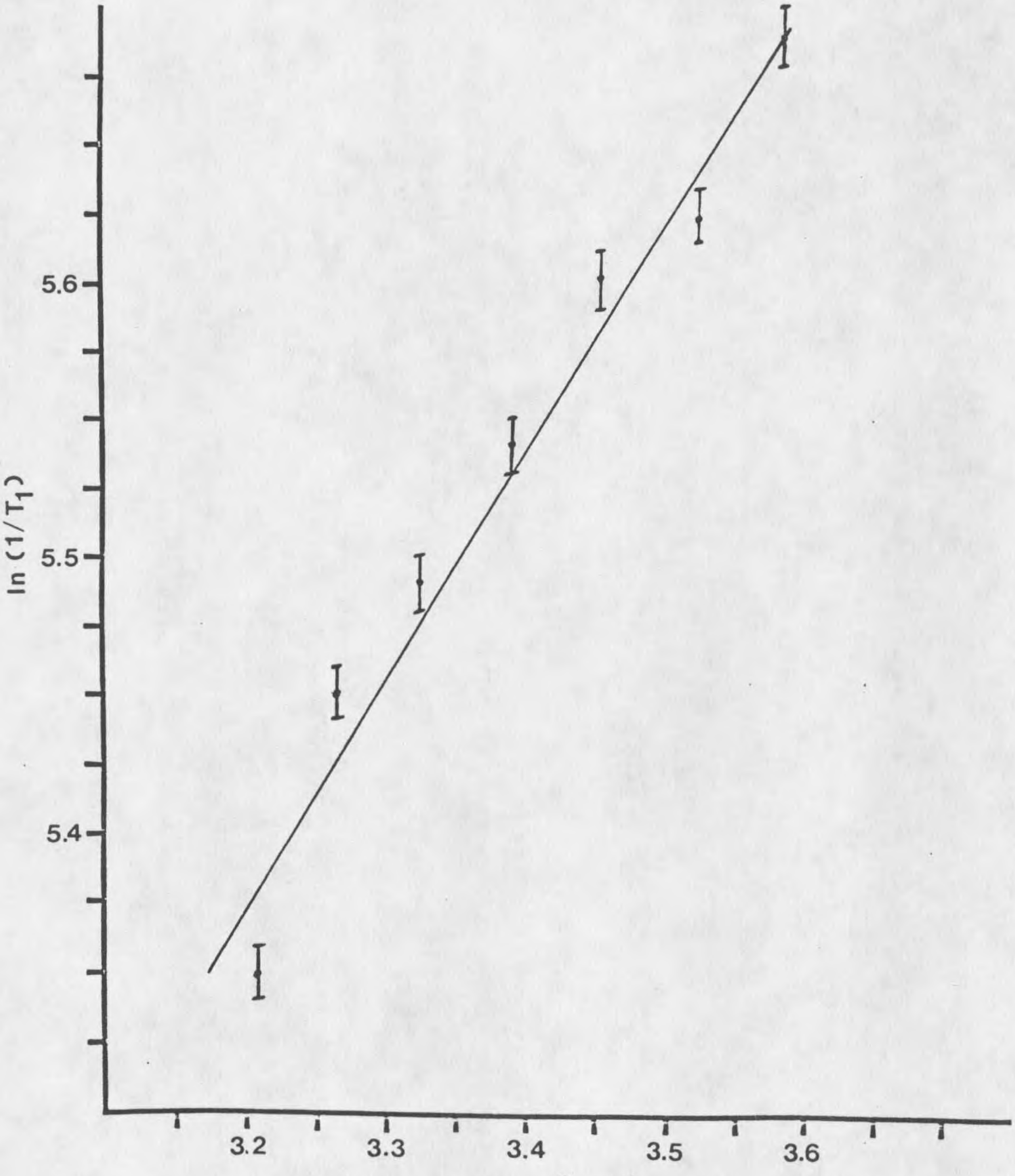


Figure 11: ^{59}Co ln(1/T_1) versus 1/T of Co(acac)$_3$ in d_6-acetone.

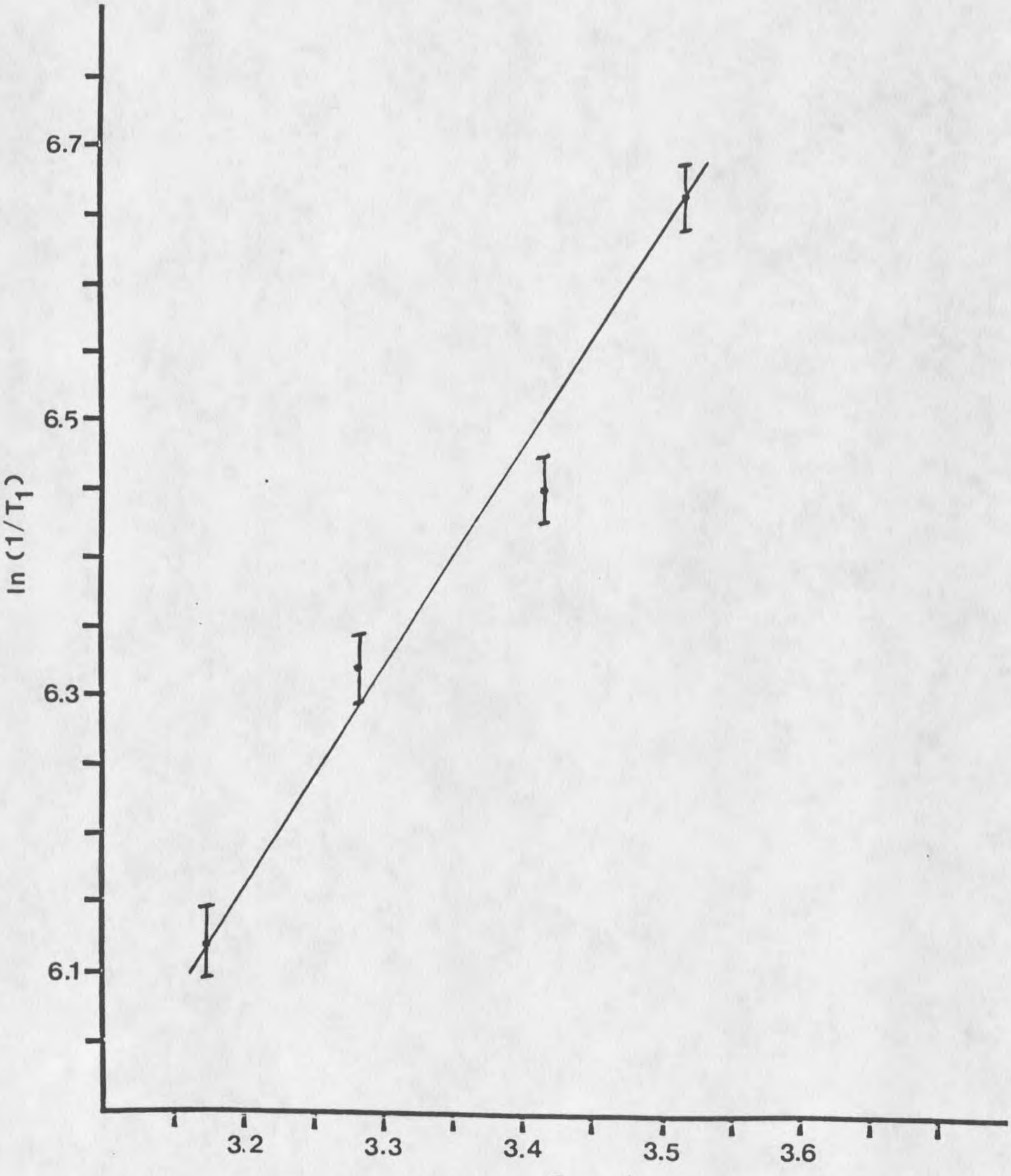


Figure 12: ^{59}Co ln(1/T$_1$) versus 1/T of Co(acac)$_3$ in diglyme.

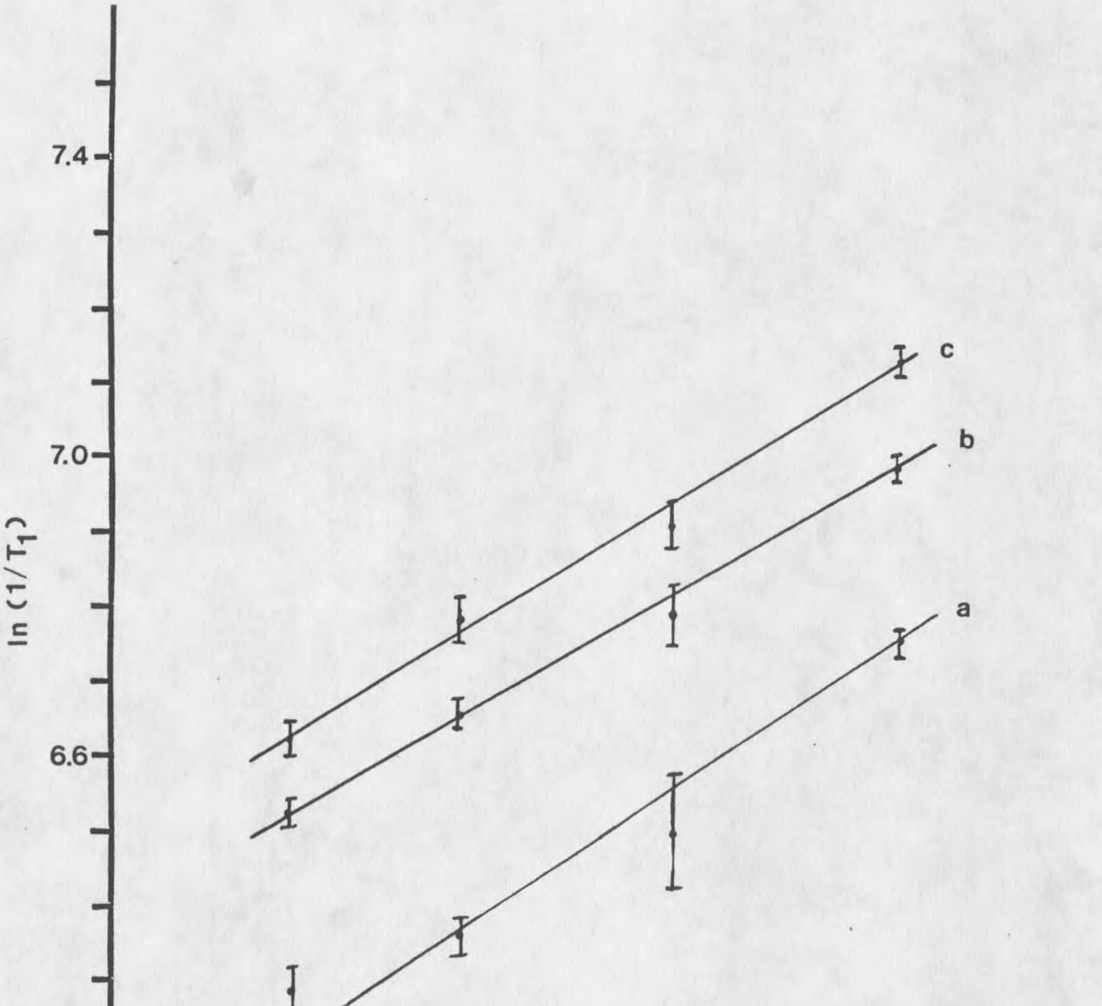


Figure 13: ^{59}C ln(1/T$_1$) versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in d$_6$-benzene.

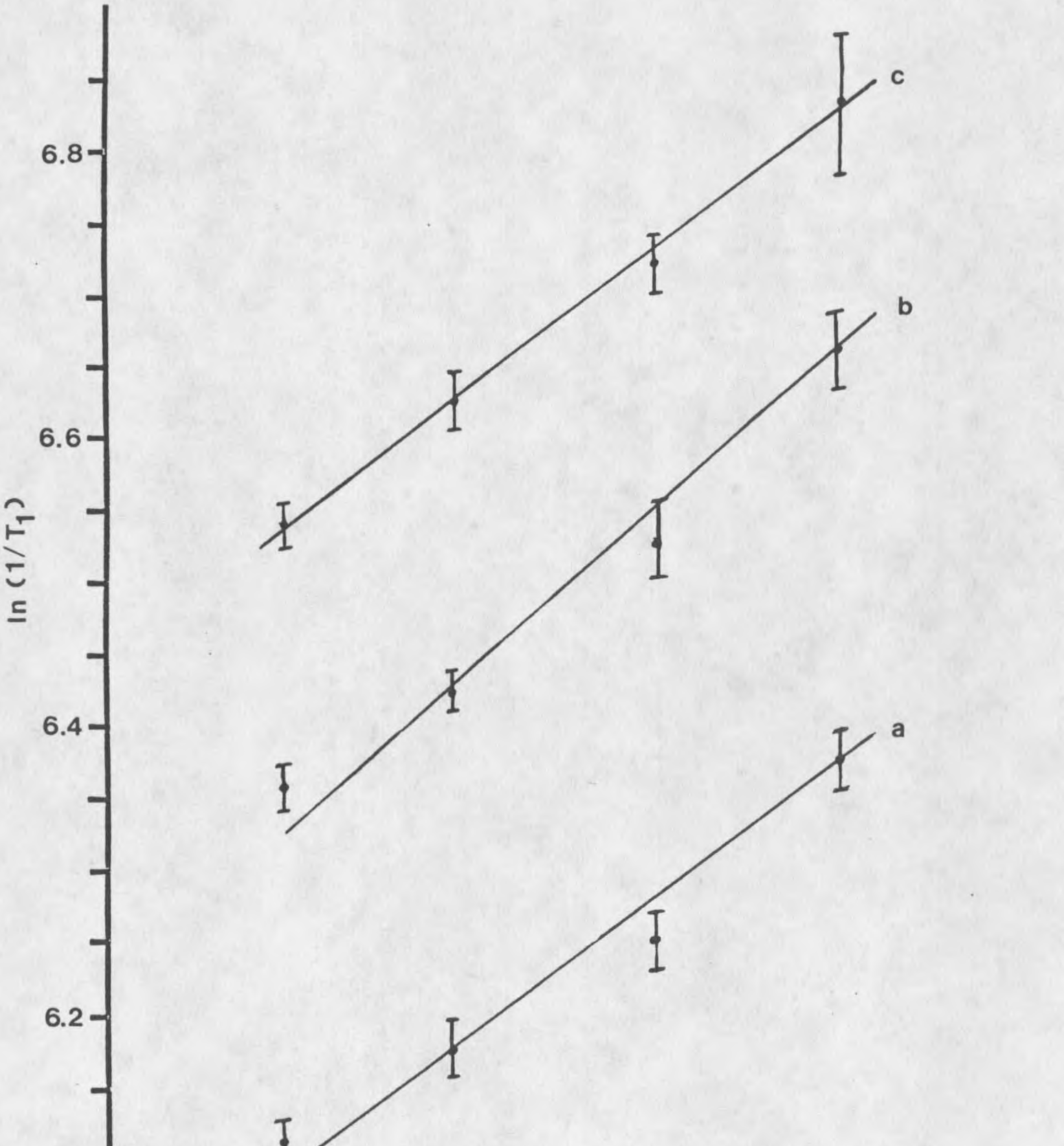


Figure 14: ^{59}Co ln $(1/T_1)$ versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in d_1-chloroform.

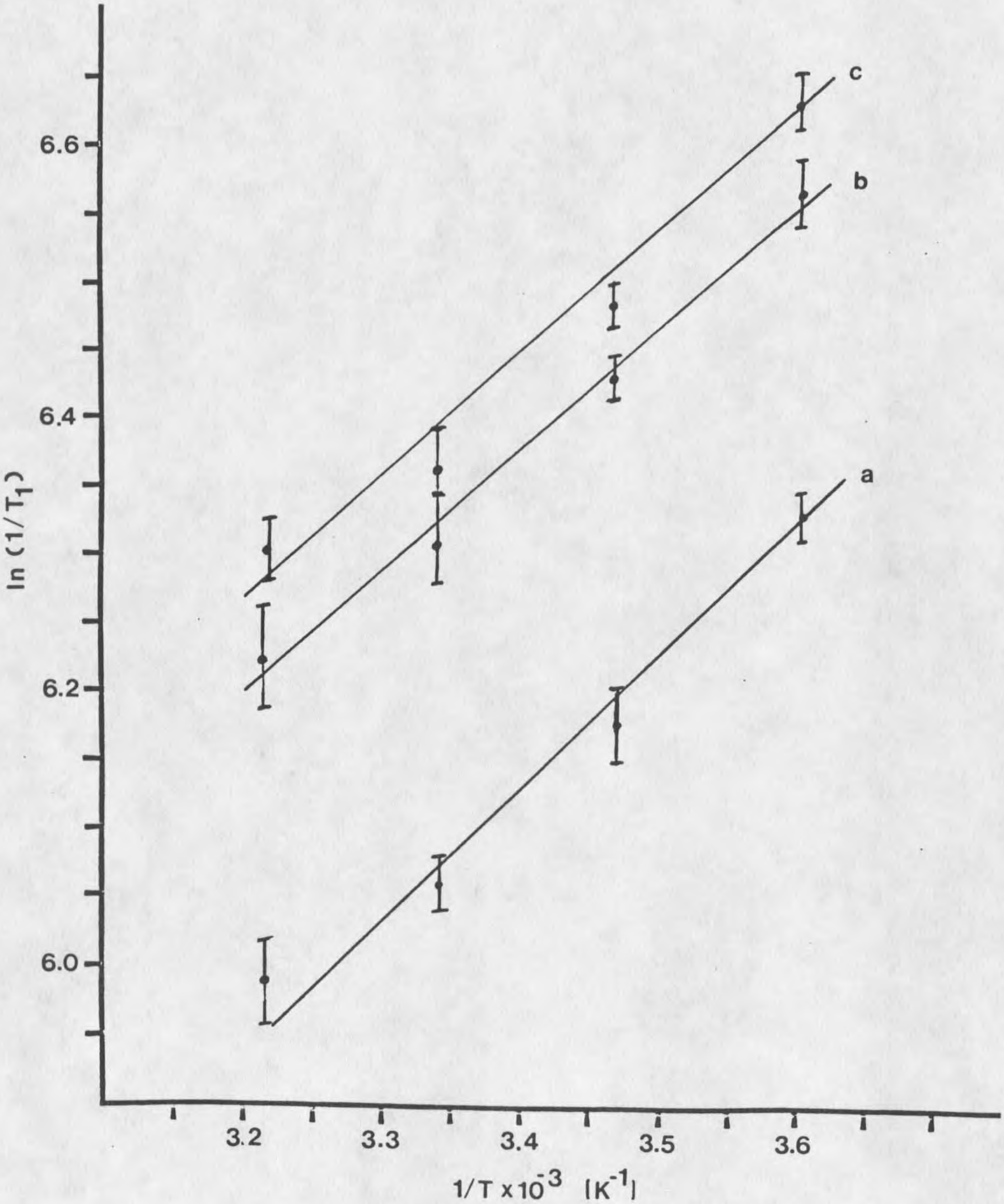


Figure 15: ^{59}Co ln(1/T_1) versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in d_6-acetone.

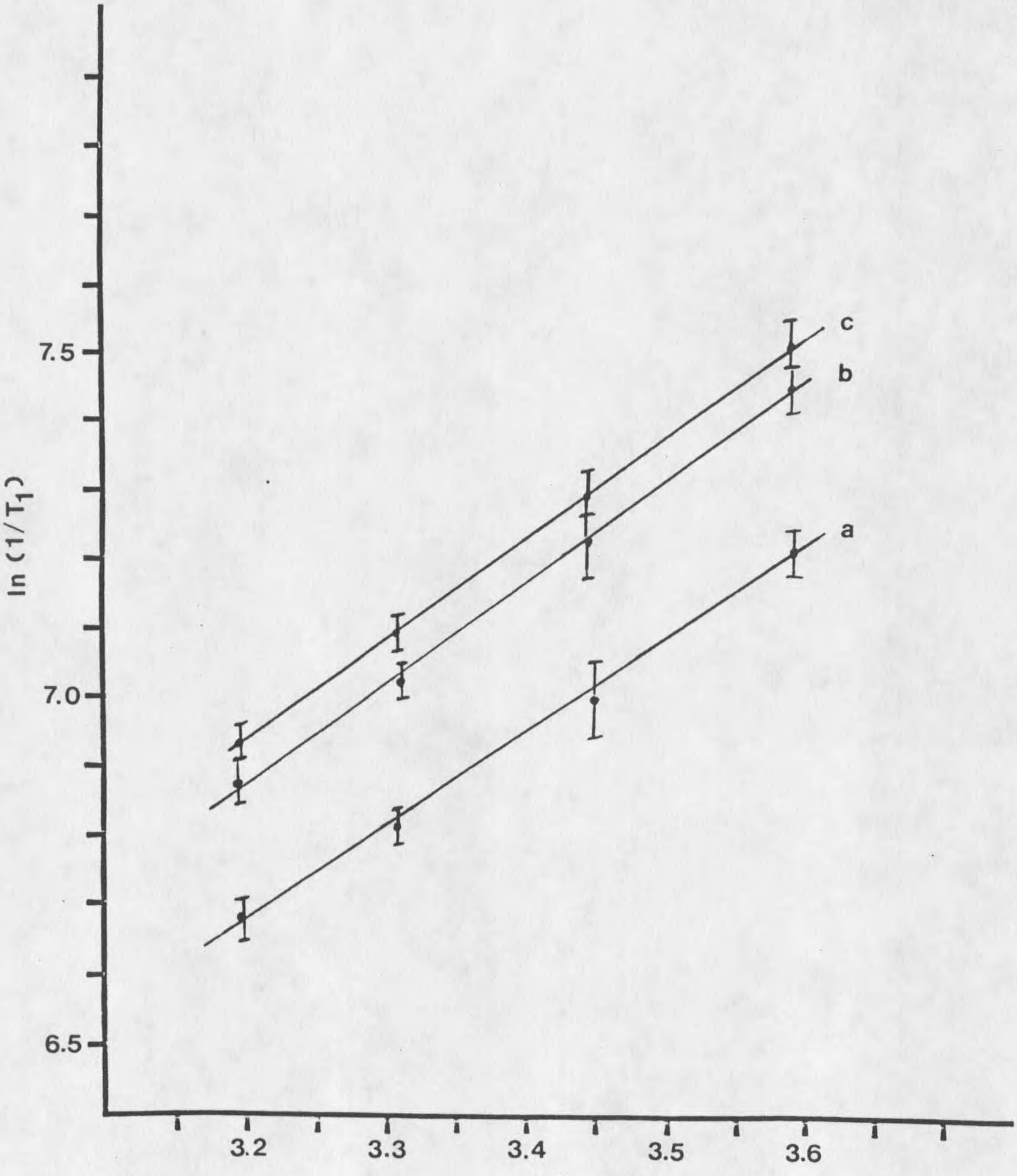


Figure 16: ^{59}Co ln(1/T$_1$) versus 1/T of a) Mono Cl; b) Bis Cl; c) Tris Cl in diglyme.

