DYNAMIC, MULTINUCLEAR NMR SPECTROSCOPY
OF
TRANSITION METAL COMPLEXES

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ABSTRACT

The use of NMR spectroscopy in inorganic chemistry is growing steadily as high-field, multinuclear, sophisticated NMR spectrometers become more readily available. NMR of transition metal complexes is developing rapidly as metal nuclei as well as nuclei of ligating atoms become more popular candidates for NMR experiments. In this thesis, dynamic, multinuclear NMR spectroscopy has been carried out on various complexes of Cobalt(III) and Zn(II) as well as on free ligand molecules found in these complexes.

The second-sphere hydrogen-bonding interaction with the hexacyanocobaltate(III) anion of substituted phenols, anilines, and benzoic acids has been studied by monitoring Co-59 NMR chemical shifts and linewidths. Analysis of the chemical shifts in order to estimate equilibrium constants has been attempted. The second-sphere complex with para-nitrophenol has also been studied by measuring H-1 and C-13 T_1's. It is shown that the lifetime of the complex is longer than its rotational correlation time indicating a complex of possible mechanistic significance.

The hexanitrocobaltate(III) anion has been studied by Co-59 NMR, IR and Raman spectroscopies in the solid state and by Raman, Co-59, N-14 and O-17 NMR, and UV-vis spectroscopies in solution. A comparison of the solid-state and solution results has shown that all six ligands are N-bonded. The primary decomposition step is concluded to be aquation with a lifetime of about three minutes. A charge transfer mechanism is suggested to explain this anomalously high rate of reaction. Analysis of the Co-59 NMR chemical shifts and optical data of related compounds shows that the ligand-field stength of the nitro ligand is markedly variable. An empirical model has been developed for predicting Co-59 chemical shifts of nitro-containing complexes and for complexes containing ligands with different orbital reduction factors. Anomalies in the field dependence of the second-order quadrupole effect in the polycrystalline Co-59 NMR of sodium cobaltinitrite are discussed. The shielding anisotropy of the same compound is shown to be less than 10 ppm.

The first application of the $T_{1\rho}$ method has been made to a metal nucleus, Co-59. Scalar relaxation in cobaltinitrite and trisethylenediaminecobalt(III) has been studied using this technique. Proton $T_{1\rho}$ measurements have also been carried out to study scalar relaxation in free thiourea and in $Zn(tu)_4(ClO_4)_2$. The advantages and disadvantages of this method are discussed.

"The fear of the LORD is the beginning of wisdom"

To my darling wife, Liz

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GLOSSARY OF ABBREVIATIONS AND SYMBOLS

B_1	- spin-locking field (strength)
CE	- chemical exchange
FID	- free induction decay
FT	- Fourier Transform
Hz	- Hertz
J	- indirect coupling constant
K	- equilibrium constant
k′(k)	- orbital reduction factor (squared)
(D)NMR	- (Dynamic) Nuclear Magnetic Resonance
NOE	- Nuclear Overhauser Enhancement (Effect)
ppm	- parts per million
(I),S	- nuclear magnetic spin quantum number
S_L	- chemical shift parameter for ligand L
S/N	- signal/noise ratio
SF	- spectrometer frequency (Bruker)
SR	- spectral reference (Bruker)
SR1(2)	- scalar relaxation of the first (second) kind
SY	- synthesizer frequency (Bruker)
T	- Tesla
T_1	- spin-lattice relaxation time
$T_{1\rho}$	- relaxation time in the rotating frame
T_2	- spin-spin relaxation time

GLOSSARY (Cont'd)

UV-vis - ultraviolet-visible

α - fraction complexed

γ - gyromagnetic ratio

δ - chemical shift (ppm)

$\delta\nu$ - frequency difference (Hz)

μ_o - permeability of free space

$\nu_o(\omega_o)$ - resonant frequency in Hz (rad/s)

$\sigma(d)$ - diamagnetic shielding constant

τ_c - rotational correlation time

τ_e - exchange lifetime

Chapter 1

Introduction

1.1.1 Basic Theory of Nuclear Magnetic Resonance

In this brief opening section, some basics of NMR theory will be presented. A nucleus having non-zero nuclear spin ($I > 0$) when placed in a magnetic field, B_0 (Tesla), experiences a net torque and begins to precess about the axis (z) of the field with a characteristic frequency, ν_0, given by the formula: $\nu_0 = \gamma_0 . B_0$, where γ_0 is the gyromagnetic ratio (MHz/T) which is different for each isotope. As well, for say $I=1/2$, the $+1/2$ spins are raised in energy relative to the $-1/2$ spins so that by the Boltzmann distribution law there will be an excess of $-1/2$ spins and a net magnetic moment from all the spins will result leading to a net longitudinal magnetization along the z-axis at equilibrium. In contrast, the x-y or transverse component of the magnetization will be zero at equilibrium since there is no net phase coherence perpendicular to the field. The detection of Nuclear Magnetic Resonance is accomplished by applying a radiofrequency field, B_1. In simple terms, absorption of energy will occur when the frequency of the applied field matches the resonant frequency, ν_0, of the spins under observation. One can then calculate the chemical shift (δ) of the signal relative to a preassigned reference signal frequency (ν_{ref}):

$$\delta \text{ (ppm)} = \frac{\nu_0 - \nu_{ref}}{\nu_0} \times 10^6 \text{ ppm}$$

As well, the lineshape of the signal can yield important information. For a discussion of the types of lineshapes obtainable in solid-state spectra, see Ch. 5. In solution, in the absence of indirect spin-spin coupling, one usually obtains a single line with Lorentzian lineshape. The linewidth is equal to $(\pi T_2)^{-1}$ if inhomogeneity in the applied field is subtracted. T_2 is known as the spin-spin relaxation time and represents the time constant for the exponential decay of x-y magnetization. A similar time constant for the decay of z-magnetization back to its equilibrium value is known as the spin-lattice relaxation time, T_1.

Two basic types of NMR spectrometer have been commonly used. In the early days of NMR, the continuous wave (cw) method was usually implemented. In this type of spectrometer, a fairly small B_1 field was used and either the applied magnetic field kept constant and frequency swept through the area of resonance or vice versa. The signal was then detected in a secondary coil arranged to detect transverse magnetization. A new method was developed some time later. In this method, a strong B_1 field is applied over the space of 1 - 100 μs and then turned off. This so-called pulse of energy excites all the spins in the sample and the free precession of the resulting x-y magnetization is again detected by a receiver coil. Since a Fourier Transform is required to produce a spectrum in the frequency domain, this method is known as the FT method.

1.1.2 Historical Introduction to Some Important Concepts in Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) experiments were first carried out by two groups of physicists working independently, F. Bloch's group at Stanford (Bloch et al, 1946; Bloch, 1946) and R.V.Pound's at M.I.T. (Purcell et al, 1946). It is interesting to note that one of these experiments was carried out on solid paraffin wax and that solid state NMR of metals and alloys was already well developed by 1953 (Bloembergen and Rowland, 1953). One of the original motivations for NMR research was the determination of nuclear magnetic moments previously determined only by atomic beam measurements (Abragam, 1961). However, it was fairly quickly noticed that gyromagnetic ratios were dependent on the environment of the nucleus. The first example of such an effect was discovered by Knight (1949) who found an appreciable difference in the resonant frequencies of pure metals compared to those in ionic salts. Large shifts of a purely chemical origin were discovered independently by Proctor and Yu (1950, 1951) and by Dickinson (1950a) for several nuclei with the largest effects (almost 1%) being observed for Co-59. Chemical effects on nuclei with smaller shift ranges such as H-1 were not appreciated until the development of high resolution spectrometers in which the field inhomogeneity was reduced to a very small fraction (<1 Hz) of the total field strength. With this development, spin-spin couplings of small magnitude could also be detected. The first example of such a coupling was detected by Proctor and Yu (1951) in SbF_6 where the Sb resonance was thought to be a quintet (actually a septet).