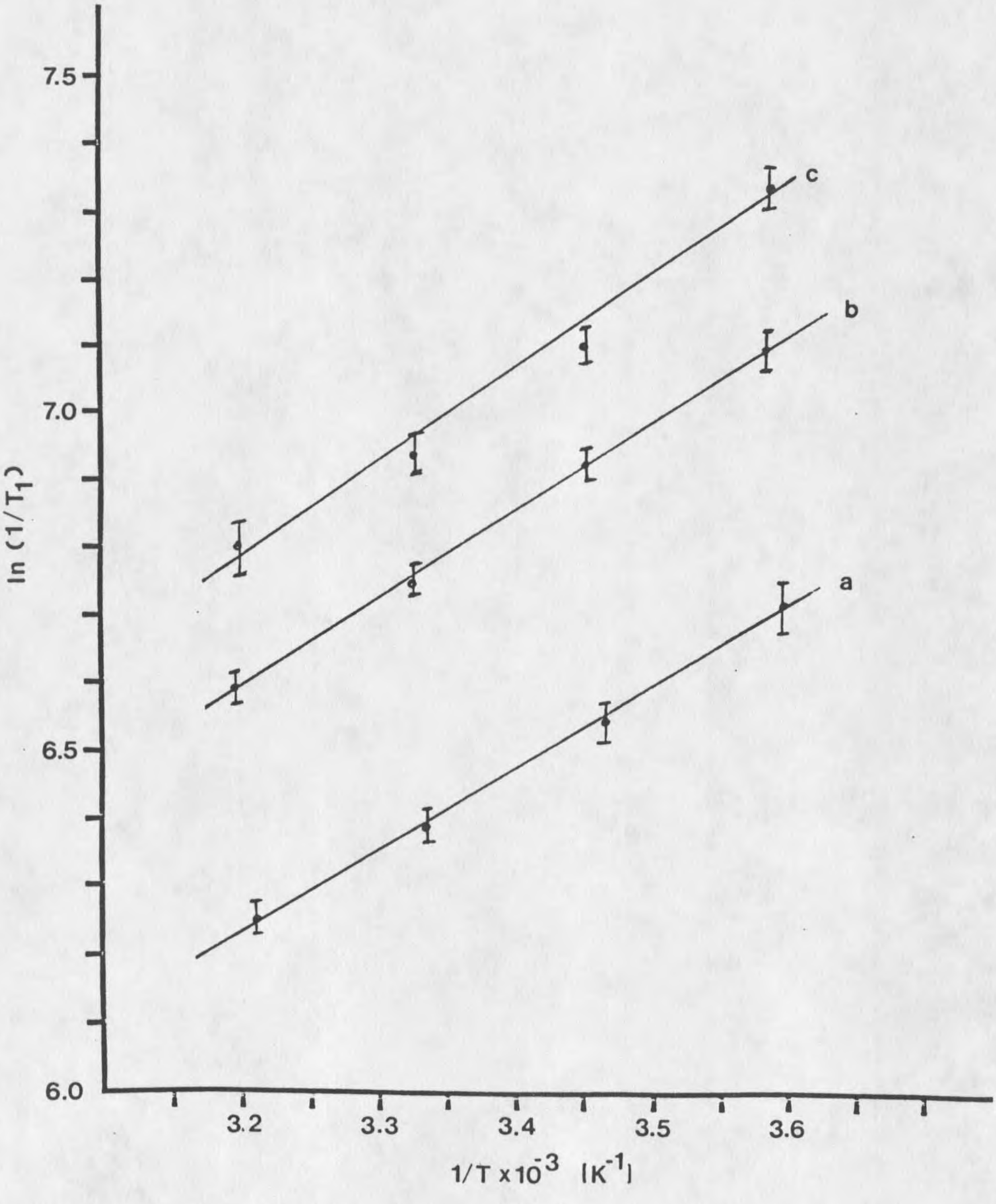


Figure 17: ^{59}Co ln(1/T_1) versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in d_6-benzene.

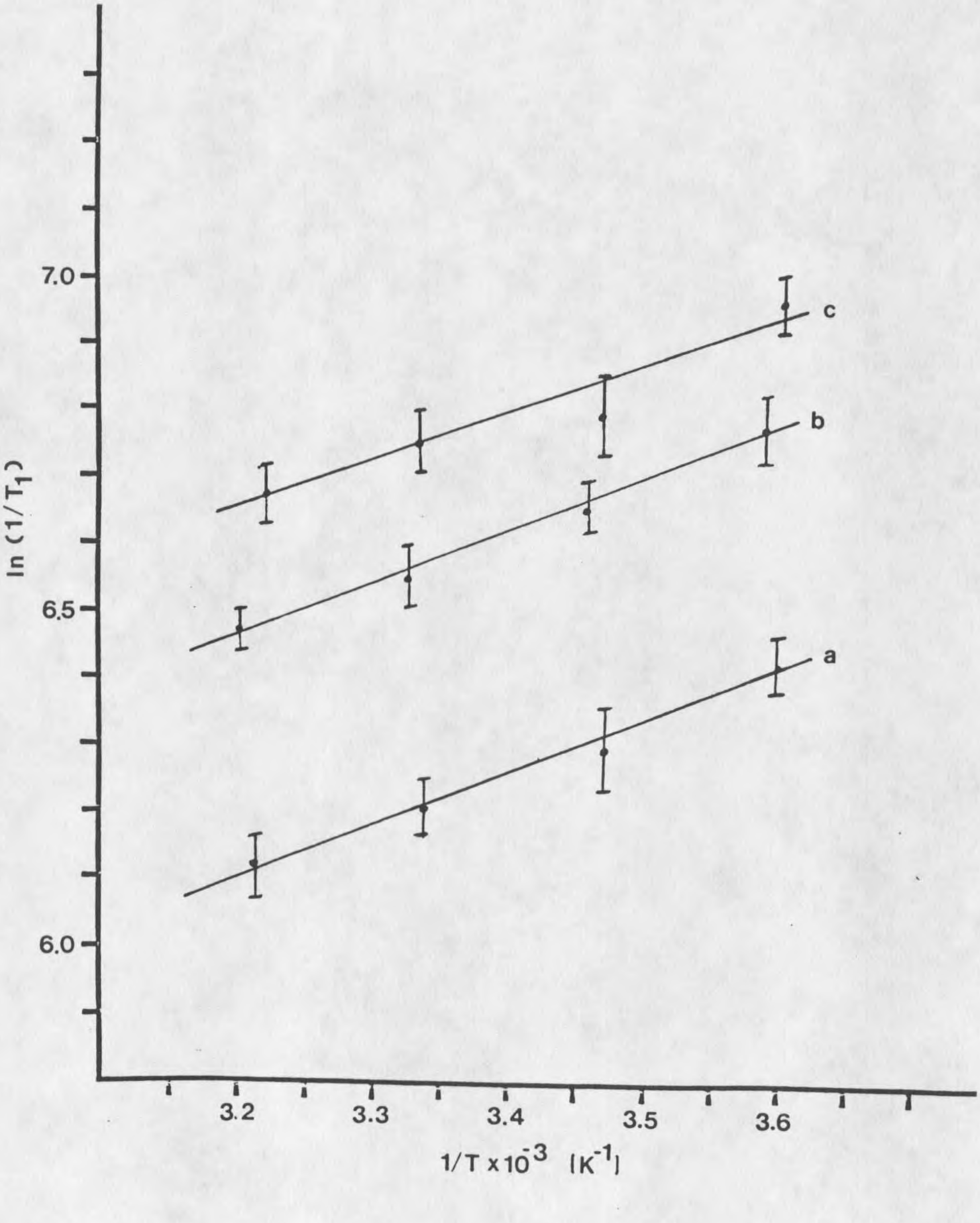


Figure 18: ^{59}Co ln(1/T_1) versus 1/T of a) Mono Br; B) Bis Br; c) Tris Br in d_1-chloroform.

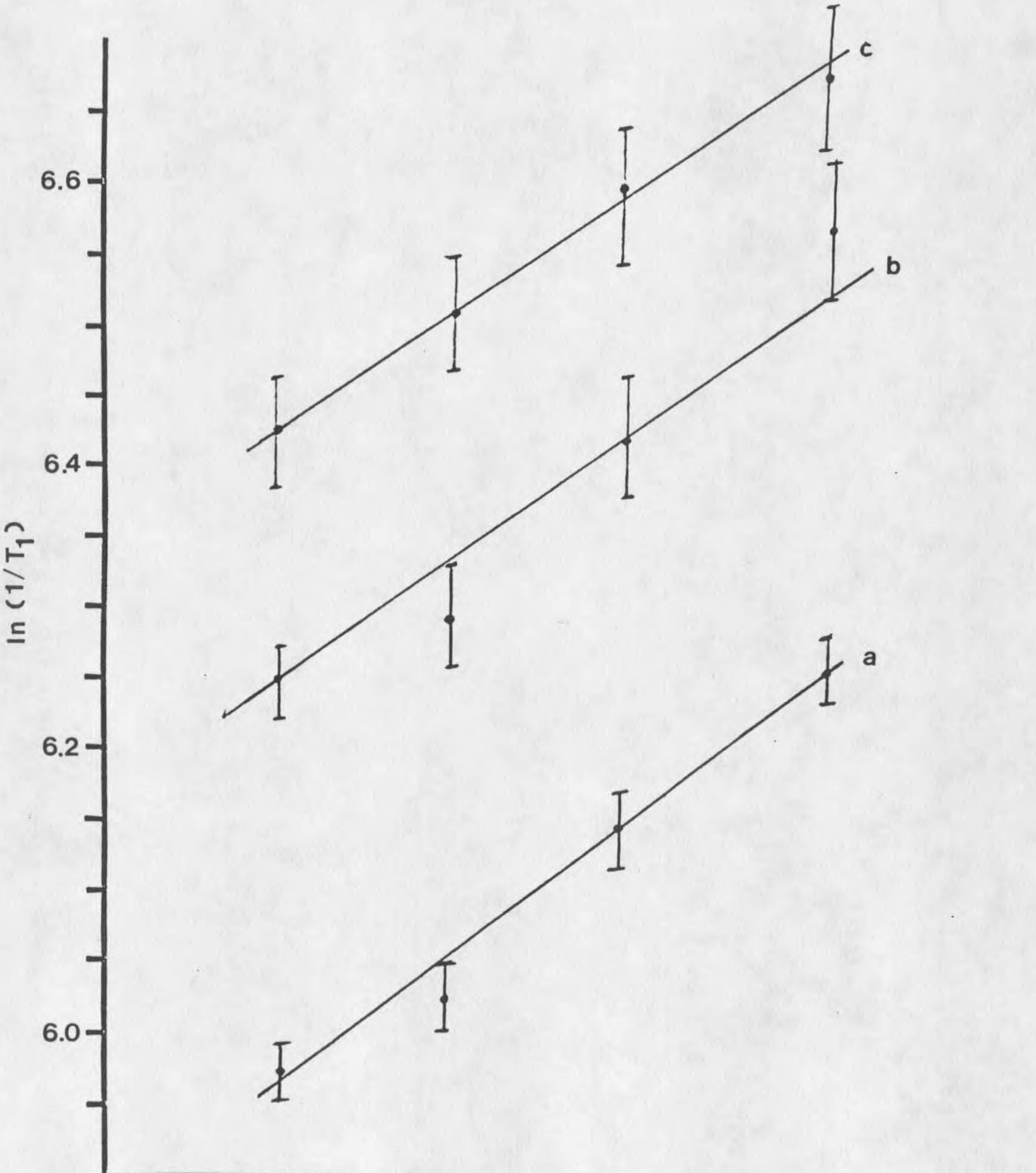


Figure 19: ^{59}Co ln(1/T$_1$) versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in d$_6$-acetone.

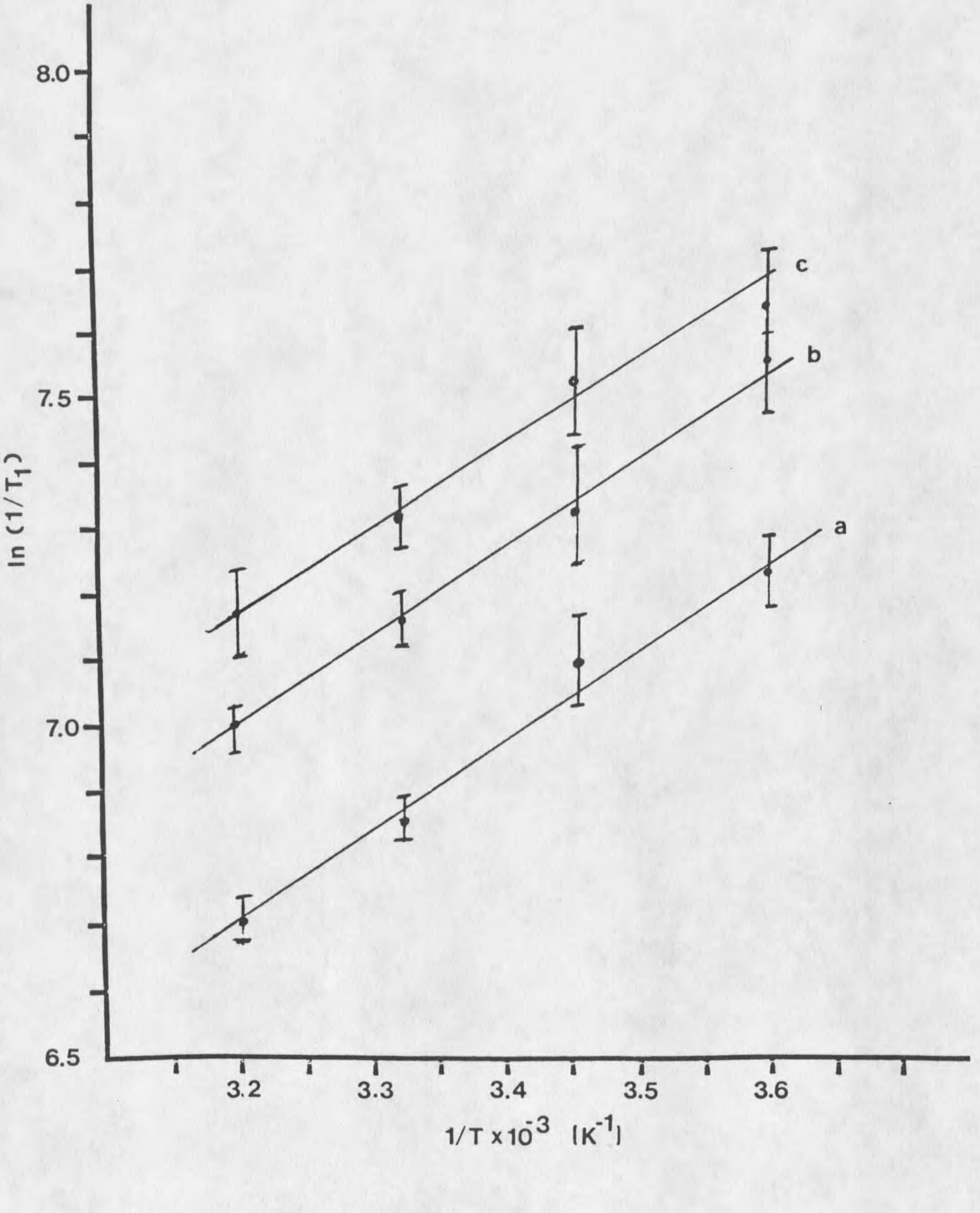


Figure 20: ^{59}Co ln(1/T_1) versus 1/T of a) Mono Br; b) Bis Br; c) Tris Br in diglyme.

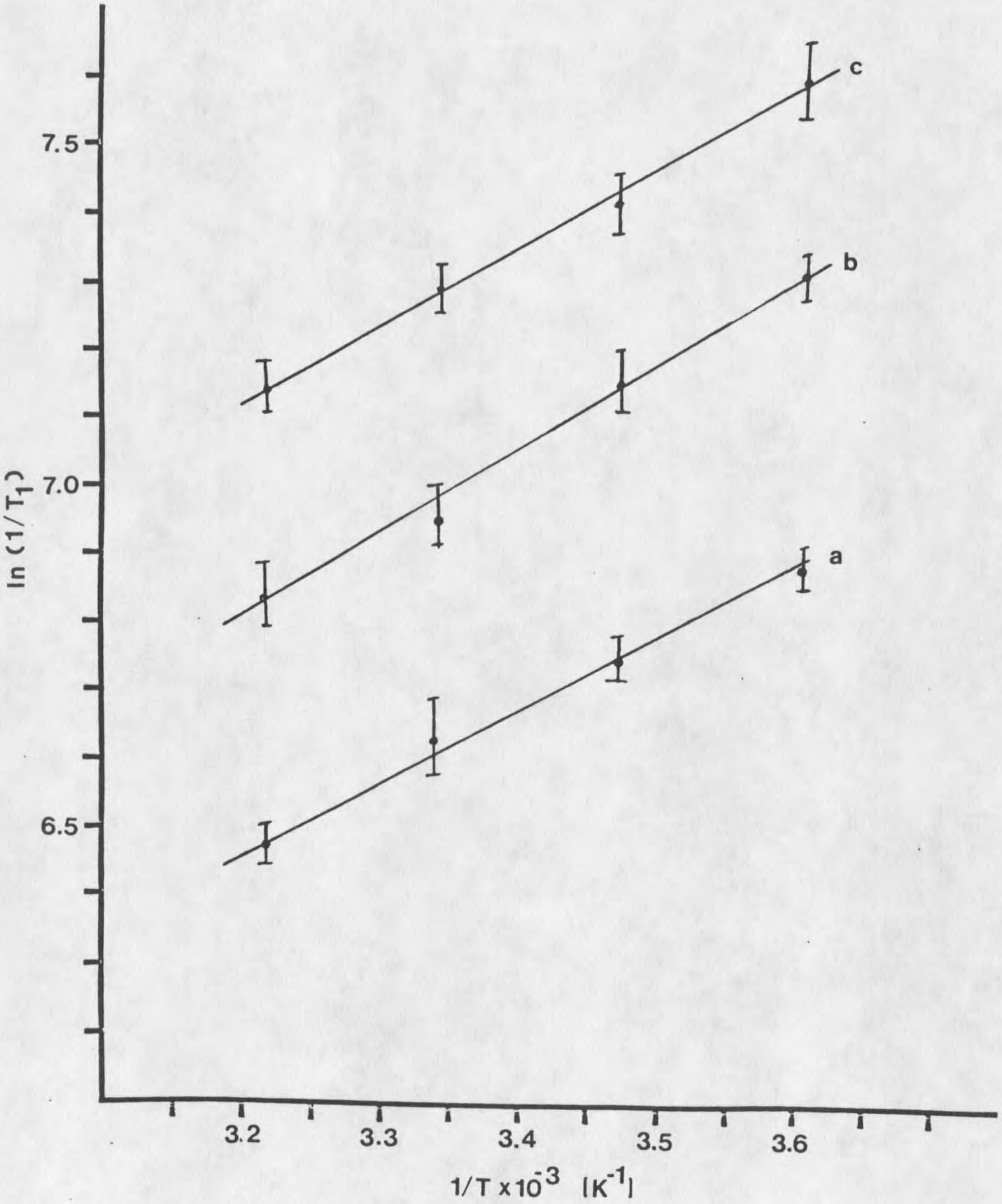


Figure 21: ^{59}Co ln(1/T_1) versus 1/T of a) Mono I; b) Bis I; c) Tris I in d_6-benzene.

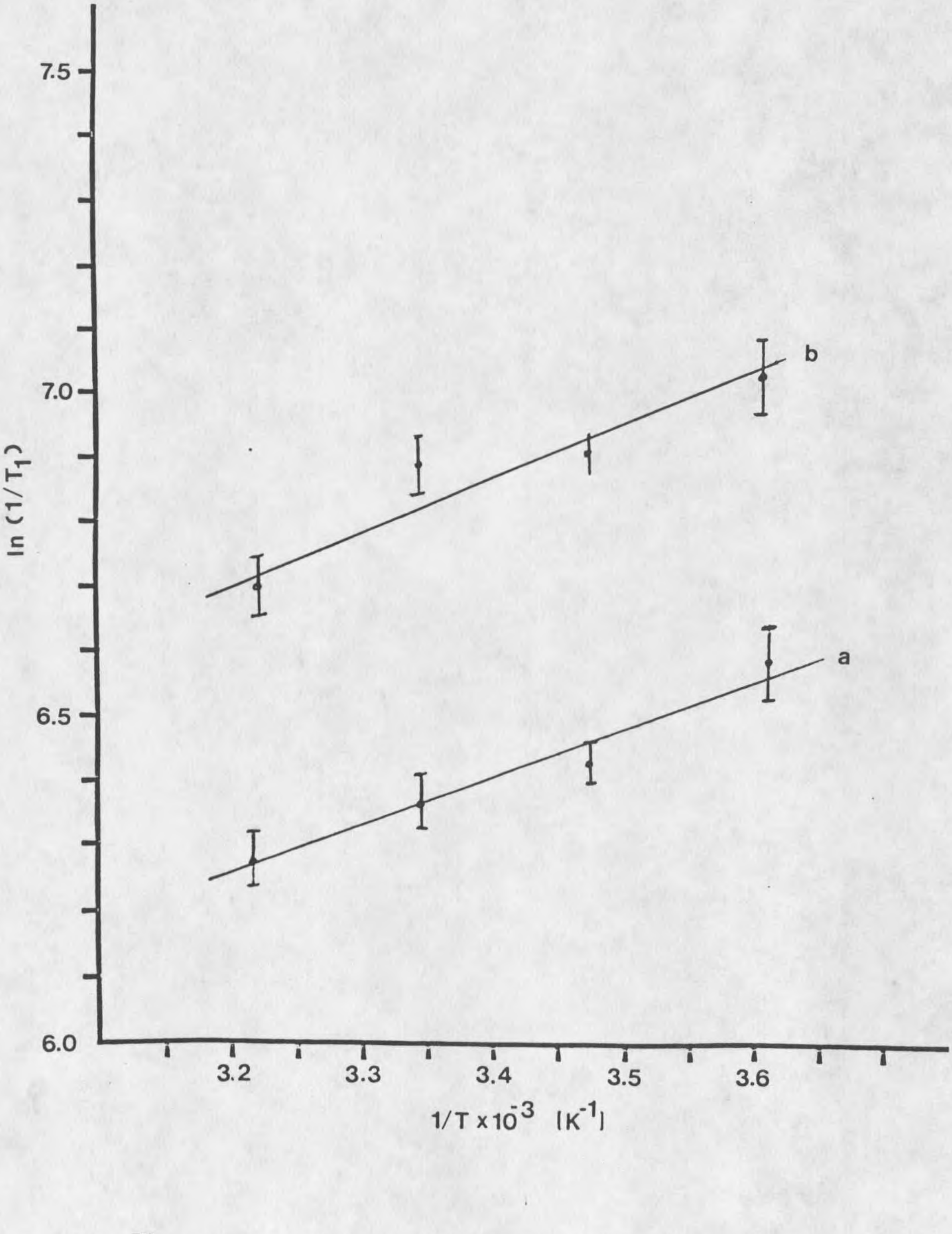


Figure 22: ^{59}Co ln(1/T$_1$) versus 1/T of a) Mono I; b) Bis I in d_1-chloroform.