The effect of motional narrowing on NMR spectra was soon appreciated as the temperature dependence of linewidths in liquids and solids was observed. Relaxation phenomena were described first by Bloch (Bloch, 1946; Wangsness and Bloch, 1953) who introduced the phenomenological relaxation equations incorporating as parameters T_1, the so-called spin-lattice relaxation time and T_2, the spin-spin relaxation time. A detailed theory for dipole-dipole relaxation in liquids was worked out by Bloembergen, Purcell and Pound (1948) and Kubo and Tomita (1954). Since then, elucidation of relaxation mechanisms and development of relaxation theories for many different situations has become an important component of NMR research (Spiess, 1978). Also a good deal of effort has been put into improving the accuracy of relaxation time measurements both through technological advances in improving instrument design and in developing new experimental methods. In particular, two important methods originated in the early days of NMR, namely the method of spin echoes due to E.L. Hahn (1950) and the method of forced transitory precession or measurement of relaxation in the rotating frame ($T_{1\rho}$) due to I. Solomon (1959). The former has proved of great importance in the development of two-dimensional (2D) NMR (Bax, 1982) while the latter is well known for studying slow molecular motions in the solid state (Look and Lowe, 1966). The $T_{1\rho}$ method has been used to a lesser extent in liquids, a situation which this thesis attempts to help redress.

1.2 Introduction to Dynamic NMR

One of the two principal applications of $T_{1\rho}$ in liquids has been in the study of chemical exchange. The study of this behaviour by NMR belongs to the area known as Dynamic NMR (DNMR) Spectroscopy which we will now briefly review. The best known type of DNMR is that in which chemical processes with modestly high activation barriers lead to the exchange of sites with different chemical shifts (Johnson, 1965; Binsch and Kessler, 1980). The term 'sites' here is commonly defined to be either nuclei with different chemical shifts or, if coupling exists, energy levels within the coupling pattern. The effect of a time-dependent process on an NMR spectrum is easy to understand if one considers that frequency, which is basically the crucial variable in spectroscopy, is in units of the inverse of time. To put it another way, the frequency difference of two sites in a molecule, $\delta\nu$, can only be observed if the lifetime of that state of the molecule is appreciably longer than the inverse of $\delta\nu$. Classical DNMR concerns itself with the study of spectra in which the two times are of the same order of magnitude.

The first published example of a bona fide case of DNMR was that of a study of compounds exhibiting scalar coupling (Gutowsky et al, 1953). The absence of scalar coupling in the H-1 spectrum of HF, HBF_4 and HPF_6 and in the F-19 spectrum of HF and HBF_4 led to the proposal that, although the coupling constants were likely large enough to be observable (600 Hz in HF), the presence of rapid intermolecular exchange of fluorines would lead to modulation of the coupling, rendering it unobservable. This was confirmed for HF by preparation of a rigorously anhydrous sample in which acid-catalysed exchange was effectively retarded and the H-1 - F-19 coupling was observed (Solomon and Bloembergen, 1956). A theoretical description of this effect was accomplished by a fairly straightforward modification of the Bloch equations by C.P. Slichter (1978). However, the first determination by NMR of an activation energy for a chemical exchange process was for a different type of process namely internal rotation about the C-N bond in N,N-dimethlyformamide exchanging cis and trans methyl groups (Gutowsky and Holm, 1956). We will not describe the analysis involved here since it is well-known and explained cogently in many basic treatises of NMR (see e.g. Pople et al, 1959). More detailed and thorough treatments of all aspects of DNMR may be found in a number of recent books including a highly informative treatise edited by Jackman and Cotton (1975) as well as shorter books by Kaplan and Fraenkel (1980) and by Sandström (1982). Regular reviews of DNMR studies and indeed of all aspects of NMR may be found in "Annual Reports on NMR Spectroscopy" edited by G.A. Webb (1968-), "NMR Basic Principles and Progress" (Diehl et al, 1969-), "Progress in NMR Spectroscopy" (Emsley et al, 1966-), "Nuclear Magnetic Resonance: Specialist Periodical Report" (Harris, 1971-) and "Advances in Magnetic Resonance" (Waugh, 1965-).

A far less used and less understood type of DNMR is that in which the exchange process studied occurs at a rate comparable to the rotational correlation time(s) (τ_c) of the molecule(s). In this way the spin-lattice relaxation time T_1 is affected as well as the spin-spin relaxation time T_2 and thus measurement of T_1 in particular can give rate information not obtainable from the classical DNMR method hereafter known as DNMR-I. The second type of DNMR, known now as DNMR-II, which has been reviewed recently by P. Laszlo (1979), allows the measurement of rates very much faster than by DNMR-I since the exchange lifetimes, being comparable to τ_c, can be of the order of 10^{-12} to 10^{-9} for small molecules. The reactions involved here are naturally ones with quite small activation enthalpies and involve weak second-sphere complexes of various types.

The principal application of DNMR-II has been to systems involving exchange between two sites with considerably different relaxation rates such as a small free ion or molecule moving on and off a bound site on a larger molecule such as a protein or some other biologically important macromolecule with binding sites (Sykes, 1969b). Thus typical studies have involved complexation of the omnipresent sodium ion by the ionophore antibiotic monensin (Degani, 1977) or inhibition by monosaccharides of enzymes such as lysozyme (Sykes, 1969a). However, association of two small molecules is also relatively easily detected (Hertz et al, 1976) and e.g. it has been found by Anderson (1969) that DMSO-$CHCl_3$ form a distinct complex as distinguished from a fleeting encounter better known as a collision complex (Mulliken and Orgel, 1957). The DNMR-II method of either quantitating equilibrium constants or qualitatively identifying true complexes has been shown to be far superior to other methods, such as NMR chemical shift variation (Engler and Laszlo, 1971), in evaluating complexation characteristics since the very nature of the method is such that a precise definition of a true complex is provided ipso facto. The crucial criterion to be applied here is that a bona fide complex must undergo orientation as a single discrete unit. Therefore the lifetime of the complex must at least be equal to the τ_c of the more slowly rotating partner. Of course, any definition is somewhat arbitrary but anything weaker would surely render the concept of complexation somewhat redundant. This method, which will be described in greater detail in Chapter 3, has been used in this thesis to confirm hypotheses about the lifetimes of second coordination sphere complexes of the hexacyanocobaltate(III) anion. Here Co-59 shifts were used to determine equilibrium constants for outer sphere binding but H-1 and C-13 T_1's were necessary to confirm complex formation.

1.3 The $T_{1\rho}$ method

In this thesis there is also made use of a technique which belongs in the class of DNMR-I experiments but which is not widely used. This is the use of $T_{1\rho}$ to obtain both $\delta\nu$ and τ_m in one set of experiments. $T_{1\rho}$ is the relaxation time of transverse magnetization measured in the presence of a strong radiofrequency field also known as the spin-locking field (B_1). As such it can be considered a cross between T_1 and T_2 since T_2 is measured when B_1 is relatively small while T_1 is obtained when B_1 is large. Alternatively, the method can be considered a type of field dispersion since the contributions to relaxation which make R_2 ($1/T_2$) greater than R_1 $(1/T_1)$ are dispersed to zero when the strength of B_1 becomes larger than the correlation time for the process involved. This is precisely the same effect obtained when one exceeds the extreme narrowing condition that $\omega_o^{-1} \ll \tau_C$ in which case R_1, after reaching a maximum, falls back to zero. In liquids and gases the relaxation processes dispersed by $T_{1\rho}$ are chemical exchange (CE) in the fast exchange region and scalar relaxation of the first (SR1) and second kinds (SR2) (Abragam, 1961). Scalar relaxation is so named because it is the result of a modulation of a scalar coupling to an X-nucleus. This modulation can be caused either by an intermolecular chemical exchange (SR1) or by rapid relaxation of the X-nucleus which is usually quadrupolar (SR2).