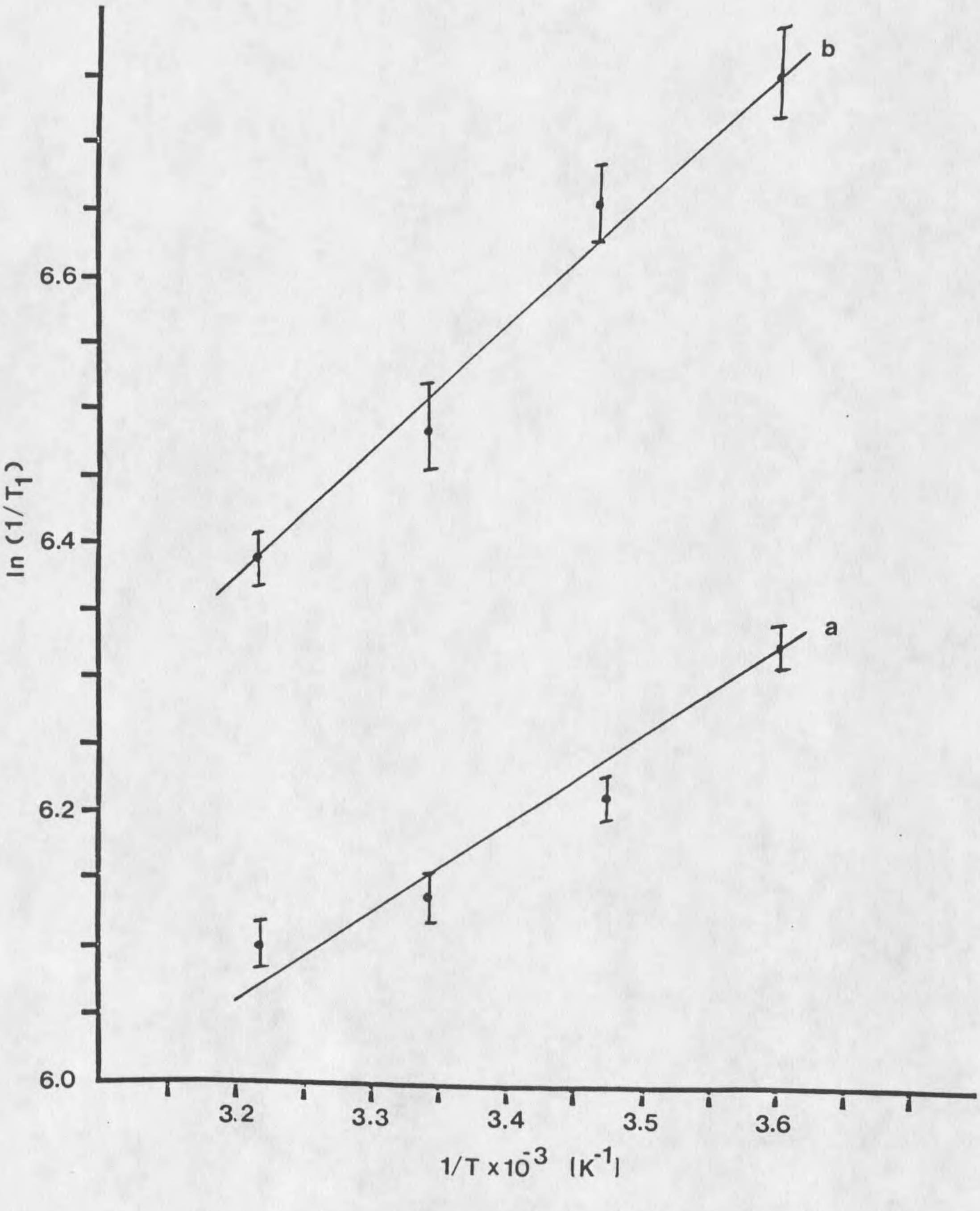


Figure 23: ^{59}Co ln(1/T$_1$) versus 1/T of a) Mono I; b) Bis I in d$_6$-acetone.

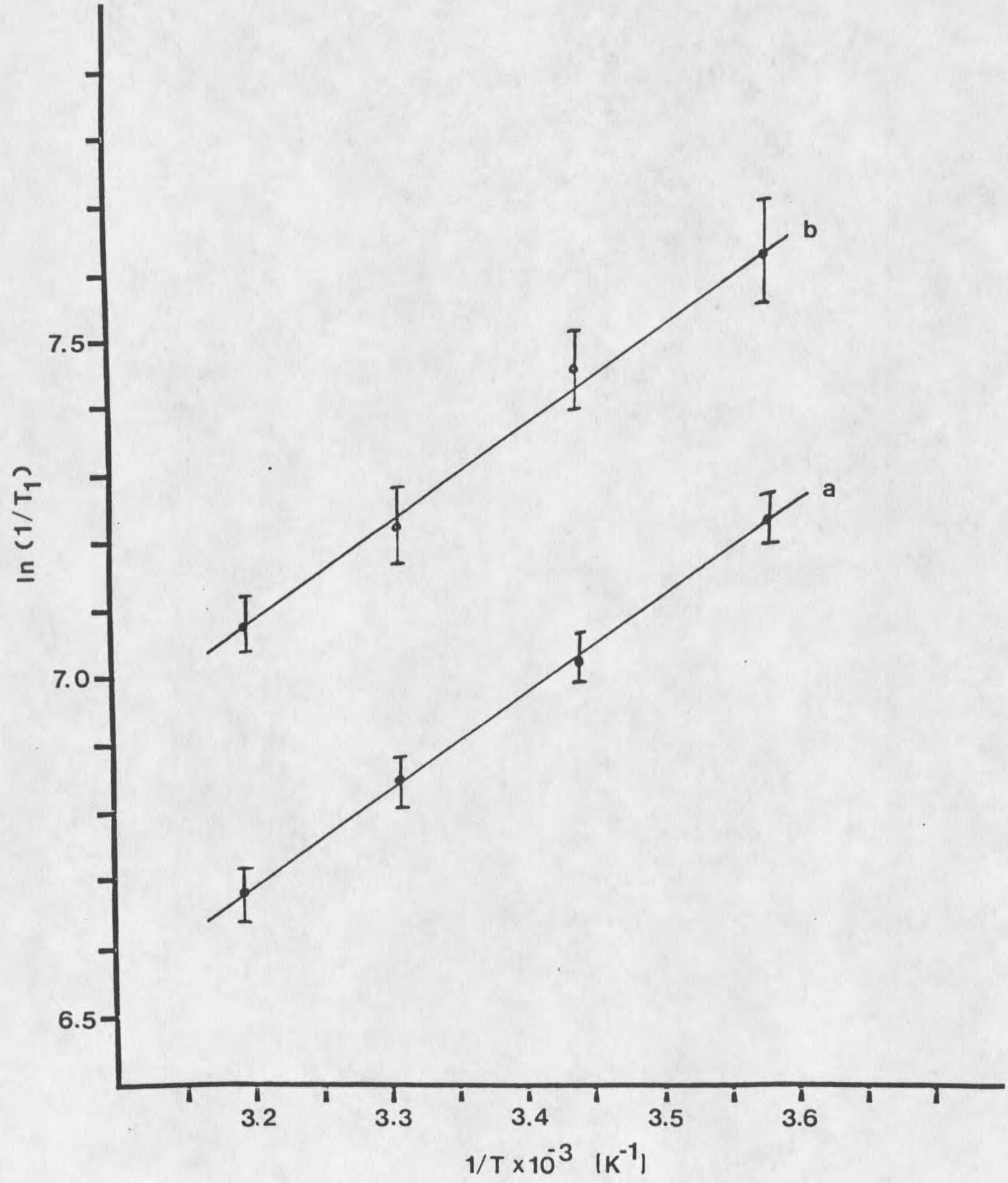


Figure 24: ^{59}Co ln(1/T_1) versus 1/T of a) Mono I; b) Bis I in diglyme.

Table 2. Activation energy ($KJmol^{-1}$) from ^{59}Co relaxation rate.

	solvent			
complex	d_6-benzene	d_1-chloroform	d_6-Acetone	Diglyme
$Co(acac)_3$	10	6	7	12
Mono Cl	8	5	6	10
Bis Cl	8	7	7	11
Tris Cl	8	6	6	11
Mono Br	8	6	5	11
Bis Br	10	6	6	11
Tris Br	11	5	4	8
Mono I	6	6	3	11
Bis I	8	6	8	12
Tris I	8	--	--	--

The activation energy of the ^{13}C relaxation is a measure of the temperature dependence of the rotational motion of the $Co(acac)_3$ molecule. Comparing the ^{13}C rotational activation energy and the ^{59}Co activation energy of $Co(acac)_3$ it is found that in d_6-acetone and diglyme the temperature dependence of the ^{59}Co relaxation is the same as that for the rotational motion of the $Co(acac)_3$ molecule. In d_6-benzene and d_1-chloroform the ^{59}Co activation energy is respectively 17% and 45% less than that for the rotational motion of $Co(acac)_3$. For the halogenated complexes there is a slight drop in the ^{59}Co activation energies in d_6-benzene, d_6-acetone and diglyme as compared to the ^{59}Co activation energy of $Co(acac)_3$. In d_1-chloroform there is no decrease in the ^{59}Co activation energies for the halogenated complexes.

The comparisons of the ^{13}C and ^{59}Co activation energies suggests that the fluctuation in the EFG at the cobalt is due to rotational reorientation in d_6-acetone and diglyme. In d_6-benzene and d_1-chloroform the difference in the activation energies of ^{13}C and ^{59}Co suggests a motion other than rotation is responsible for the fluctuations in the EFG. However, because the ^{59}Co activation energy in d_6-benzene, $d_6$acetone and diglyme is lower for the halogenated complexes than for $Co(acac)_3$ and in d_1-chloroform there is no difference it appears that whatever motion is responsible for the fluctuation in the EFG in d_6-benzene it is not the same in d_1-chloroform.

In Yamatera's paper[33] on the rotational motion of $Co(en)_3$ he found that the rotational correlation time followed the Stokes-Einstein relation[15]

$$\tau_c = V\eta/kT \quad (14)$$

where τ_c is the rotational correlation time, V is the molecular volume, η is the viscosity, k the Boltzman constant and T the temperature. Because $Co(acac)_3$ is similar to $Co(en)_3$ in size and shape it is reasonable to assume that the rotational correlation time for $Co(acac)_3$ will also follow equation (14).

Since $1/T_1$ τ_c equation (14) can be rewritten as

$$1/T_1 = A\ V\eta/kT \quad (15)$$

where A is the proportionality constant. Equation (15) can be used to study the viscosity or volume dependence of the ^{13}C and ^{59}Co relaxation. Because of problems in determining the molecular volume[39] of

$Co(acac)_3$ and the different halogenated complexes a study of the viscosity dependence is undertaken. The relaxation rate (either ^{13}C or ^{59}Co) is determined[40] at 298K for a given complex in each of the solvents since A, V, k and T in equation 15 are all constant a plot of $1/T_1$ in each solvent versus the viscosity of the solvent will be linear if equation (15) holds.

Figure 25 shows a plot of $1/T_1$ versus viscosity for the ^{13}C relaxation of $Co(acac)_3$. As expected the plot is linear, this further supports the use of the ^{13}C relaxation of the methine carbon as a means of looking at the rotational motion of the $Co(acac)_3$ molecule.

Equation (15) can also be used to examine the ^{59}Co relaxation of $Co(acac)_3$ and possibly determine if d_6-benzene behaves like d_1-chloroform or d_6-acetone and diglyme. The activation energy study suggests that the ^{59}Co relaxation is due to rotational reorientation in d_6-acetone and diglyme, in d_6-benzene and d_1-chloroform the relaxation appears to be via another mechanism. The dependence of the activation energy on halogenation however seems to put d_6-benzene, d_6-acetone and diglyme together with the ^{59}Co activation energy dropping while in d_1-chloroform there is no change. If the data point for d_6-benzene is linear with d_6-acetone and diglyme it would support the idea that the ^{59}Co relaxation of $Co(acac)_3$ in d_6-benzene is due to rotational motion. If d_6-benzene is not co-linear with d_6-acetone and diglyme it would suggest that rotational motion is not important in the ^{59}Co relaxation of $Co(acac)_3$.

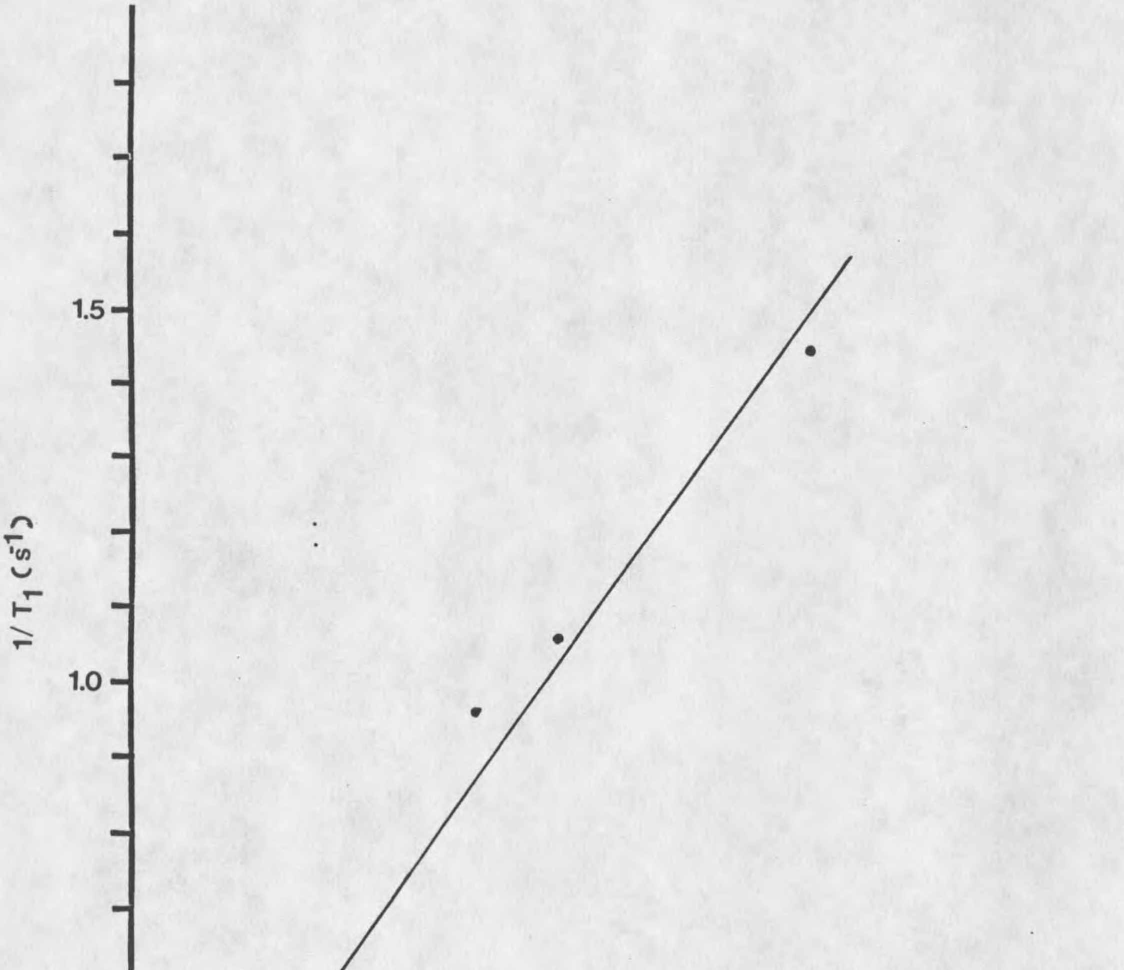


Figure 25: ^{13}C $1/T_1$ versus viscosity of Co(acac)$_3$.

Figure 26 shows a plot of $1/T_1$ versus viscosity for the ^{59}Co relaxation of Co(acac)$_3$. It can be seen that within experimental error it is possible to draw a straight line through the point for d_6-acetone, d_6-benzene and diglyme. The linearity of the d_6-benzene, d_6-acetone and diglyme points suggests that the ^{59}Co relaxation is due to rotational reorientation in d_6-benzene. Figure 26 also shows the d_1-chloroform point falling well below the line which is to be expected if the ^{59}Co relaxation of Co(acac)$_3$ in d_1-chloroform is not due to rotational reorientation.

Plots of $1/T_1$ versus viscosity for the Cl series, the Br series and the I series are shown in Figures 27-29 respectively. The plots display the same trends as the ^{59}Co relaxation of Co(acac)$_3$ with d_6-acetone, d_6-benzene, and diglyme being linear and d_1-chloroform falling below the line. The linearity of the d_6-acetone, d_6-benzene and diglyme points is much more evident for the tris complexes than for the mono and bis complexes. This could be due to the fact that the rotational motion of the mono and bis complexes is anisotropic and equation 15 might not hold while the rotational motion of the tris complexes is isotropic and equation 15 holds.

Both the temperature and viscosity dependence of the ^{59}Co relaxation rate of Co(acac)$_3$, the Cl series, the Br series and the I series in d_6-acetone, diglyme and possibly in d_6-benzene, indicate that the fluctuations of the EFG at the cobalt nucleous is due to rotational reorientation. The fluctuation in the EFG in d_1-chloroform appears to be via a different mechanism possibly vibrational or solvent reorganization. From figure 26 the ^{59}Co relaxation rate of Co(acac)$_3$

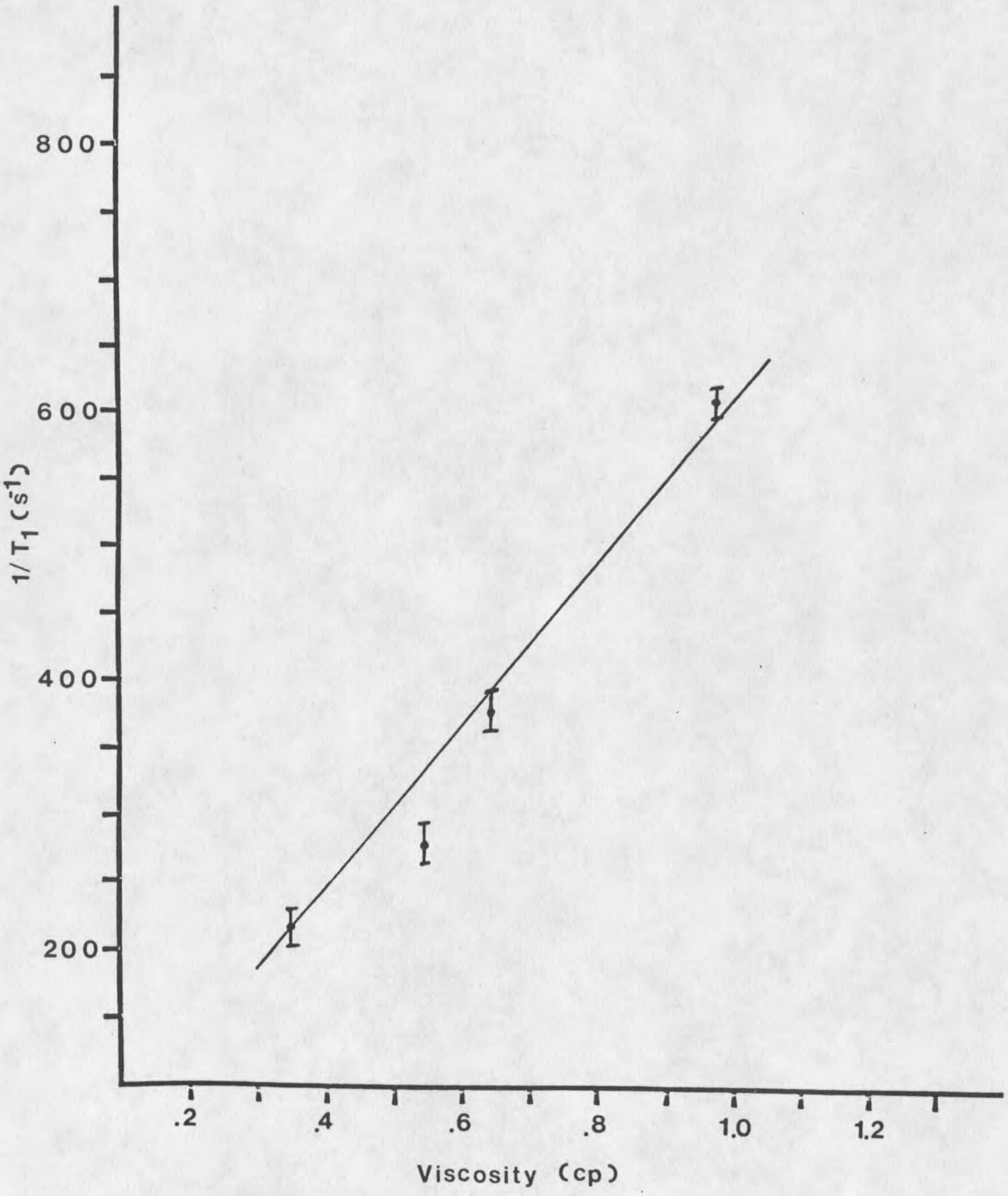


Figure 26: ^{59}Co $1/T_1$ versus viscosity of Co(acac)$_3$.

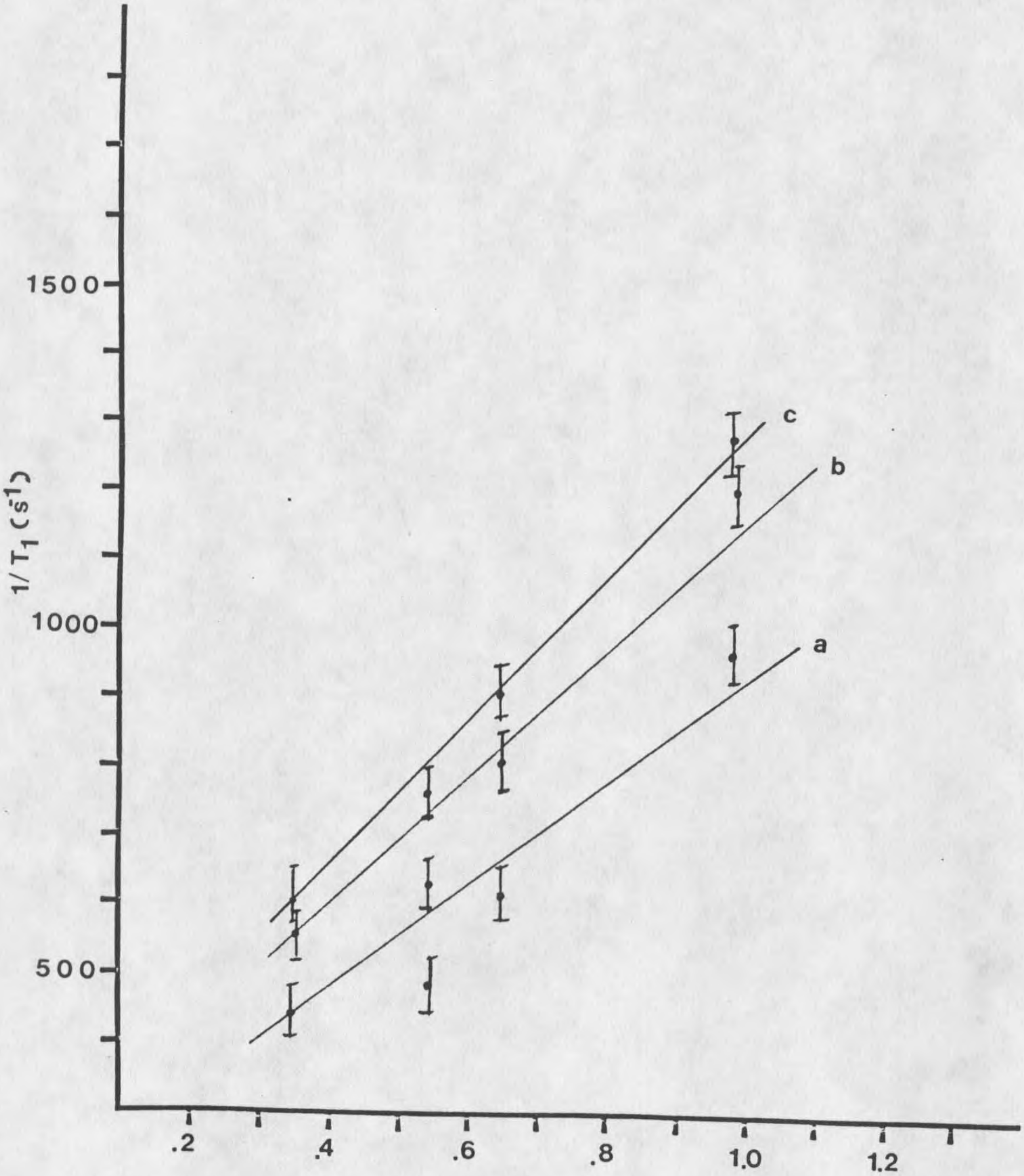


Figure 27: ^{59}Co 1/T$_1$ versus viscosity of a) Mono Cl; b) Bis Cl; c) Tris Cl.