The first application of $T_{1\rho}$ measurement was accomplished by Solomon (1959b) who used it to measure the N-14 - H-1 coupling constant and T_1^N in formamide. The next application, by Meiboom (1961), was noteworthy in several respects since it involved one of the most common liquids known to man, water. True to form, the analysis turned to be rather unique for several reasons. First of all, the source of line-broadening in naturally occurring H_2O was shown to be due to the small amount of O-17 (.037%) present in the water. Furthermore, a fortuitous combination of several factors was shown to be necessary, namely the presence of quadrupolar relaxation for the O-17 nucleus which collapsed the .037% H_2(O-17) to a single line, the presence of intermediate proton exchange measurable due to the very small amount of catalysing H^+ and OH^-, and finally the whole experiment was interpretable only because of the simplification that only one of the exchanging sites was dominant precisely because of the low abundance of O-17. Strictly speaking, this is an example of scalar relaxation of both the first and second kind since scalar coupling is being modulated by chemical exchange (SR1) as well as by quadrupolar relaxation (SR2). Thus this example can hardly be considered a typical one but it has in fact spawned at least three other studies of H_2O by $T_{1\rho}$, namely the study of the temperature, pH and density dependence of the exchange lifetime and of J(H-1 - O-17) by Burnett and Zeltmann (1974), by Knispel and Pintar (1975) and by Lamb et al (1981).

The first example of the use of $T_{1\rho}$ to study chemical exchange (CE) between two distinct chemical shifts was by Deverell et al (1970) who studied chair-to-chair isomerization in cyclohexane. A few other examples involve molecules such as cis-decalin (Ohuchi et al, 1979), the tautomers of meso-tetraphenylporphine (Hennig and Limbach, 1979), ureas (Stilbs and Moseley, 1978) and benzaldehydes (Doddrell et al, 1979a). Examples of studies of scalar relaxation of the second kind (SR2) include those on nitrobenzene and pyridine(J C-13 - N-14) (Mlynarik, 1982), chlorocarbons(J C-13 – Cl-35,37) (Ohuchi et al, 1979) and on liquid HCl and HBr (Morgan and Strange, 1969). The general formula applicable for all these cases is the following:

$$\frac{1}{T_{1\rho}} = \frac{1}{T_1} + \sum_n \frac{\pi\,\tau\,\delta^2\,P_n}{1 + \omega_1{}^2\tau_c{}^2}$$

where for CE (and SR1) τ = exchange lifetime, for SR2 τ = $T_1^{\blacksquare}$; for CE $\delta = \delta\nu$, for SR2 $\delta^2 = S(S+1)(2\pi J)^2/3$; ω_1 is the strength of B_1 in rad/s and P_n is the fraction of magnetization at each site in the case of CE. Use of this formula will be illustrated in Chapter 5. Further aspects of the accuracy of $T_{1\rho}$ measurements will be discussed in the Experimental Section.

To complete this review of rotating frame experiments, we should finally mention the pioneering work of Hennig and Limbach (1979) who were the first to apply $T_{1\rho}$ measurements in the slow exchange region and have since invented a new method also applicable to slow exchange which combines the $T_{1\rho}$ method with the Forsen and Hoffman (1963, 1964; Hoffman and Forsen, 1966) magnetization transfer technique (Hennig and Limbach, 1982). Bleich and Wilde (1984) have since converted this technique into a two-dimensional (2D) experiment thus complementing the well known 2D NOE method for slow chemical exchange (Jeener et al, 1979). A still more recent extension of the $T_{1\rho}$ technique has been made by Jordan and co-workers (Chopra et al, 1984) who have used it to analyze the paramagnetic relaxation of solvent molecules by paramagnetic ions. Jordan has shown that, under the appropriate conditions, the number of molecules in the solvation shell can be determined as well as the paramagnetic chemical shift and the exchange lifetime.

1.4 Multinuclear NMR

$T_{1\rho}$ measurements have been carried out almost exclusively on common nuclei such as H-1, C-13, and P-31. This thesis reports the first example of Co-59 $T_{1\rho}$ measurements. This extension of $T_{1\rho}$ work into the so-called multinuclear field is typical of recent developments in NMR to establish facilities which vastly broaden the scope of NMR research into multinuclear NMR, solid-state and gas phase work, and any NMR experiment more complicated than a simple one-pulse acquisition (Turner, 1984). A brief description of solid-state NMR developments will be given shortly but now it would be appropriate to briefly review advances in multinuclear applications. Several monographs have recently appeared which specifically address this topic (Harris and Mann, 1978; Brevard and Granger, 1981; Laszlo, 1983). The title of one of these monographs expresses very well the aim of this type of NMR application. The title is "NMR and the Periodic Table", affectionately known as "NMR and the P.T.", and the aim then is to be able to do efficient and useful NMR research observing any nucleus in the periodic table. And in fact this is theoretically possible since all elements in the periodic table have at least one naturally occurring nuclide that is NMR active.