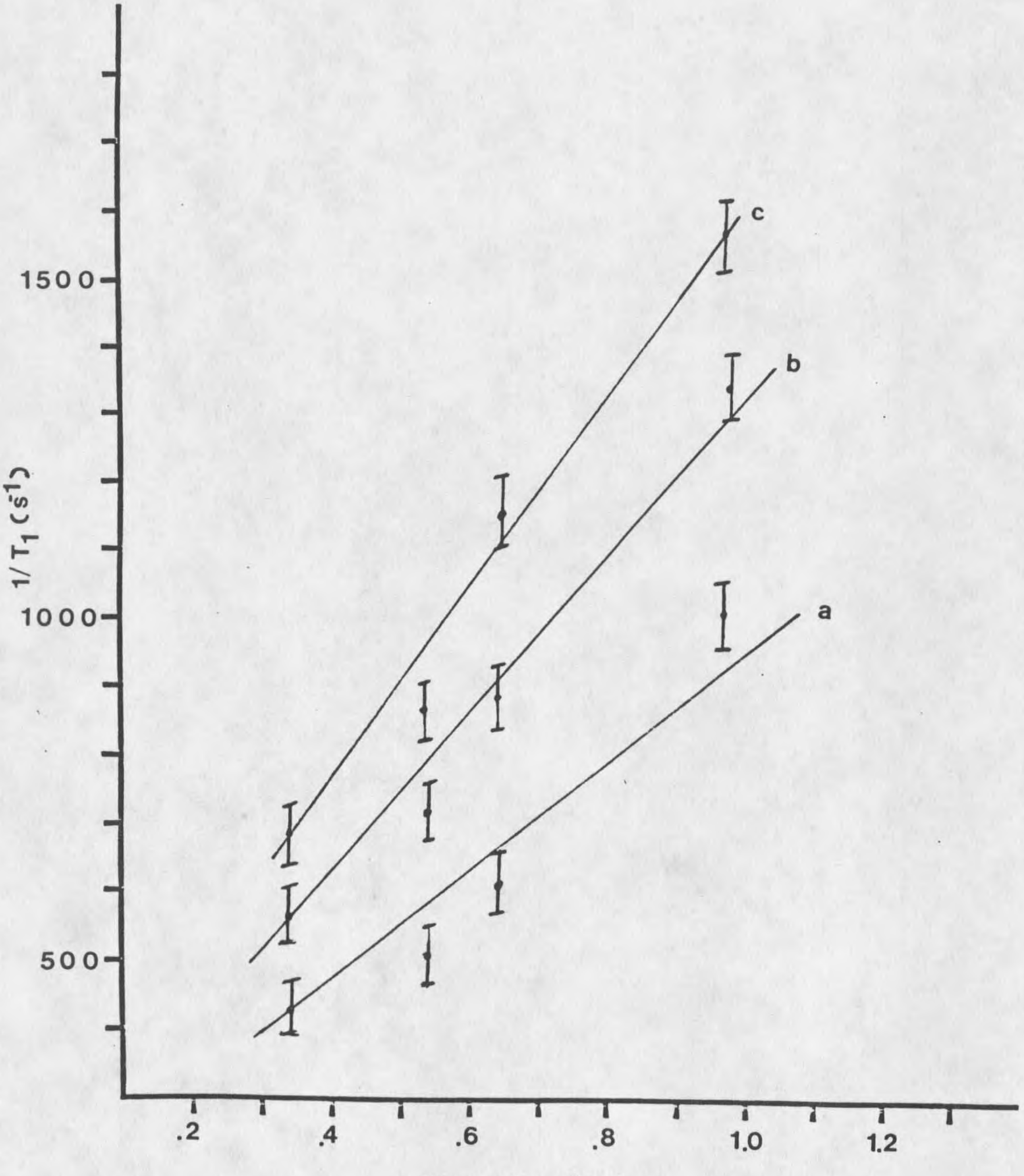


Figure 28: ^{59}Co $1/T_1$ versus viscosity of a) Mono Br; b) Bis Br; c) Tris Br.

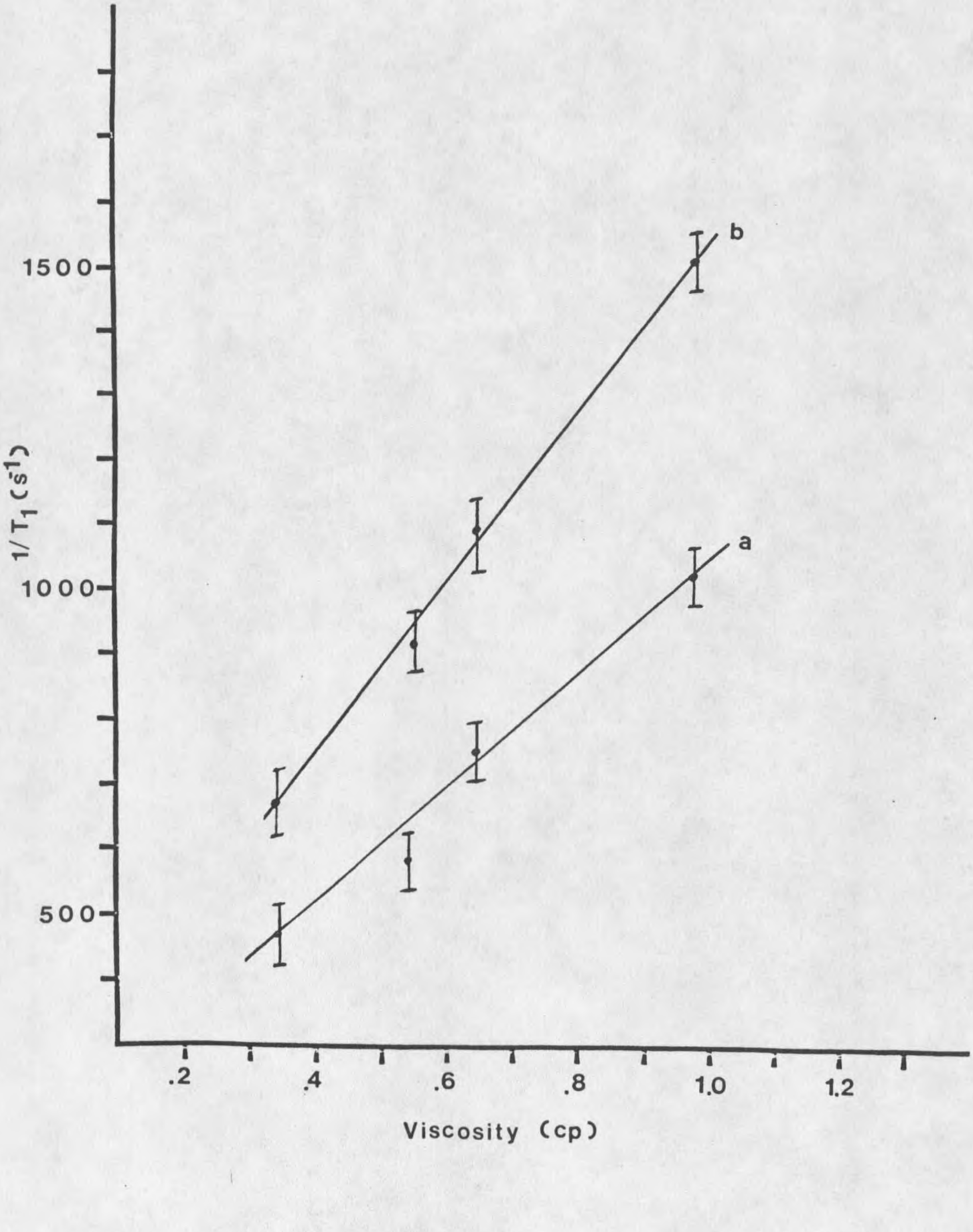


Figure 29: ^{59}Co $1/T_1$ versus viscosity of a) Mono I; b) Bis I.

in d_1-chloroform is found to be 18% slower than what would be expected from d_1-chloroform's viscosity. The slower relaxation rate could be caused by either a smaller EFG or a faster correlation time. The EFG being 18% smaller in d_1-chloroform than the other solvents is unlikely so a faster correlation time is assumed to be the cause of the slower relaxation rate.

In both the vibrational theory and the solvent reorganization theory predicts correlation times for the fluctuations of the EFG that are less than the rotational correlation time of the $Co(acac)_3$ molecule. For solvent reorganization the correlation time is that of the chloroform molecule which is smaller than $Co(acac)_3$ and therefore the rotational correlation time will be faster. Since the correlation time is solvent dependent the difference in the ^{59}Co relaxation rates for any two complexes should depend only on the difference in the EFG of the complexes. This is definitely not the case as can be seen from Table 3 which lists the ^{59}Co relaxation rate for the cobalt complexes in each of the solvents. Although Mono Cl and Bis Cl should have the largest EFG it is Mono I and Bis I that have the fastest relaxation rate.

Table 3. ^{59}Co relaxation rate (s^{-1}) at 298K.

	solvent			
complex	d_6-benzene	d_1-chloroform	d_6-Acetone	diglyme
$Co(acac)_3$	375	274	216	605
Mono Cl	620	493	446	978
Bis Cl	804	636	561	1212
Tris Cl	907	767	605	1287
Mono Br	608	505	431	1007
Bis Br	893	724	570	1346
Tris Br	1153	871	682	1572
Mono I	750	584	469	1022
Bis I	1097	921	677	1510
Tris I	1473	--	--	--

The question to ask now is does the fluctuations in the EFG at the cobalt nucleus arise from vibrational motion. Colpa[6] and Doddrell[18] have both determined equations for correlation times due to vibrational motions. Determining the correlation time from Colpa's equation,

$$\tau_V^{-1} = \tau_R^{-1} + \tau_2^{-1} \quad (16),$$

involves the estimation of τ_2 which is the time constant for the fluctuation of the coefficients of the wave functions for vibrational motion. The estimation of τ_2 is beyond the scope of this study but it is determined that the vibrational correlation time, τ_V, will be shorter than the rotational correlation time τ_R.

Doddrell determined a vibrational correlation time that is given by,

$$\tau_V^{-1} = K_1 \, a_1^{-5} \tau_R^{-1} \quad (17)$$

where K_1 is a constant within similar classes of complexes, a_1 is the radius of the complex and τ_R is the rotational correlation time of the complex. From equation 17 Doddrell derived the following relationship for two complexes of a class

$$\frac{(T_1)_i}{(T_1)_j} = \frac{(\tau_R a_1^5)_j}{(\tau_R a_1^5)_i} \quad (18).$$

Combining equation (14) and equation (18) and assuming the volume is given by $3/4\pi a^3$ the following relationship is determined

$$\frac{(T_1)_i}{(T_1)_j} = \frac{(a_1^8)_j}{(a_1^8)_j} \quad (19).$$

The radius of the $Co(acac)_3$ molecule (taken to be from the cobalt to the methine carbons hydrogen) is estimated to be 3.5 A from a crystal structure of $Co(acac)_3$ published by Hon and Pfluger[10]. The radius of the tris complexes were determined by subtracting .3 A for the hydrogen then adding values of .99 A, 1.14 A, and 1.33 A for chlorine, bromine and iodine respectively. The resultant radii are 4.19 A for Tris Cl, 4.34 A for Tris Br and 4.53 A for Tris I. The ^{59}C T_1 at 298K for the complexes in d_1-chloroform are listed in Table 4. Because Tris I was not soluble in d_1-chloroform the ^{59}Co relaxation rate was estimated to be 1100 s^{-1}.

Table 4. ^{59}Co T_1 in d_1-chloroform at 298K.

complex	T_1 (seconds)
Co(acac)$_3$	3.6×10^{-3}
Tris Cl	1.3×10^{-3}
Tris Br	1.1×10^{-3}
Tris I	9.1×10^{-4}

The ratio of a_1^8 for Co(acac)$_3$/Tris Cl, Co(acac)$_3$/Tris Br and Co(acac)$_3$/Tris I are .24, .18 and .13 respectively. This compares to .36, .31, and .25 for the ratios of the T_1's for each of the respective ratios. The ratios of T_1 and a_1^8 are not equal as is expected from equation (19), this could be due to the fact that the complexes are not spherical or that the estimates of the radii are not correct. Even though the a_1^8 and T_1 ratios are not equal it is interesting that there is an average difference of .055 in going from the Co(acac)$_3$/Tris Cl ratio to the Co(acac)$_3$/Tris Br ratio to the Co(acac)$_3$/Tris I ratio for either a_1^8 or T_1. This fact suggests that there is a relationship between a_1^8 and T_1 but that the estimates of the radii are not correct.

So far the study has examined the time dependence of the EFG and has not been concerned with the origins of the EFG. According to the three theories of the quadruple relaxation at symmetric center the EFG is either static and due to slight distortions from perfect symmetry, or is time dependent and due to solvent reorientation or solvent assisted vibration. If the EFG is time dependent its magnitude should be solvent dependent because the EFG is due to solvent collisions or reorientation. The nuclear quadruple coupling constant (NQCC) is directly proportional to the EFG so an examination of the NQCC of Co(acac)$_3$ could possibly help determine the origins of the EFG at the cobalt nucleous.

To calculate the ^{59}Co NQCC of Co(acac)$_3$ from the equation for quadruple relaxation both the relaxation rate and the correlation time must be known. The rotational correlation time determined from the ^{13}C relaxation of Co(acac)$_3$ can be used as the correlation time for Co(acac)$_3$ in d$_6$-acetone and diglyme because the ^{59}Co relaxation appears to be due to rotational motion. The rotational correlation time was calculated for Co(acac)$_3$ in each solvent and is listed in Table 5, also listed is the ^{13}C relaxation rate determined[40] at 298K.

Table 5. ^{13}C Relaxation rate and rotational correlation time for Co(acac)$_3$.

	solvent			
	d$_6$-benzene	d$_1$-chloroform	d$_6$-acetone	diglyme
$1/T_1(s^{-1})$	1.06	.97	.53	1.45
10^{11} $_R$(s)	5.2	4.8	2.6	7.1

The experimental value for τ_R can be compared to a theoretical determined values calculated using equation 14 and using a molecular volume determined for a sphere with a radius of 3.5 A. Values of τ_R calculated from equation 14 are, 2.7 x 10^{11}, 2.4 x 10^{11}, 1.4 x 10^{11} and 4.3 x 10^{11} for Co(acac)$_3$ in d$_6$-benzene, d$_1$-chloroform, d$_6$-aceton and diglyme respectively. These values are about a factor of 2 lower than the experimental values but considering the rough estimate of the molecular volume they are in quite good agreement.

The rotational correlation times from Table 5 were used to calculate the ^{59}Co NQCC from equation 1. An asymmetric parameter equal to 0 was used because of the symmetric octahedron of oxygens. Values of 3.7 MHZ, 3.3 MHZ, 4.0 MHZ and 4.0 MHZ were determined for Co(acac)$_3$ in d$_6$-benzene, d$_1$-chloroform, d$_6$-acetone and diglyme respectively. The ^{59}Co NQCC in d$_6$-acetone and diglyme are equal, this indicates that the ^{59}Co relaxation of Co(acac)$_3$ is due to a static EFG that fluctuates because of rotational reorientation. As expected the NQCC in d$_1$-chloroform is less than that in d$_6$-acetone and diglyme because the correlation time used in the calculation of the NQCC was too long. The NQCC determined in d$_6$-benzene is smaller than the NQCC in d$_6$-acetone and diglyme but not as small as in d$_1$-chloroform. Compared to the ^{59}Co NQCC in d$_6$-acetone or diglyme the NQCC in d$_6$-benzene relates to a 7.5% drop in the EFG, since this is unlikely the low value for the NQCC is probably due to the rotational correlation time not being the correct correlation time to be used to calculate the NQCC in d$_6$-benzene.

It is possible to compare the ^{59}Co NQCC calculated for Co(acac)$_3$ in d$_6$-acetone and diglyme to the NQCC value of ^{27}Al determined by Dechter. Because the reaction of a nucleus to an external field gradient is not identical for all nuclei the NQCC must be divided by the quantity eQ(1-γ), where eQ is the nuclear quadrupole moment and (1-γ) is the Sternheimer antishielding factor. Dechter determined a corrected NQCC of 0.9 for ^{27}Al which was believed to be consistent with a slightly distorted octahedral structure. Because tables of Sternheimer antishielding factors are not available for all nuclei the value for ^{59}Co must be estimated from the values given for ^{27}Al and ^{69}Ga. Trends in the Sternheimer antishielding factors show that the value for ^{59}Co will lie between that of ^{27}Al and ^{69}Ga. Using a value of 8 for the Sternheimer antishielding factor a value of 1.25 is calculated for the corrected NQCC of ^{59}Co. This is in good agreement with the value calculated by Dechter for ^{27}Al which is consistent with a slightly distorted octahedral structure.

It would be informative to calculate the NQCC for the mono and bis complexes to determine the change in the EFG in going from Co(acac)$_3$ to a Mono or Bis complex. Because the rotational motion is not isotropic and because the asymmetric parameter is no longer equal to zero the NQCC for the mono and bis complexes can not be calculated in a straight-forward manner. Plots of $1/T_1$ versus the number of liqands halogenated were used to get a graphical picture of the dependence on the relaxation rate on substitution. Figure 30 is a plot of $1/T_1$ at 298K versus the number liqands halogenated for the Cl series, the Br series and the I series in d$_6$-benzene. The straight lines connect the point for Co(acac)$_3$ with each of the tris complexe points. Because Co(acac)$_3$ and a tris complex have the same EFG and any difference in the relaxation rate is due to a change in the correlation time, the lines represent the relaxation rates of a complex with the same EFG as Co(acac)$_3$ but an increased correlation time. The difference in the relaxation rate of the mono and Bis complexes and the relaxation rate given by the line will be a measure of the difference in the EFG of $Co(acac)_3$ and the Mono and Bis complexes. Figures 31-33 are similar plots of the Cl series and Br series in d_1-chloroform, d_6-acetone and digylme respectively.

According to a point change model the EFG for the Mono and Bis complexes of any series is identical, this means the distance above the line should be identical for a Mono and Bis complex from a given series in a given solvent. Figures 30-33 do show this trend but with some scatter due to experimental error. The error is very noticeable in figure 30 where only the Cl series shows a significant EFG and the Br series and I series fall on or below the line. The figures also shows that the EFG due to the chlorine is greater than that of bromine which is to be expected.

As another means of examining the EFG of $Co(acac)_3$ and the halogenated complexes a theory derived by Deverell[19] which relates the EFG at a nucleus to its chemical shift is used. The basis behind the theory is that any change in the electron cloud of a nucleus will give rise to an EFG and a paramagnetic shift in the chemical shift. The EFG is related to the chemical shift by the following equation

$$e^2Qq = 1/10 \quad e^2Q(\frac{\Delta\sigma_p}{\alpha_2}) \qquad (20)$$

where e^2Qq is the nuclear quadruple coupling constant (NQCC), Δ is the mean excitation energy, α is the fine structure contant and σ_p is the paramagnetic term of the magnetic shielding equation.

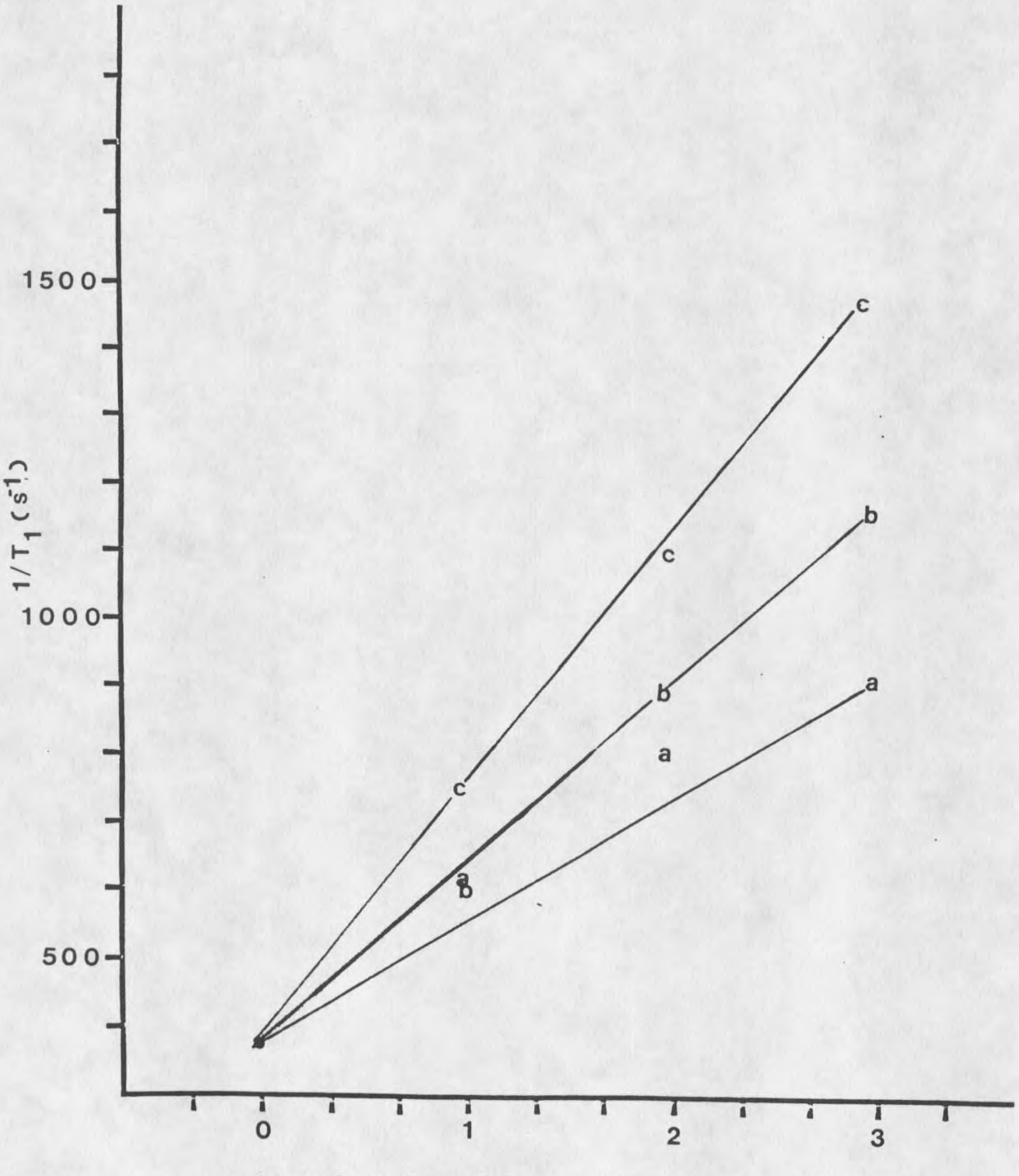


Figure 30: ^{59}Co $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series; c) I series in d_6-benzene.

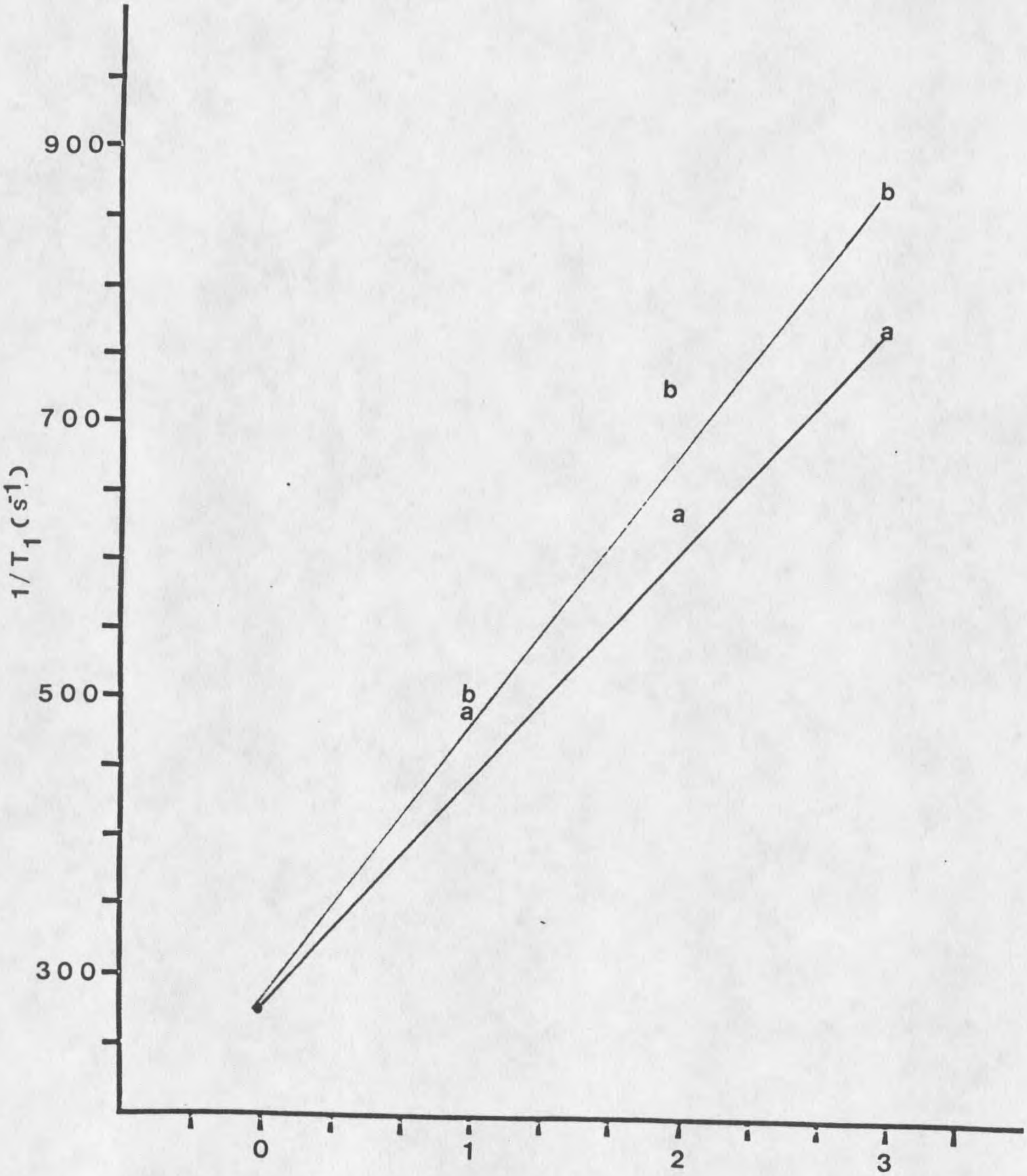


Figure 31: ^{59}Co $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series in d_1-chloroform.

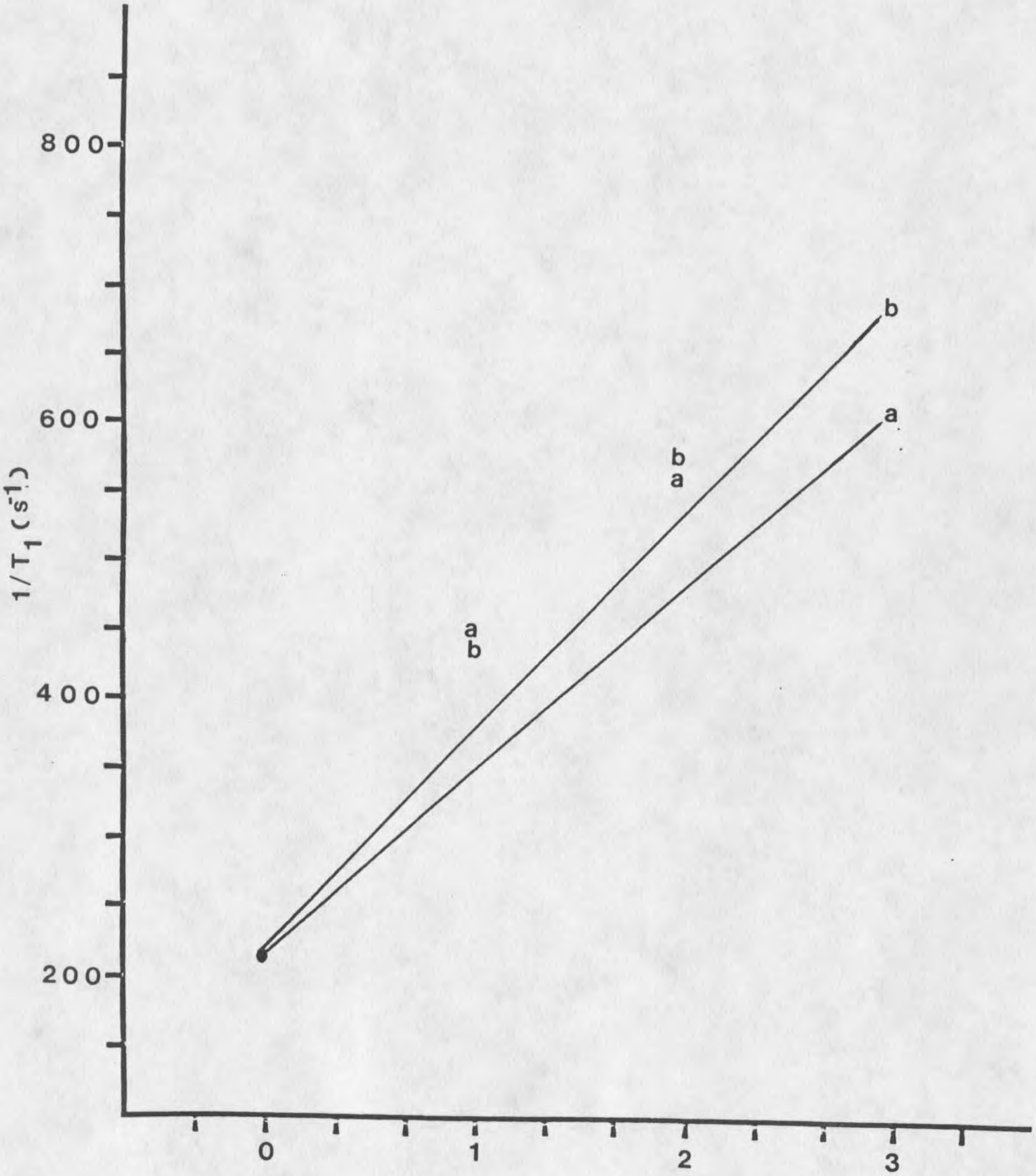


Figure 32: ^{59}C $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series in d_6-acetone.

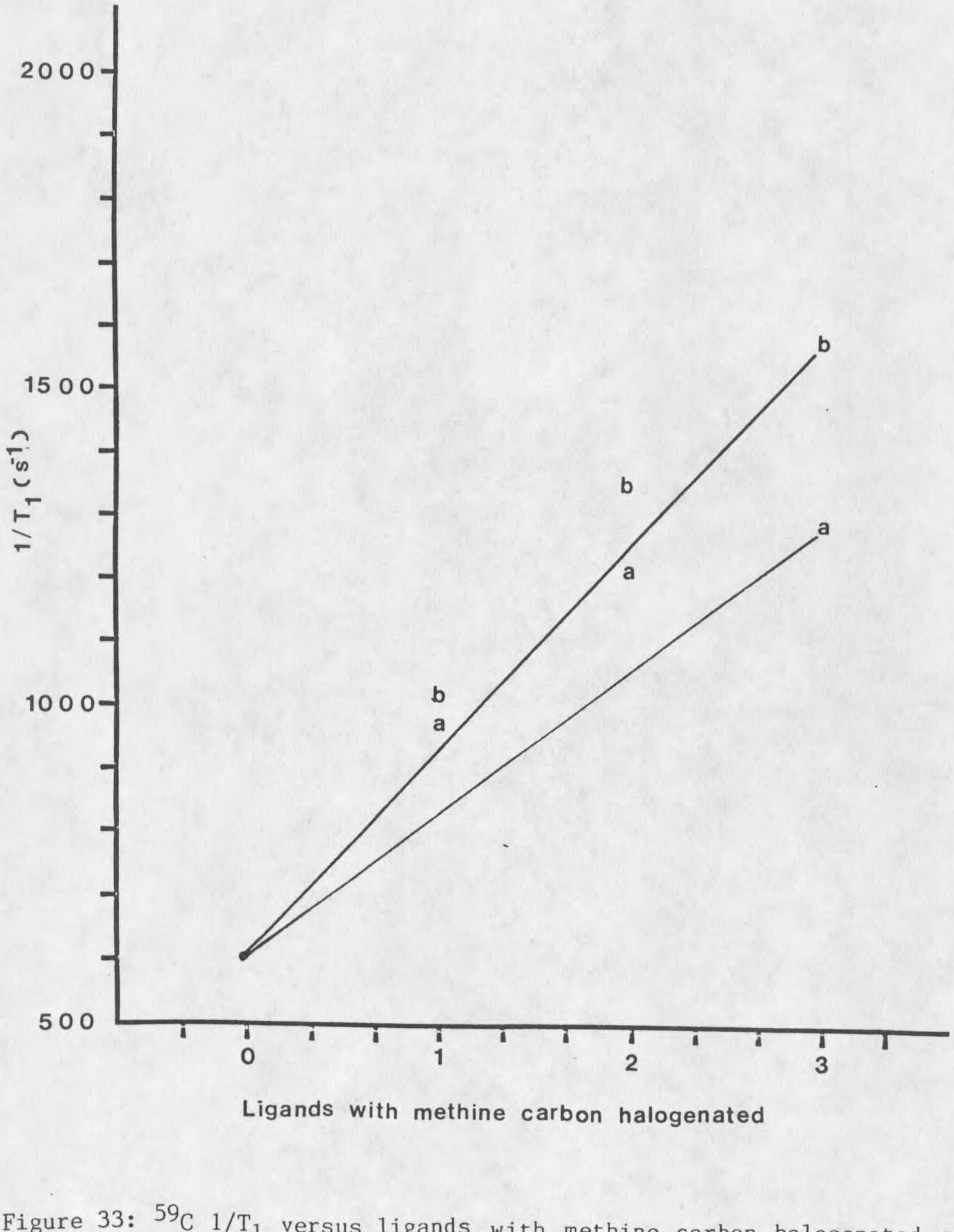


Figure 33: ^{59}C $1/T_1$ versus ligands with methine carbon halogenated of a) Cl series; b) Br series in diglyme.

In a paper on the relaxation of ^{23}Na in mixed solvents Laszlo[41] used the Deverell theory to explain the ^{23}Na relaxation. In the paper he used the following relationship

$$(\Delta^{*}_{YZ})^{1/2} \propto \delta \qquad (21)$$

where Δ^{*}_{YZ} is the linewidth at half height normalized to unit viscosity and δ is the chemical shift. Equation 21 relates the EFG which is proportional to the square root of the linewidth to the chemical shift which is mainly due to variations in σp. If equation 21 holds a plot of $(\Delta^{*}_{YZ})^{1/2}$ versus δ will be linear.

Figures 34-37 show plots of $(\Delta^{*}_{YZ})^{1/2}$ versus the ^{59}Co chemical shift[13] at 298K in d_6-benzene, d_1-chloroform, d_6-acetone and diglyme respectively. The plots are linear suggesting that the EFG is responsible for the different relaxation rate of the cobalt complexes in a given solvent. The lines for each solvent are not co-linear which supports the fact that the differences in the relaxation rate of a complex in the solvents is not due to EFG but a difference in the correlation time of the EFG fluctuations.

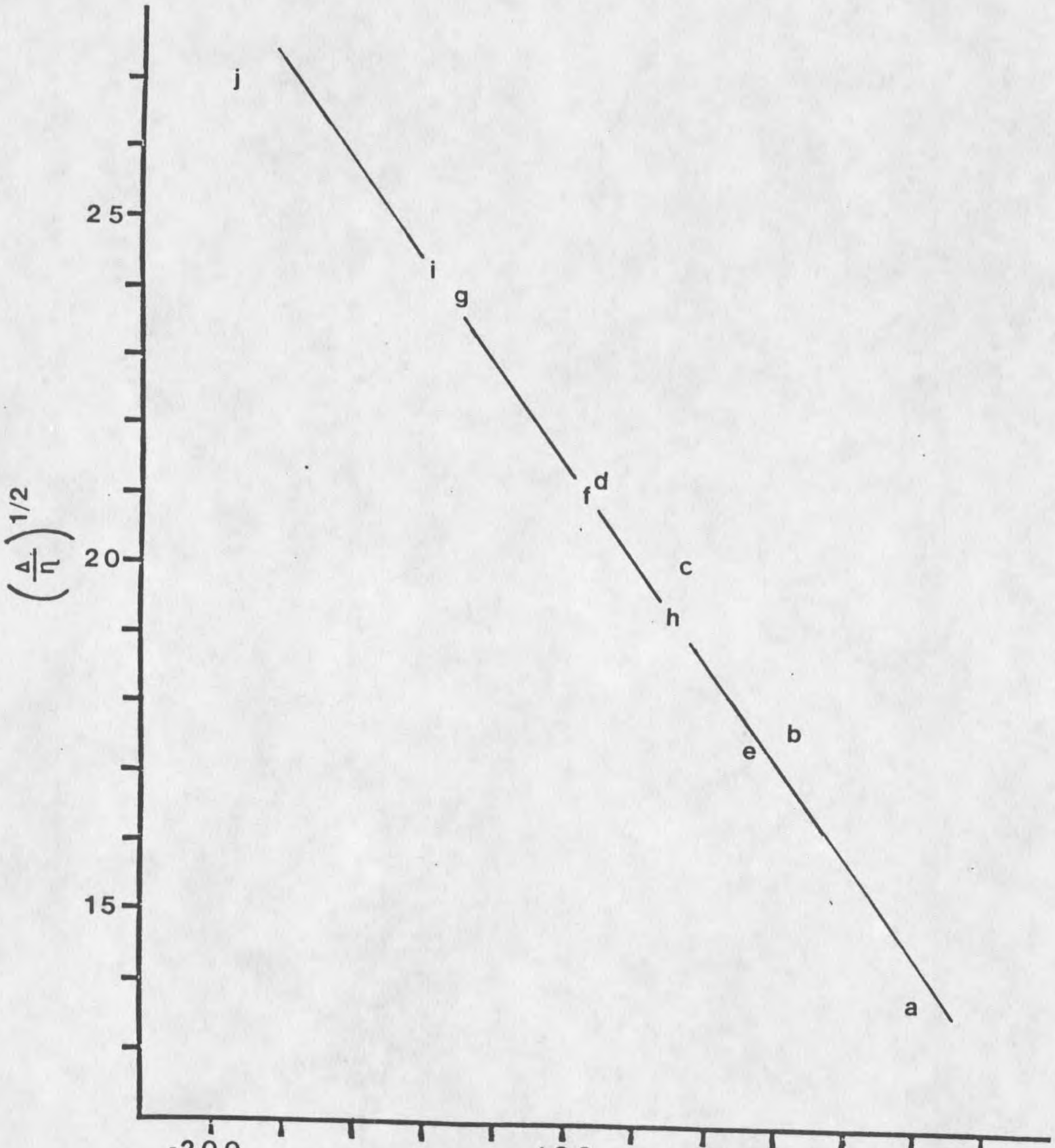


Figure 34: ^{59}Co $(\frac{\Delta}{\eta})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tri Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I; j) Tris I in d$_6$-benzene.

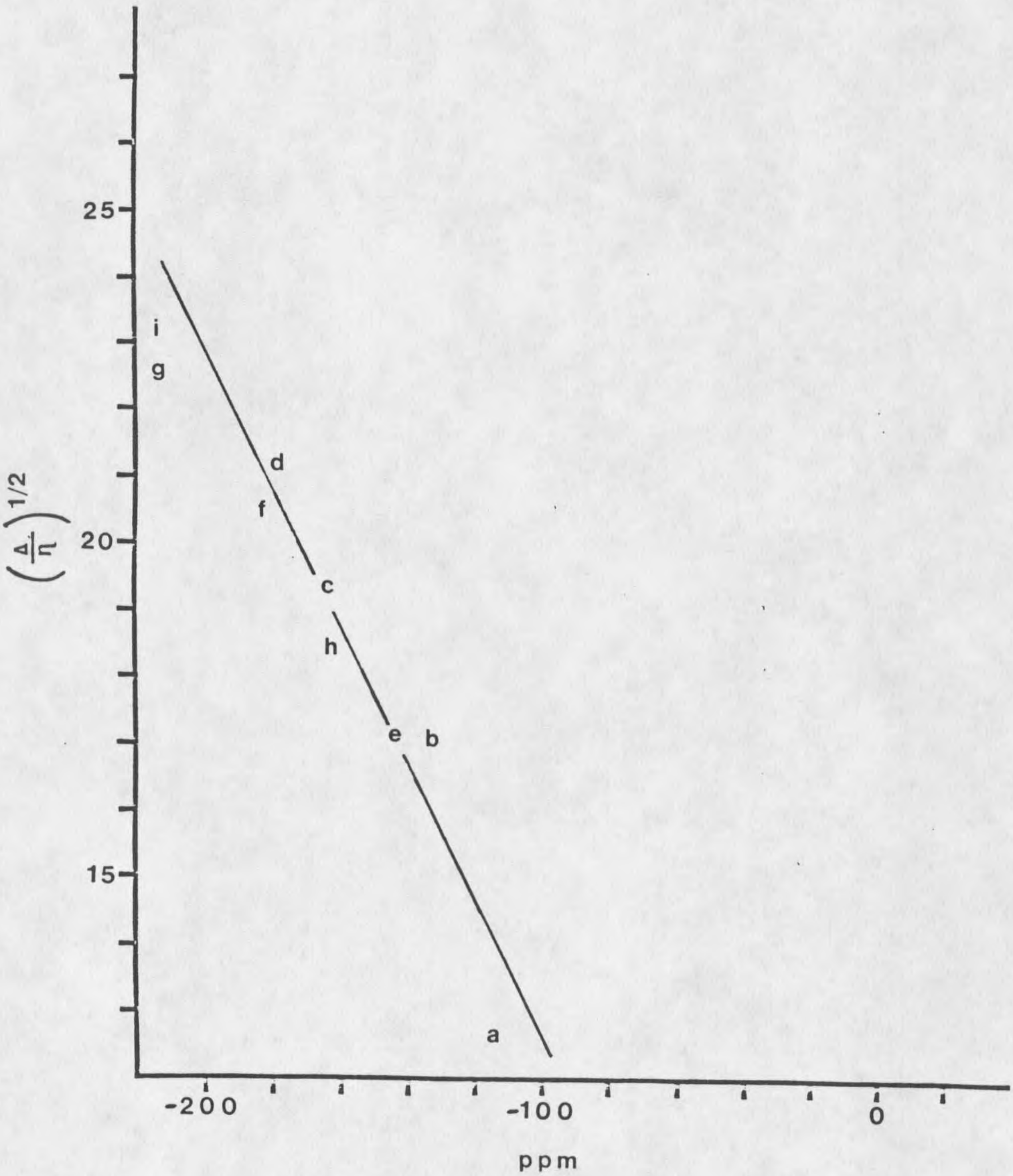


Figure 35: ^{59}Co $(\frac{\Delta}{\eta})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I in d$_1$-chloroform.

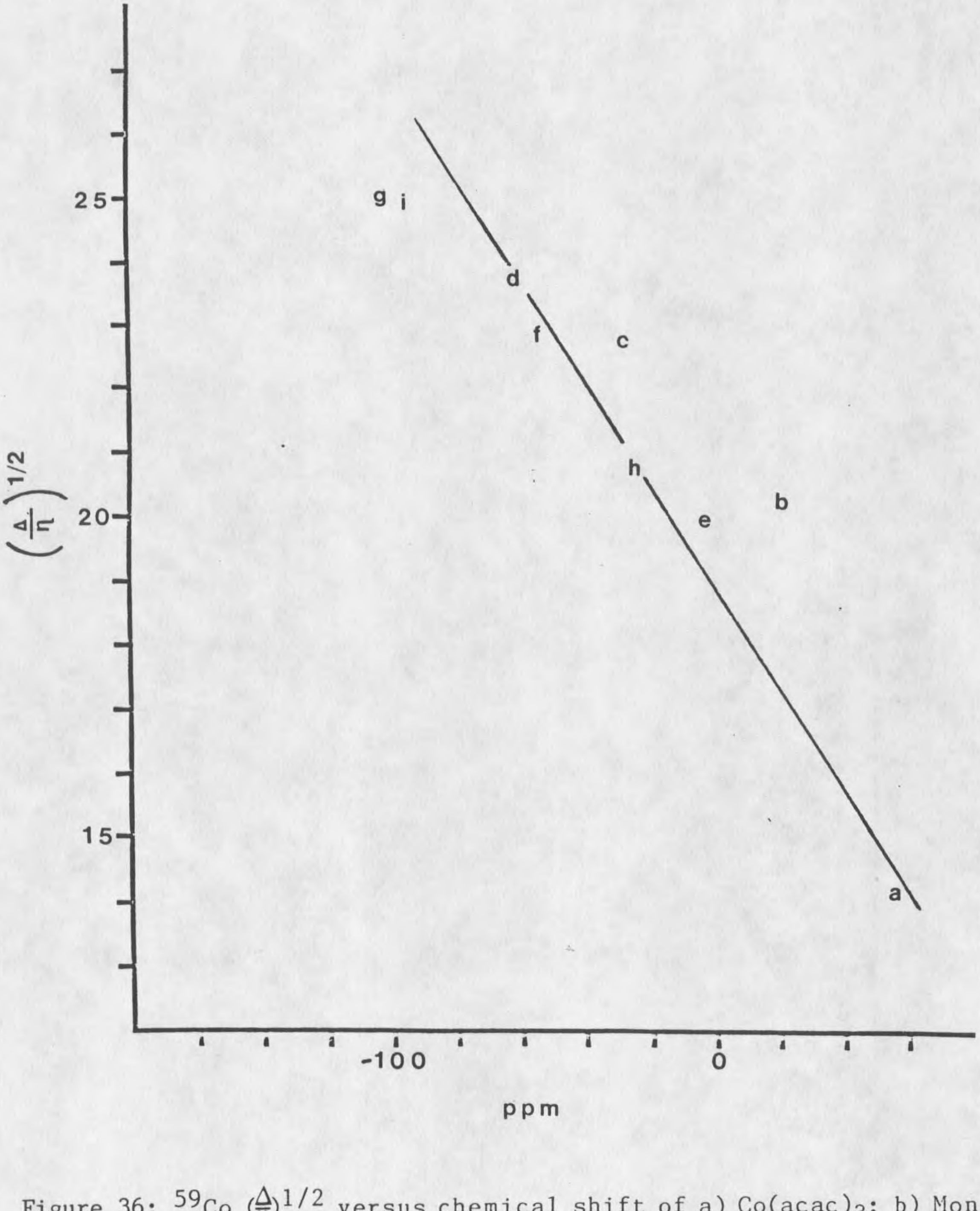


Figure 36: ^{59}Co $(\frac{\Delta}{\eta})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I in d$_6$-acetone.

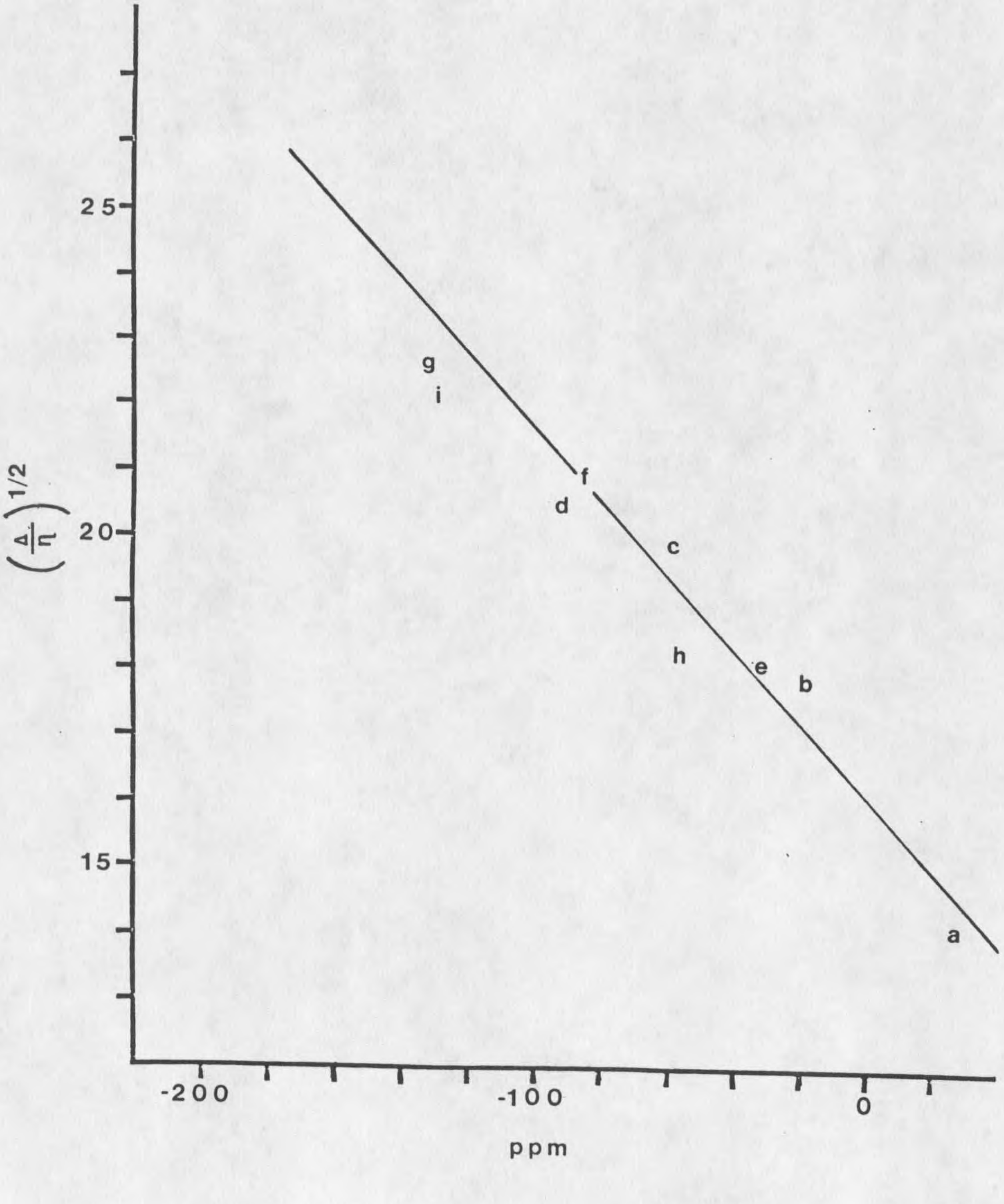


Figure 37: ^{59}Co $(\frac{\Delta}{\eta})^{1/2}$ versus chemical shift of a) Co(acac)$_3$; b) Mono Cl; c) Bis Cl; d) Tris Cl; e) Mono Br; f) Bis Br; g) Tris Br; h) Mono I; i) Bis I in diglyme.

SUMMARY AND CONCLUSION

Comparing the temperature dependence or activation energy of the ^{13}C relaxation of the methine carbon of Co(acac)$_3$ to the temperature dependence or activation energy of the ^{59}Co relaxation of Co(acac)$_3$ it appears that the ^{59}Co relaxation of Co(acac)$_3$ in d_6-acetone and diglyme is due to rotational reorientation while in d_6-benzene and d_1-chloroform it is due to vibrational motion. This conclusion is very simplified in that the relaxation is said to be either rotationally or vibrationally controlled and the possibility of the relaxation being due to a combination of rotational and vibrational motion has been ignored due to the complexity of the problem. However, it does appear that the characteristics of relaxation follow either rotational motion or vibration motion so that although not completely correct it is possible to refer to the relaxation as either one or the other. The NQCC of 4.0 OMHZ calculated for Co(acac)$_3$ in d_6-acetone and diglyme is in excellent agreement with the value of ^{27}Al(acac)$_3$ determined by Dechter which corresponded to a slightly distorted octahedral. This also leads to the conclusion that the ^{59}Co quadrupole relaxation of Co(acac)$_3$ in d_6-acetone and diglyme is due to a small static EFG due to a slight distort form O_h symmetry of the oxygen atoms which is modulated by the rotational reorientation of the Co(acac)$_3$ molecule.

The ^{59}Co relaxation of Co(acac)$_3$ in d_6-benzene and d_1-chloroform does not appear to be due to rotational reorientation, the ^{59}Co activation energy is less than the ^{13}C activation energy and ^{59}Co relaxation is less than what would be expected from the viscosities of

d_6-benzene and d_1-chloroform. The ^{59}Co relaxation could be caused by vibrational motion as the Valiev-Brown and Colpa theory suggests but a rigorous proof of this is beyond the scope of this study. It would involve the estimations of a number of quantities so that the ^{59}Co relaxation rate could be calculated from the equations derived by Valiev and by Brown and Colpa these values could be compared to the experimentally determined relaxation rates to see how the theories compare to experiment.

It is not obvious what could cause the ^{59}Co relaxation of Co(acac)$_3$ to go from rotationally controlled relaxation in d_6-acetone and diglyme to what appears to be vibrationally controlled relaxation in d_6-benzene and d_1-chloroform. The magnitude of the EFG is one idea as to the change but small increase in the magnitude of the EFG have no effect on the type of motion responsible for the ^{59}Co relaxation. Both the mono and Bis complexes have an increased EFG compared to Co(acac)$_3$ but the ^{59}Co activation energy and the viscosities dependence in d_6-benzene and d_1-chloroform are similar to those of Co(acac)$_3$ in d_6-benzene and d_1-chloroform.

The answer to the differences in the solvents may be in the excited vibrational mode of the complexes. It is possible that d_6-benzene and d_1-chloroform are able through collisions to excite the vibrational mode more efficiently than d_6-acetone and diglyme and therefore allow for relaxation due to vibrational motion. A means is then needed by which the solvent effects of the vibrational motion of the complexes can be examined and related to the ^{59}Co relaxation. It may be possible to study the excited vibrational modes of the complexes directly with the NMR, the temperature dependence of the ^{59}Co chemical shift is due to changes in the population of the excited vibrational states which changes the mean excitation energy in the paramagnetic term in the Ramsey equation for the chemical shift and thereby causing the temperature dependent chemical shift. The temperature dependence of the ^{59}Co chemical shift may be different for $Co(acac)_3$ in d_6-benzene and d_1-chloroform and reveal the reason for the different quadrupole relaxation modes in the different solvents.

Plots of the ^{59}Co chemical shifts versus temperature for $Co(acac)_3$ and the halogenated complexes are shown in the appendix, the slopes were determined using a least squares fit and are listed in Table 6. It is clear that the temperature dependence of the ^{59}Co chemical shift is significantly different in d_1-chloroform as compared to the other solvents. This may be related to the reason the quadrupole relaxation is via a different mode in d_1-chloroform than in d_6-acetone or diglyme, however, the slopes in d_6-benzene agree well with those for d_6-acetone and diglyme even though the quadrupole relaxation in d_6-benzene appear to be via vibrational motion.

At least in the case of d_1-chloroform there seems to be a relationship between the temperature dependence of the ^{59}Co chemical shift and the mode of quadrupole relaxation. It is not clear the exact nature of the relationship or if any useful information can be extracted but a future study may be very enlightening.

Table 6. Slopes of plots of ^{59}Co chemical shift versus temperature.

	Solvent			
complex	d_6-benzene	d_1-chloroform	d_6-acetone	diglyme
Co(acac)$_3$	2.03	2.47	2.02	1.91
Mono Cl	2.11	2.61	2.13	1.98
Bis Cl	2.19	2.74	2.19	2.11
Tris Cl	2.26	2.89	2.28	2.22
Mono Br	2.14	2.60	2.16	2.03
Bis Br	2.21	2.72	2.26	2.15
Tris Br	2.34	2.95	2.41	2.32
Mono I	2.06	2.64	2.14	2.04
Bis I	2.17	2.82	2.27	2.22
Tris I	2.32	--	--	--

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4) The extreme narrowing condition occurs in nonviscous solvents where the relation $\omega_o \tau_c << 1$ holds, where ω_o is the larmar frequency and τ_c is the correlations time of the relaxation process.

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27) Because the ^{59}Co chemical shift is solvent and temperature dependent the chemical shift was measured using the internal standard in the NMR the standard was set so that the ^{59}Co chemical shift of Co(acac)$_3$ in d$_6$-benzene at 298K is 0 ppm.

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APPENDIX

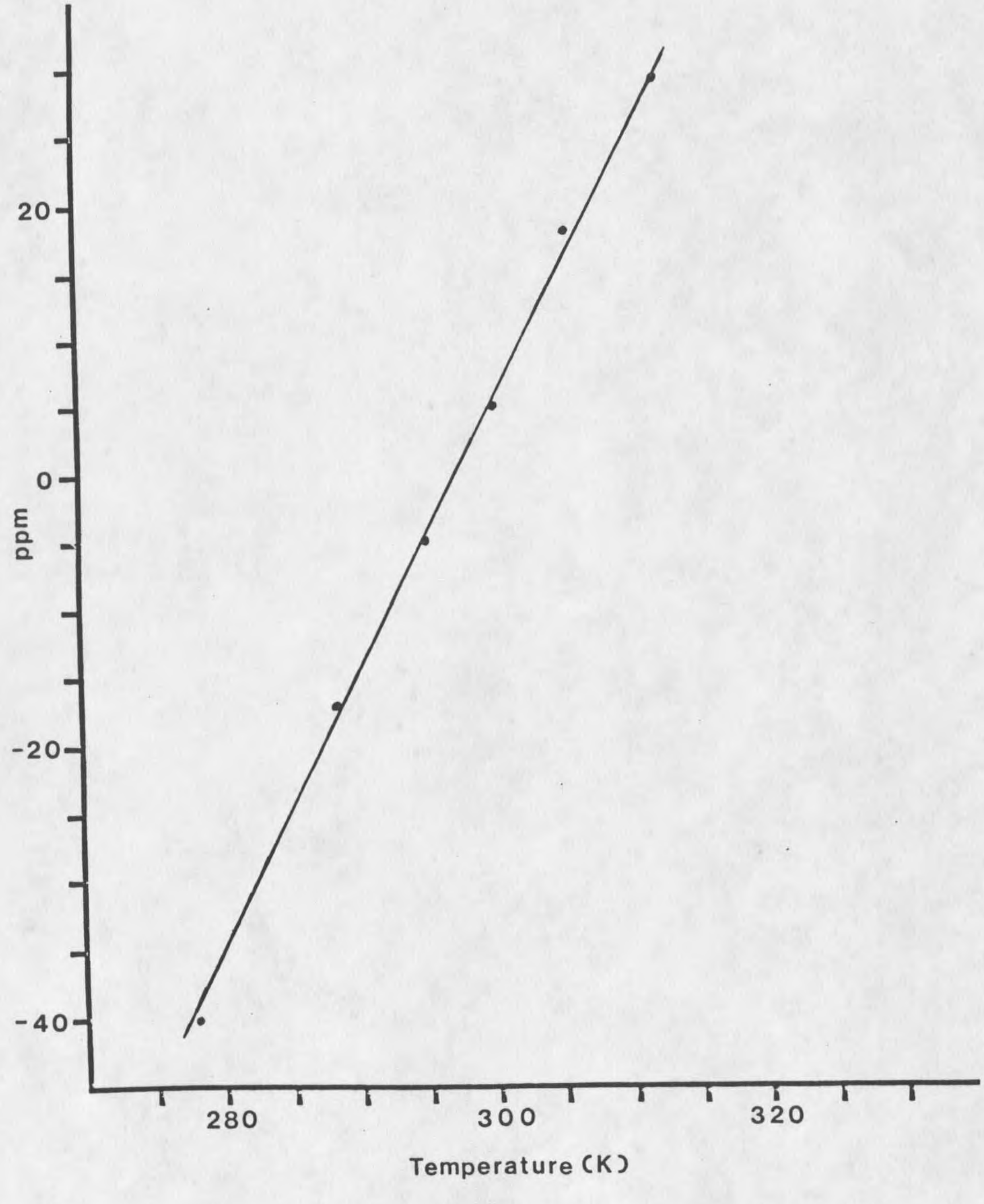

Figure 38: ^{59}Co chemical shift versus temperature of Co(acac)$_3$ in d$_6$-benzene.

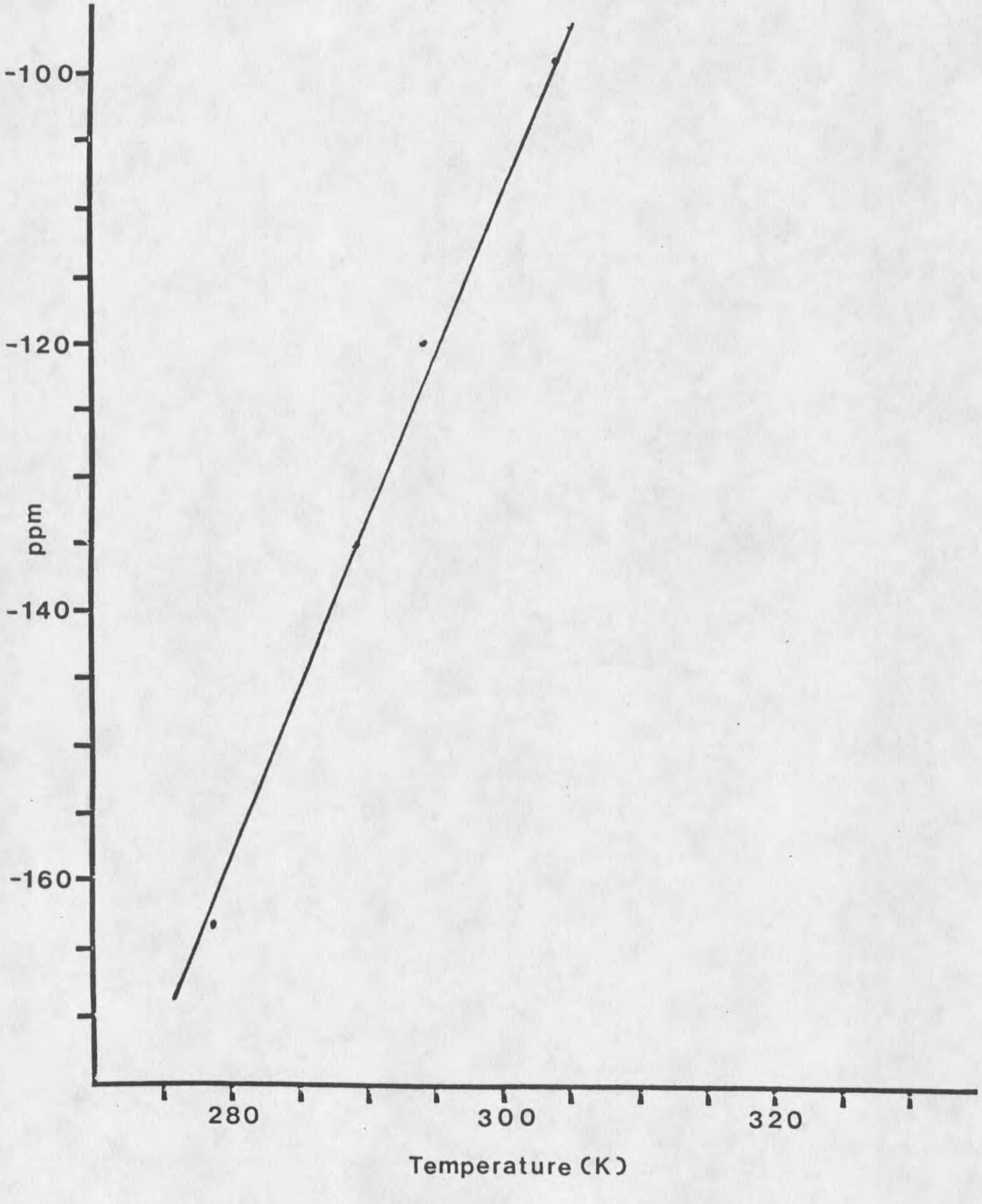

Figure 39: ^{59}Co chemical shift versus temperature of $Co(acac)_3$ in d_1-chloroform.

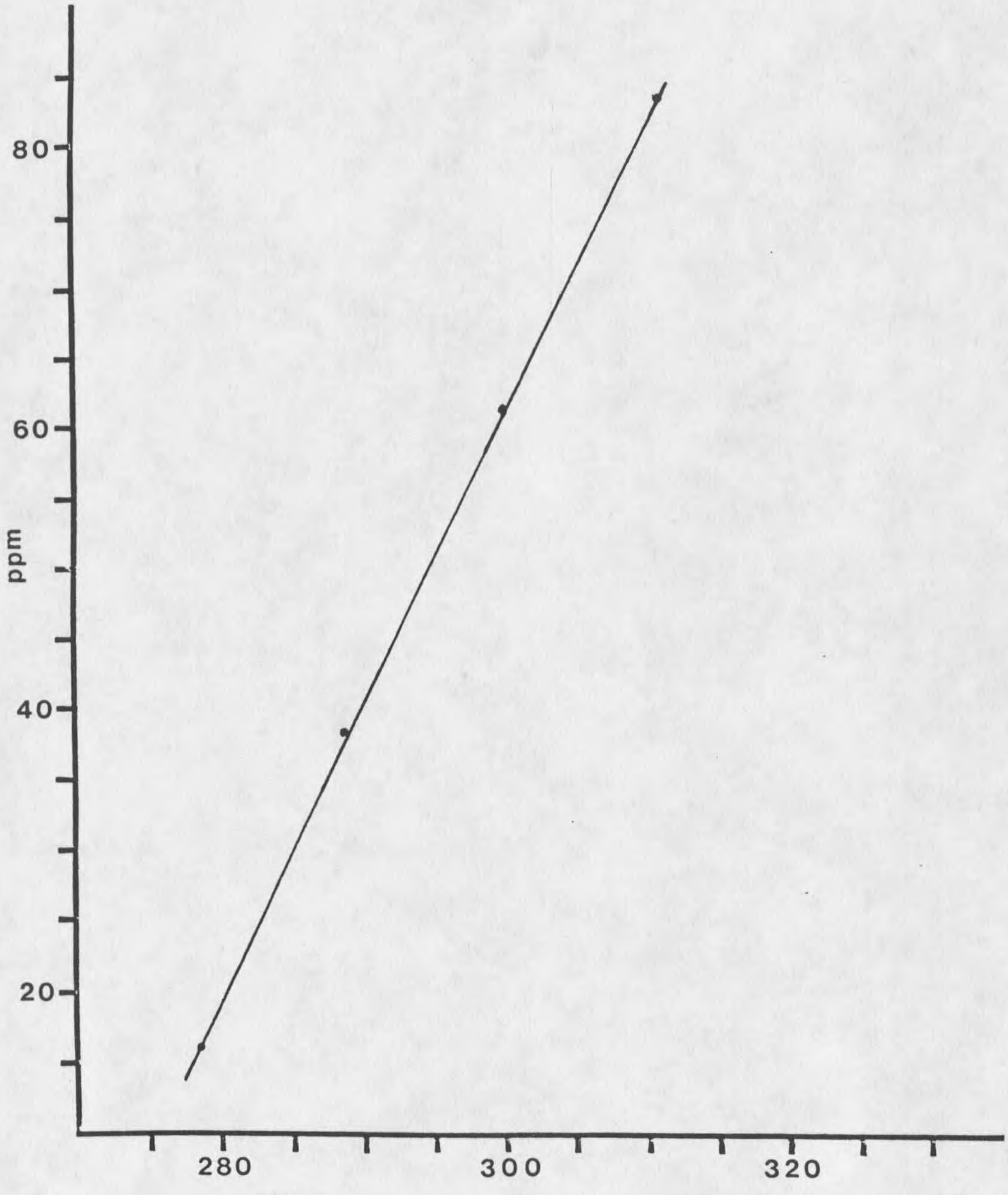

Figure 40: ^{59}Co chemical shift versus temperature of $Co(acac)_3$ in d_6-acetone.

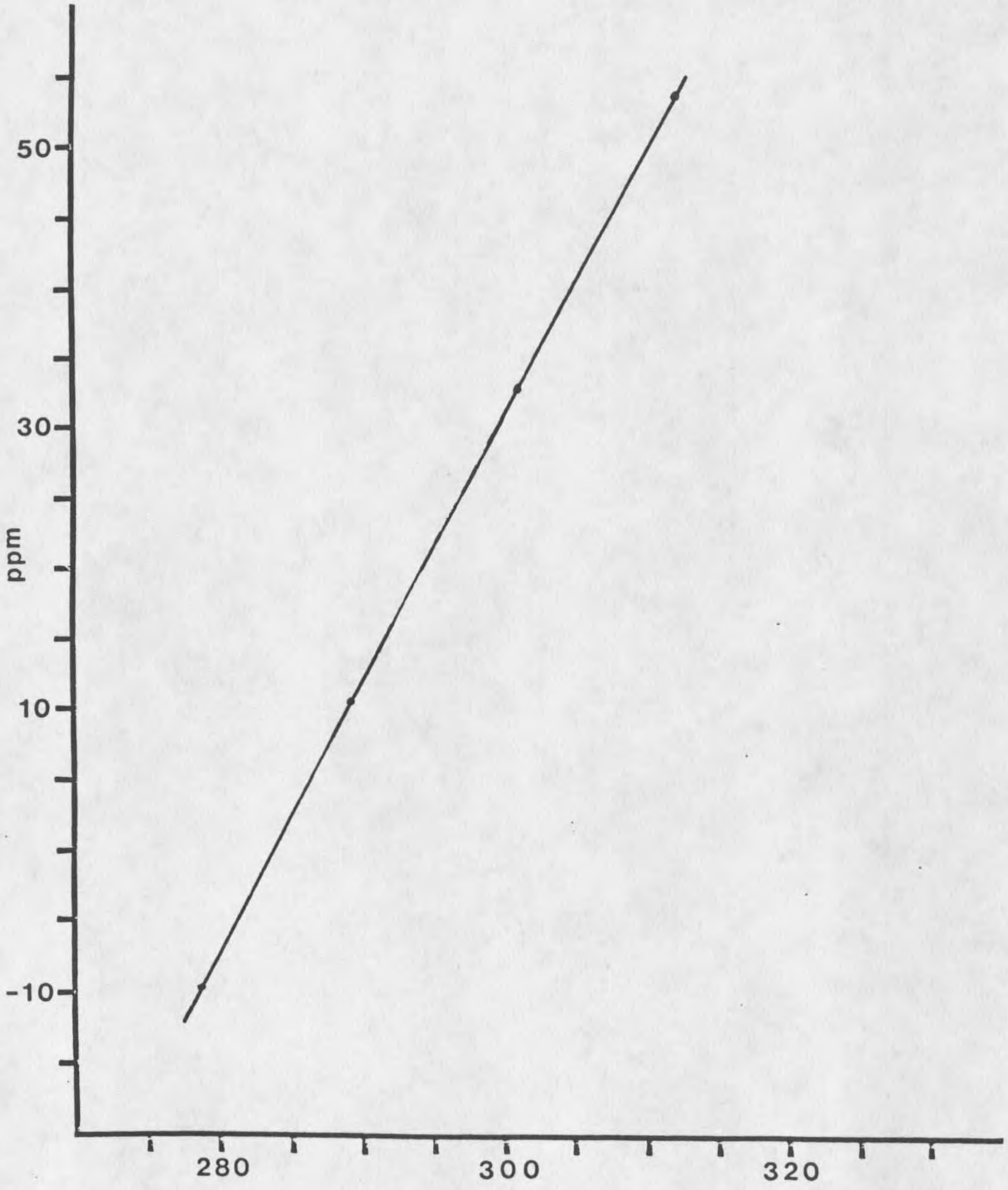

Figure 41: ^{59}Co chemical shift versus temperature of Co(acac)$_3$ in diglyme.

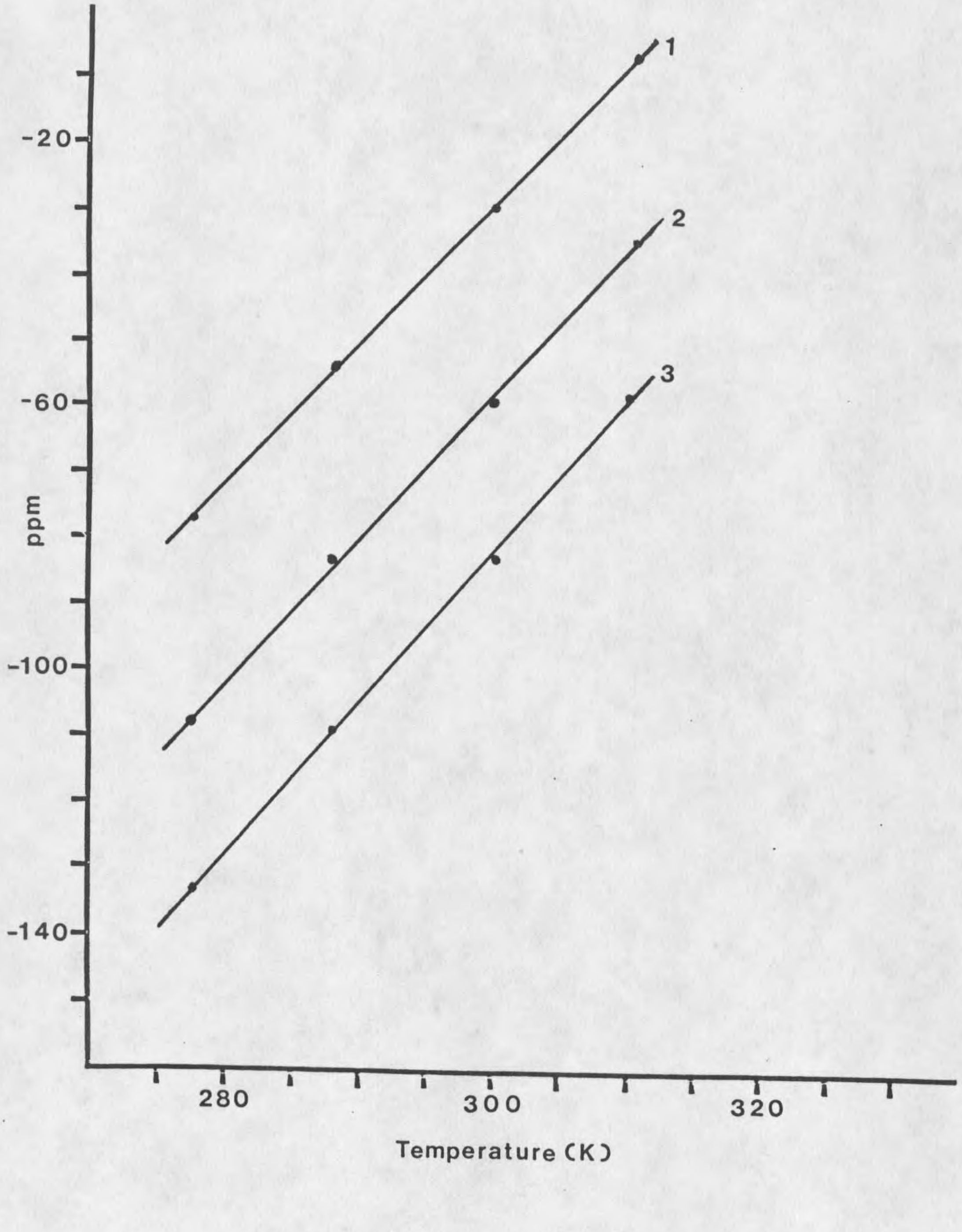

Figure 42: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in d_6-benzene.

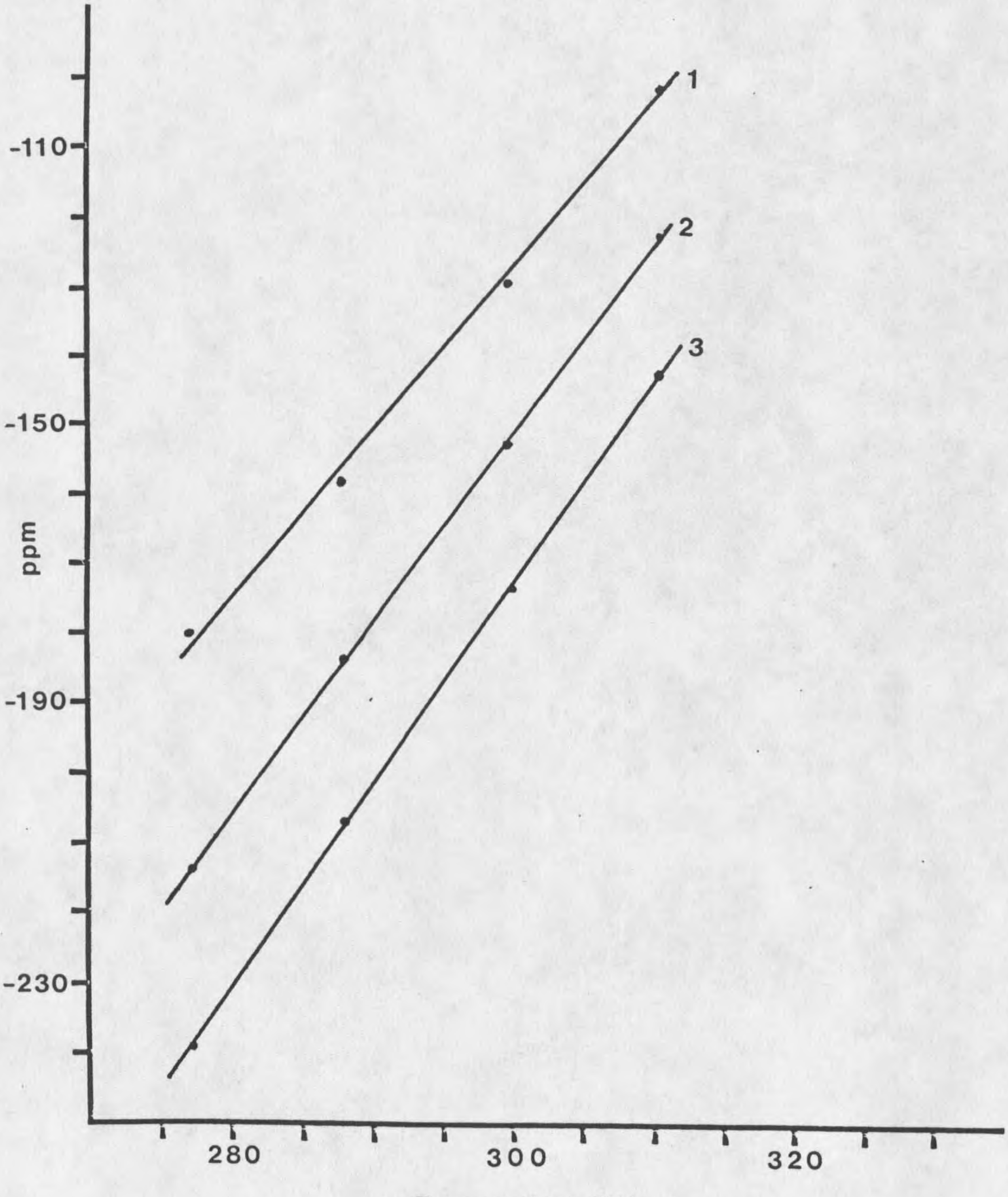

Figure 43: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in d$_1$-chloroform.

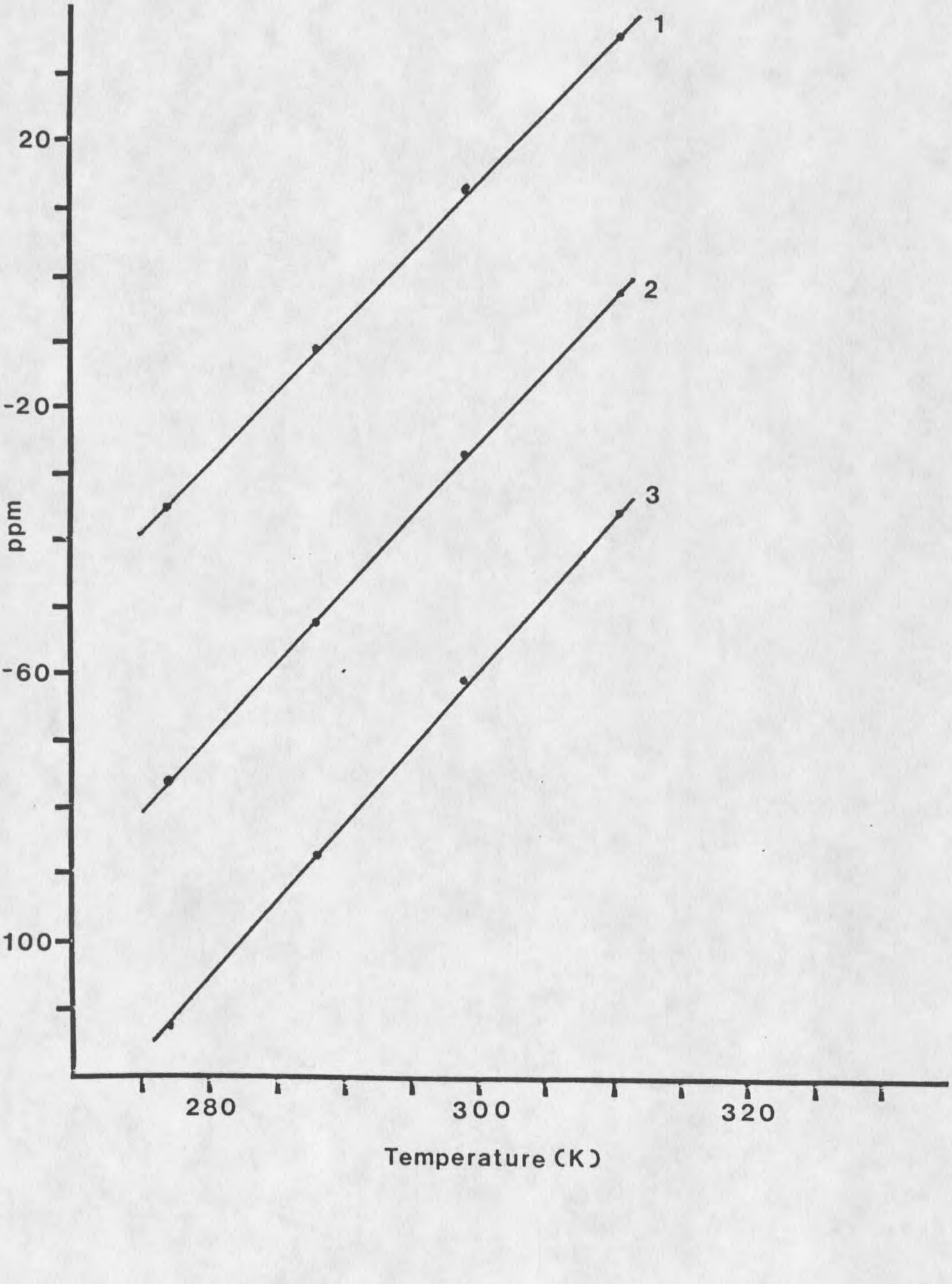

Figure 44: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in d_6-acetone.

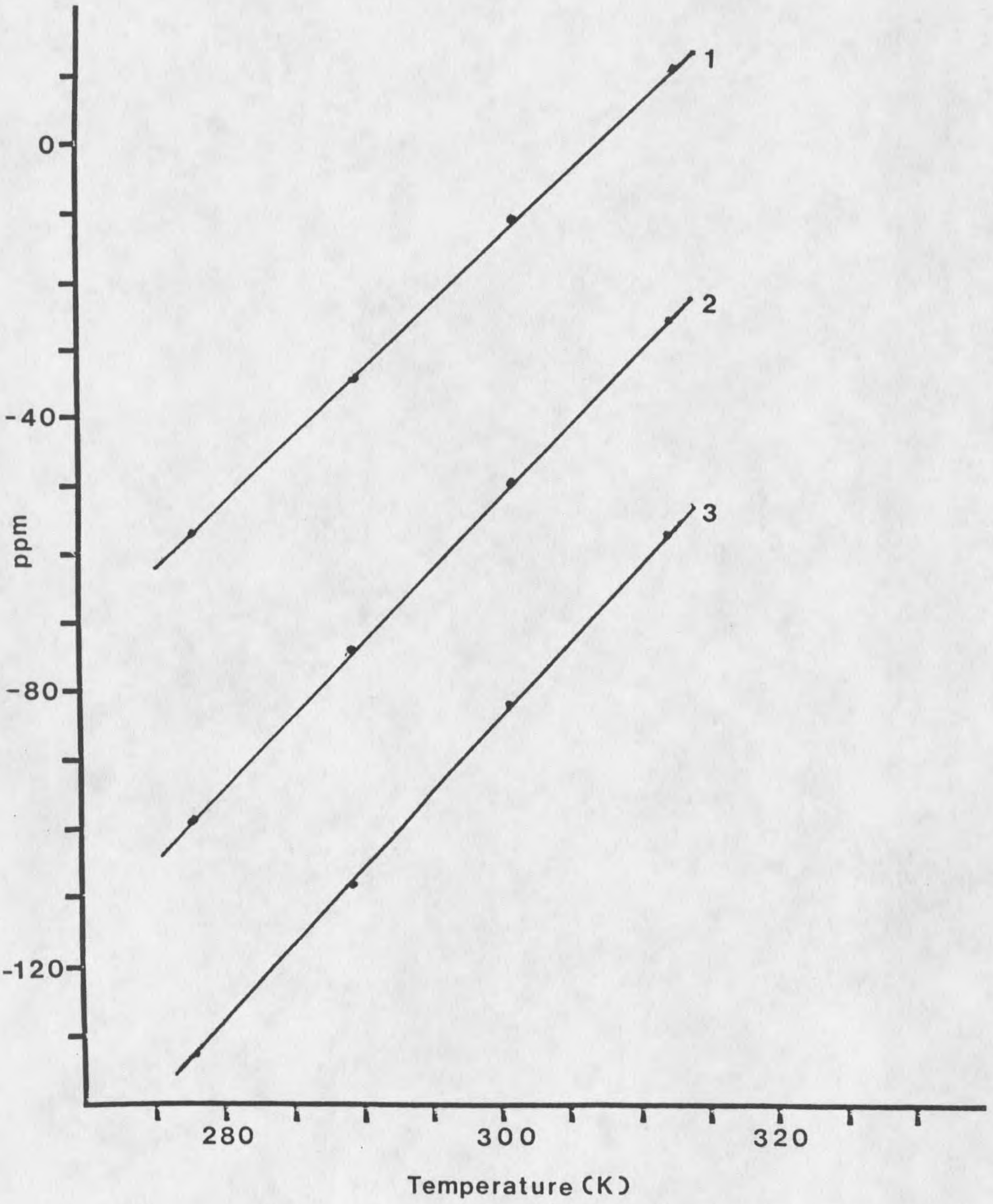

Figure 45: ^{59}Co chemical shift versus temperature of 1) Mono Cl; 2) Bis Cl; 3) Tris Cl in diglyme.

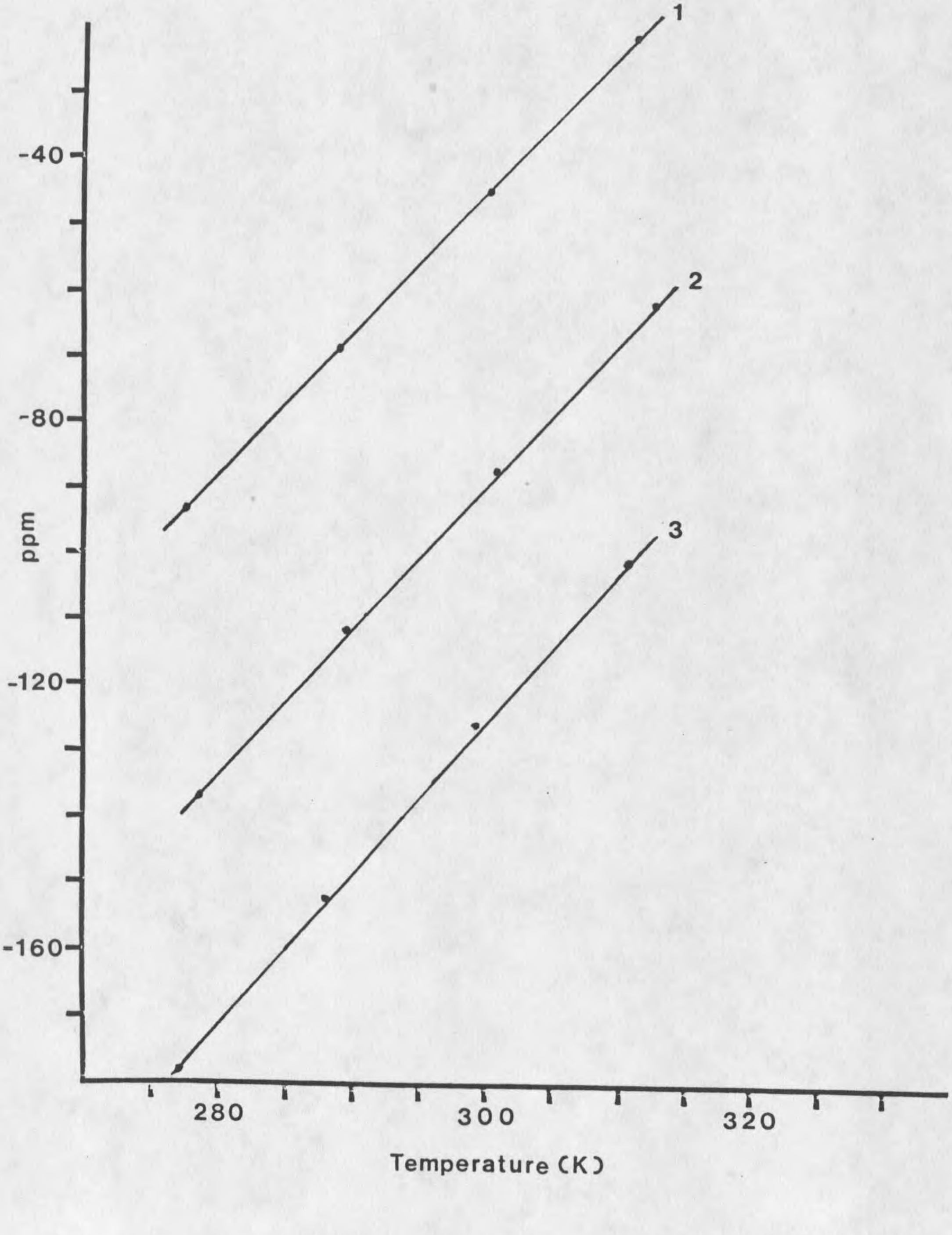

Figure 46: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in d_6-benzene.

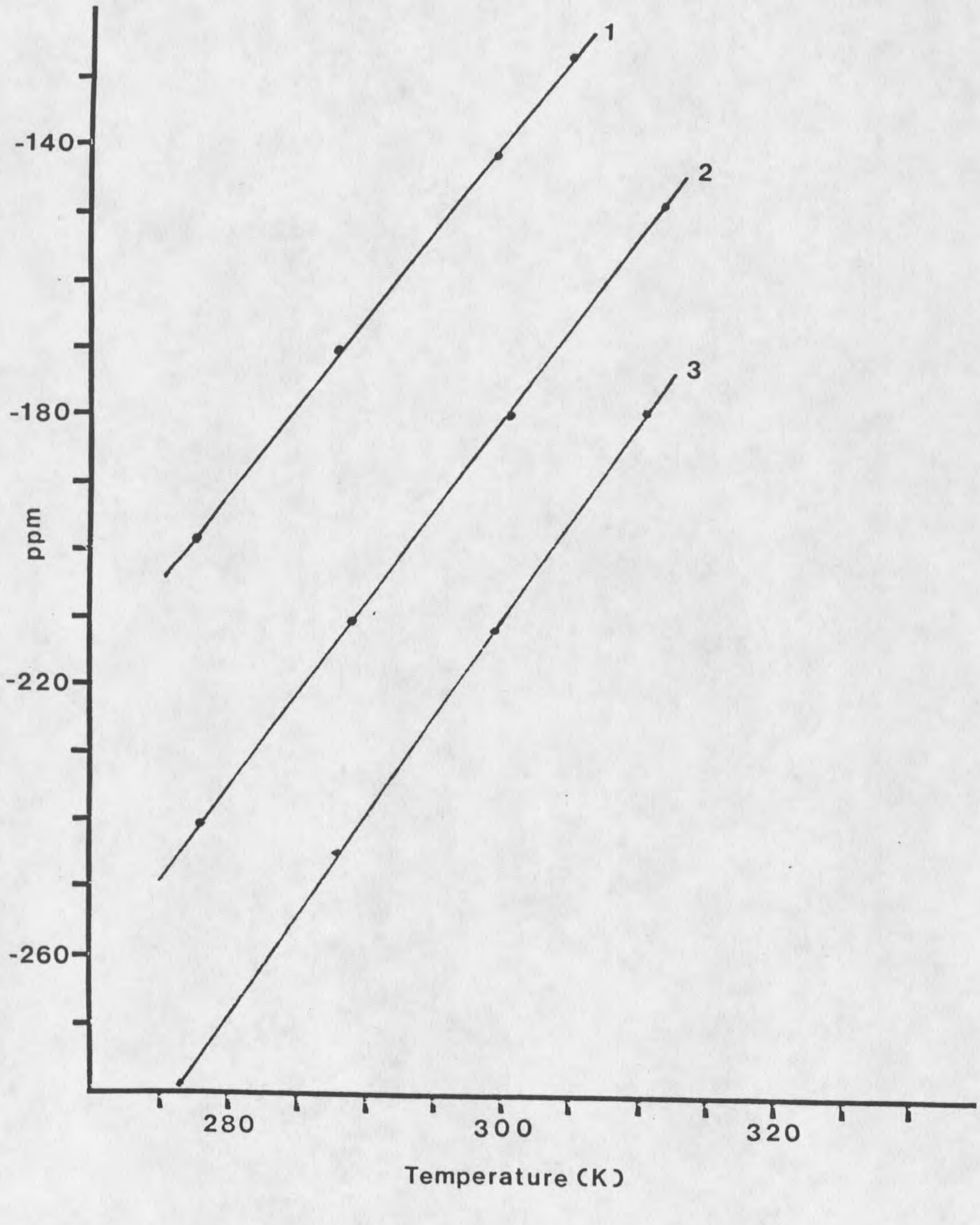

Figure 47: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in d_1-chloroform.

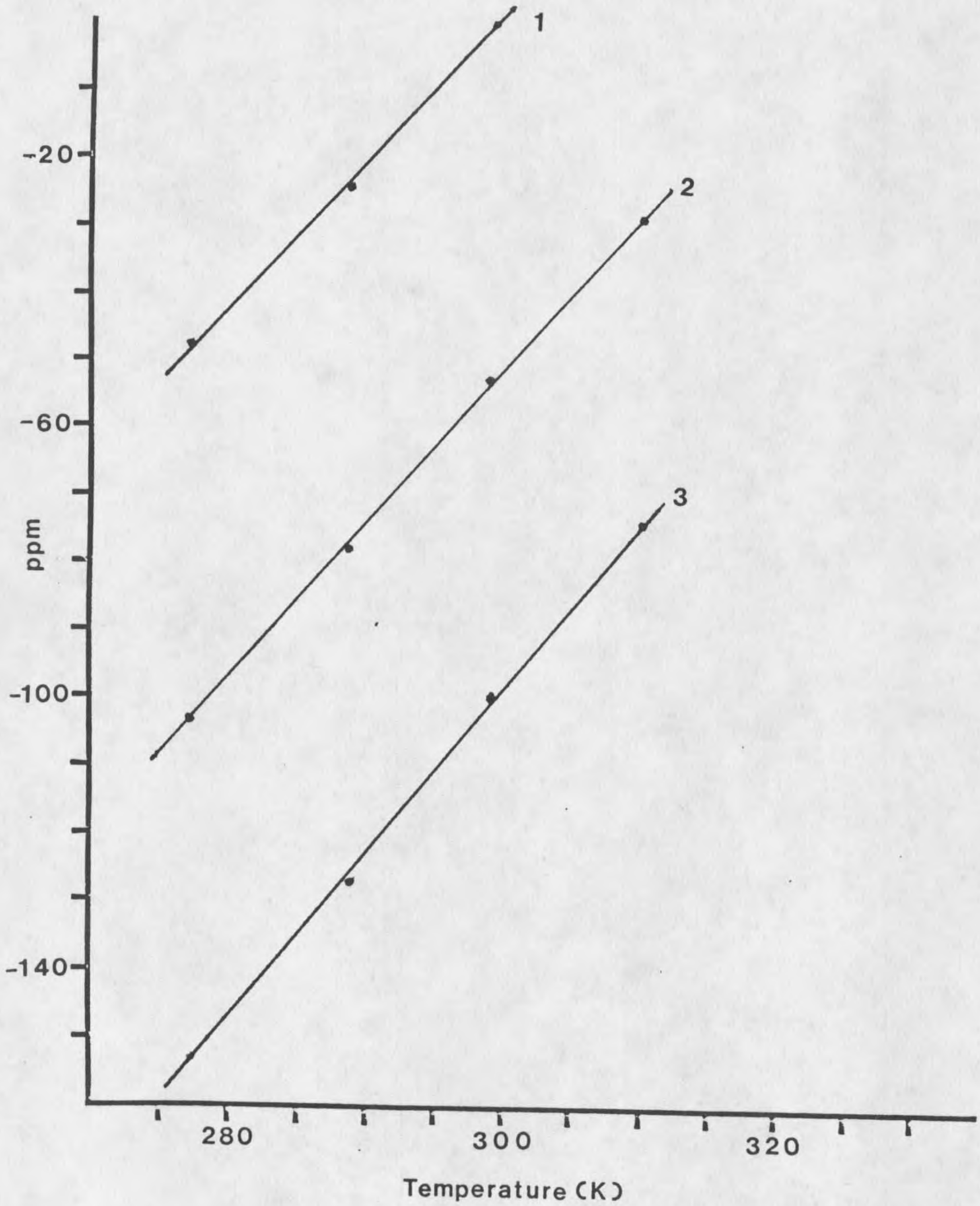

Figure 48: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in d_6-acetone.

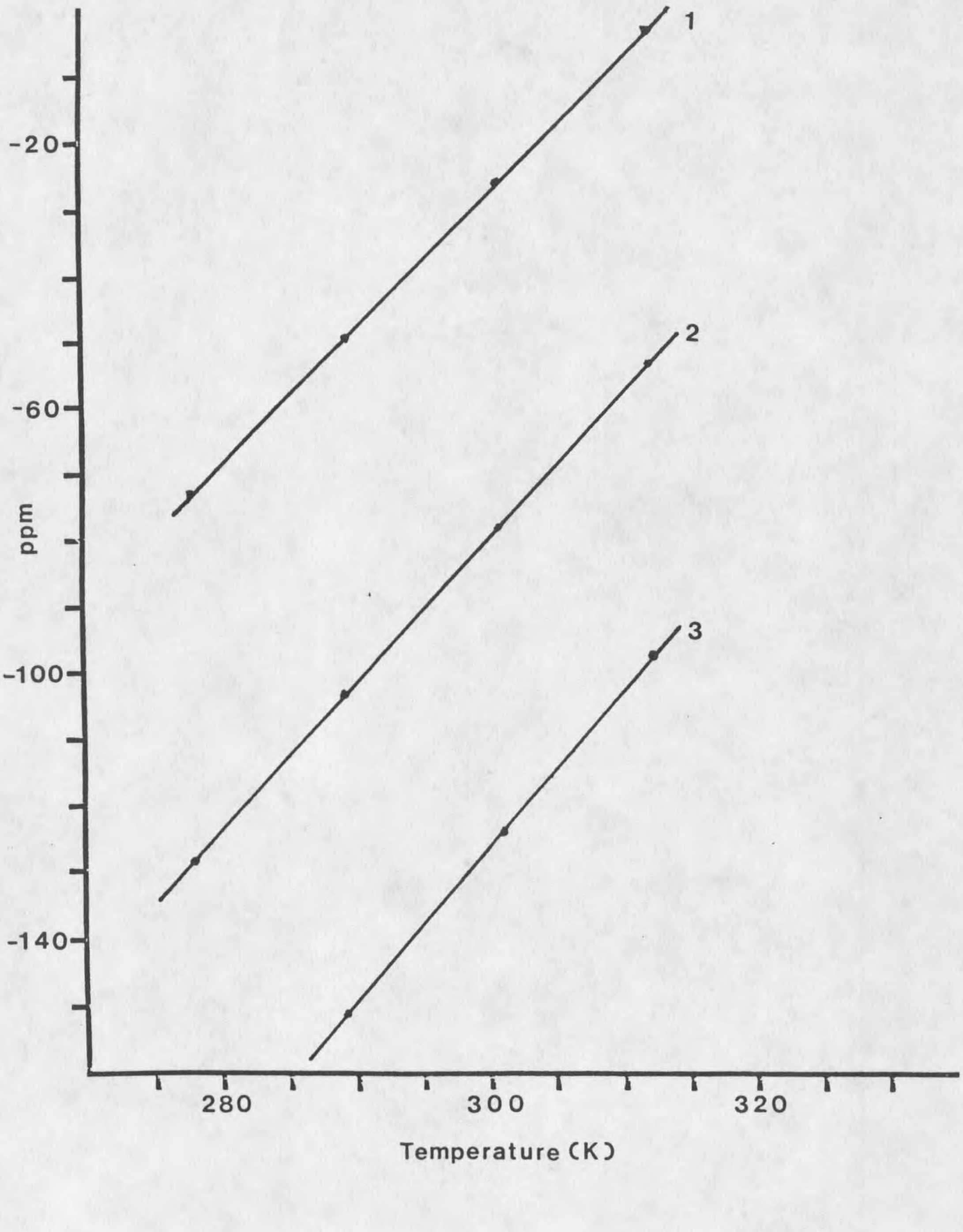

Figure 49: ^{59}Co chemical shift versus temperature of 1) Mono Br; 2) Bis Br; 3) Tris Br in diglyme.

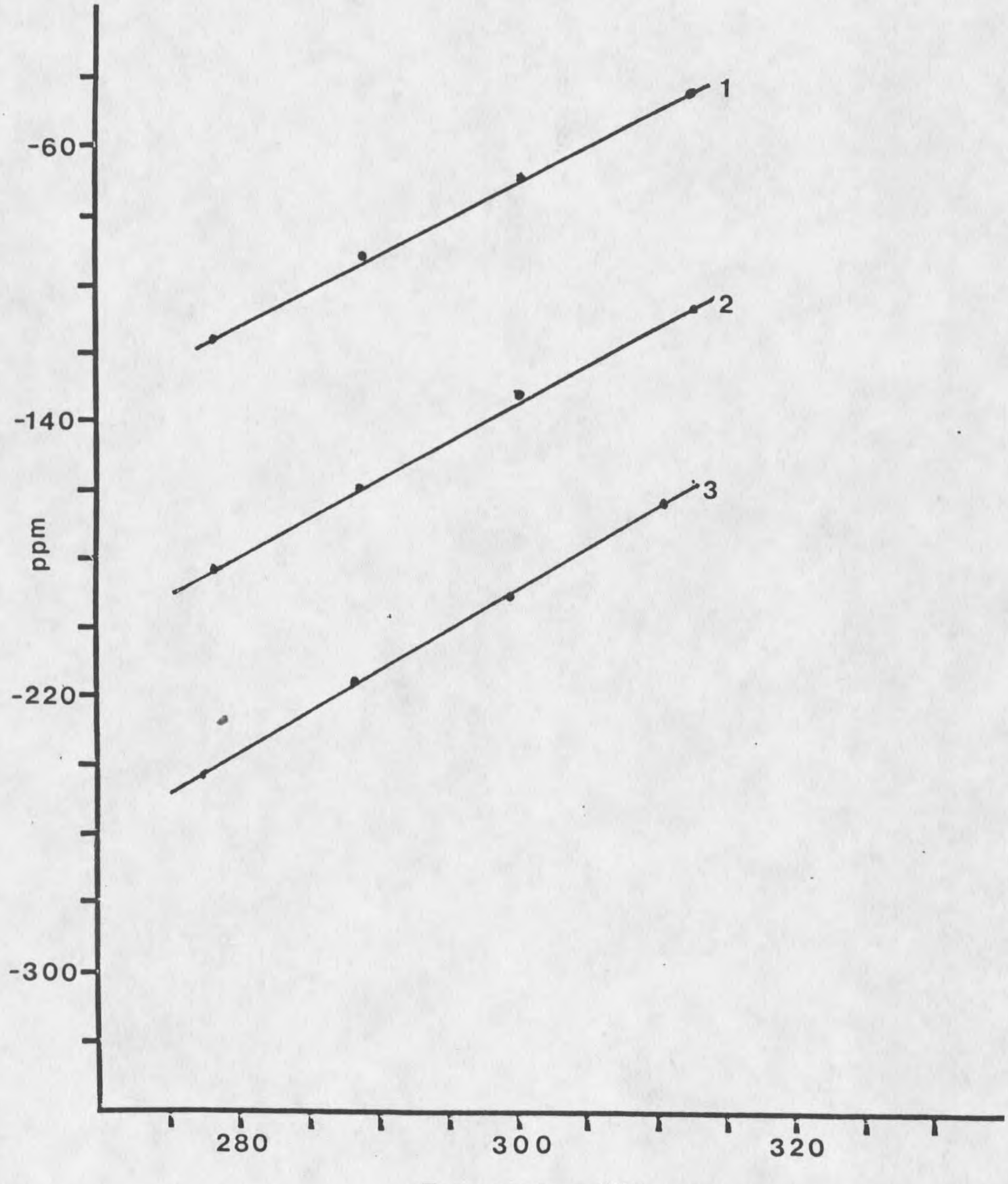

Figure 50: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I; 3) Tris I in d_6-benzene.

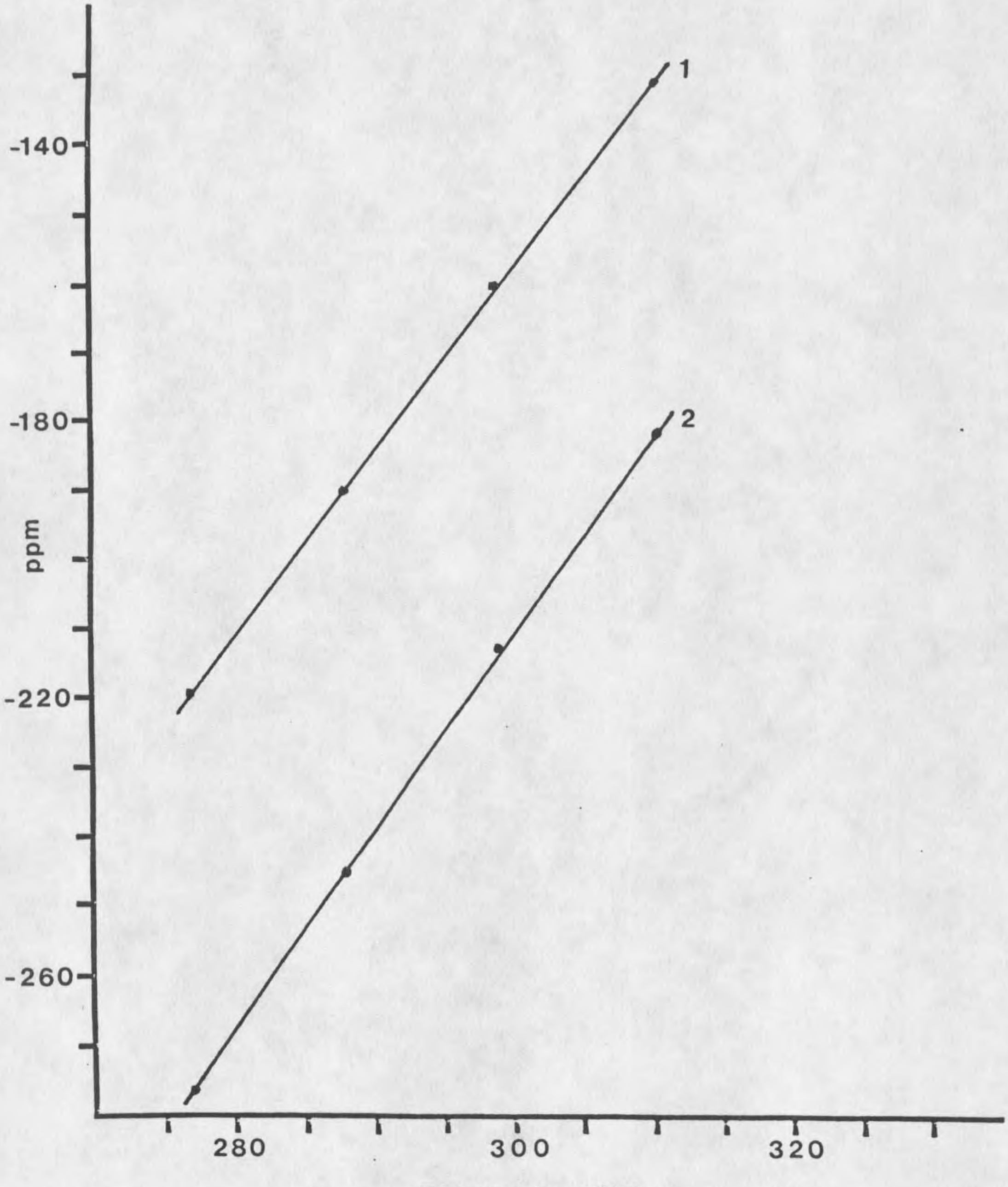

Figure 51: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I in d_1-chloroform.

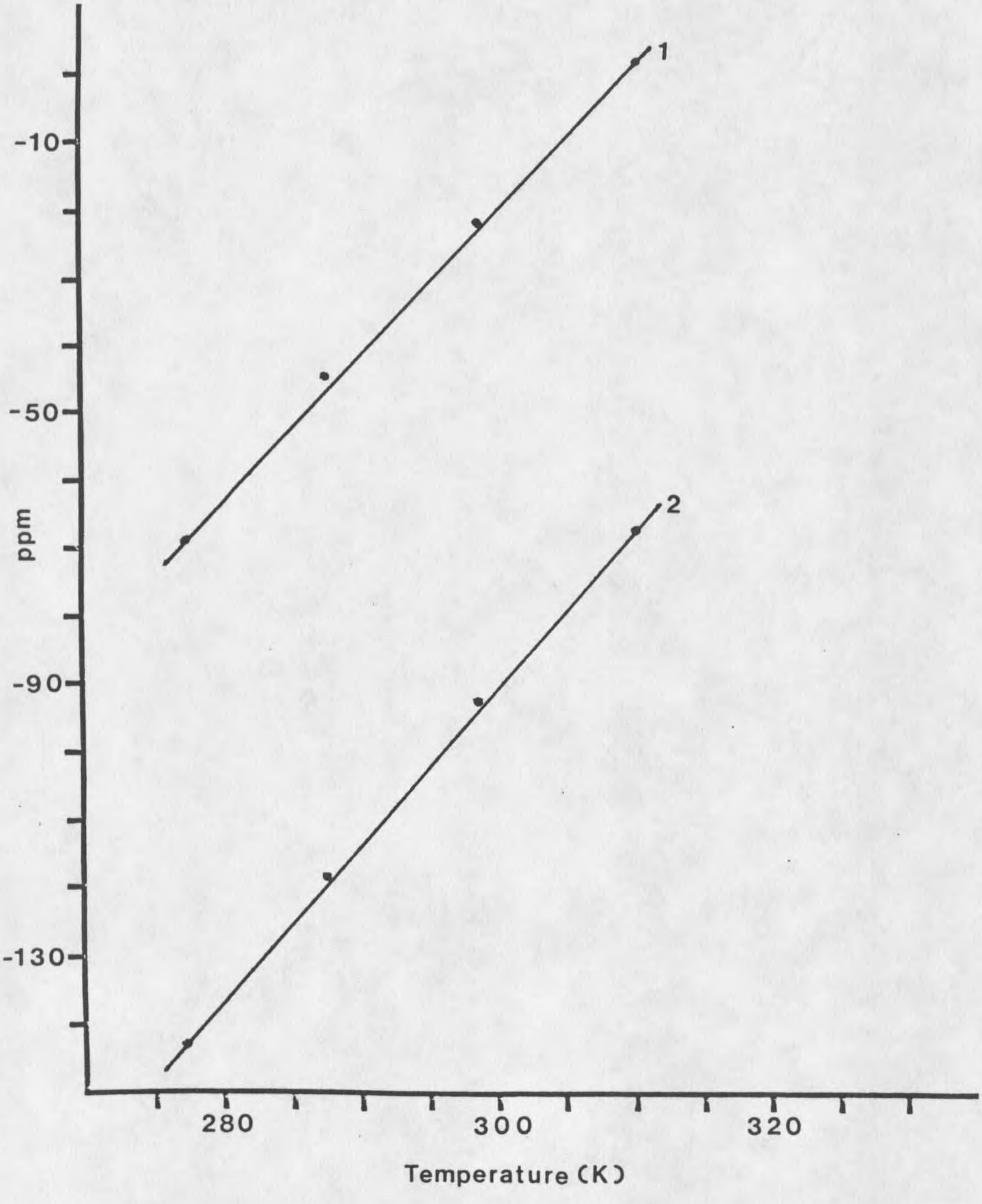

Figure 52: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I in d_6-acetone.

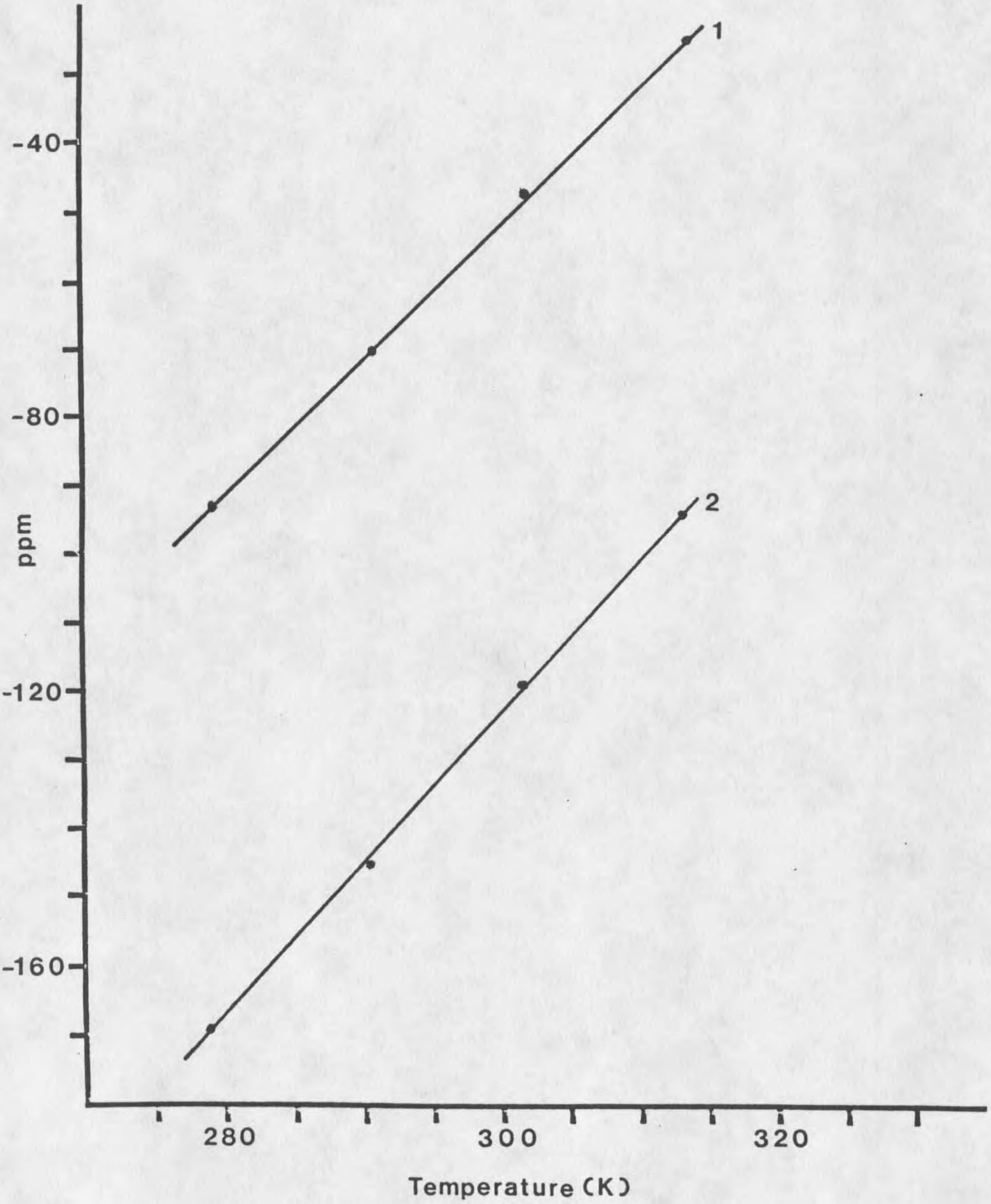

Figure 53: ^{59}Co chemical shift versus temperature of 1) Mono I; 2) Bis I in diglyme.

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