A variety of difficulties may arise making the practical use of some of these nuclides impossible in all but special cases. For instance, the natural abundance of the nuclide may be so low (e.g. .037% for O-17) that the signals for all but very concentrated samples will be very weak. If not prohibitively expensive, isotopic enrichment can be very profitable here. Another difficulty might be that the gyromagnetic ratio of the nucleus could be so small that the magnetization of even a concentrated sample will be very small. In this case, increasing the applied magnetic field by the use of superconducting magnets has been an important development since the magnetic moment of a sample is directly proportional to the field. A third type of difficulty lies in the relaxation properties of the nucleus under observation. To give two extreme examples, if the T_2 is too short (<1μs) or the T_1 too long (>1hr) the signal will be difficult to observe; in the former case the line will be too broad to be seen particularly on high resolution instruments designed to observe narrow lines; in the latter case the total observation time will be too long if more than a few dozen scans are required to see the signal. Because of these difficulties and others, multinuclear NMR is not a panacea designed to cure all problems but rather a useful tool to be exploited in a growing number of situations.

In this thesis, four 'heteronuclei' have been observed, namely C-13, N-14, O-17 and Co-59. Of these the first can be considered common enough that little needs to be said about it except to refer to standard texts on the subject such as those edited by Levy (1974-) and several other books with valuable compilations of chemical shifts and coupling constants (Stothers, 1972; Wehrli and Wirthlin, 1976). The subject of N-14 or its companion N-15 NMR has also been well reviewed (Witanowski et al, 1981) and the monographs of Witanowski and Webb (1973), Levy and Lichter (1979) and Martin et al (1981) in particular can be mentioned. O-17 NMR has also been reviewed recently (Kintzinger, 1981) and in any case has not been used extensively here. On the other hand, Co-59, by virtue of the compounds in which it is found, is much more a specialist's nucleus and requires a more thorough introduction. In this case, there are two good reviews of this subject, namely one in the chapter on transition metal NMR by Kidd and Goodfellow (1978) in "NMR and the P.T." and a recent overview by P. Laszlo in Vol. 2 of "NMR of Newly Accessible Nuclei" (1983b).

As mentioned at the beginning of this chapter, Co-59 is actually an old-timer in the NMR field being first observed by Proctor and Yu in 1950. The fact that Co-59 was one of the first nuclei for which the chemical shift effect was observed is quite appropriate since it has the largest chemical shift range of all nuclei, about 18,000 ppm. This nuclide also boasts the largest chemical shift temperature dependence as well as enormous solvent dependences and for that matter even huger substituent effects to use the parlance of the H-1/C-13 chemist. Ironically all these effects may be attributed to only one contribution to the chemical shift namely the paramagnetic shift arising from the low-lying T_{1g} ligand-field state corresponding to the excitation of one electron from a t_{2g} orbital to an e_g (Freeman, Murray and Richards, 1957). As such, the discussion of Co-59 chemical shifts is much simpler than for most nuclei for which a number of excited states contribute and where, if the paramagnetic contribution is fairly small, the diamagnetic one cannot be ignored either. The development of Co-59 shielding theory has seen a slow but steady evolution since the days of Proctor and Yu who were the first to suggest the source of the Cobalt shift as due to temperature-independent paramagnetism of the same type Van Vleck (1932) used to explain the residual magnetic susceptibility of some spin-paired complexes.

The equation relevant to magnetic shielding was first proposed by N.F. Ramsey (1950; 1951) and is given here as presented by Griffith et al (1957) who were the first to discuss the importance of Ramsey's equation for Co-59 shifts:

$$\sigma(\text{para}) = \frac{-e^2 \langle 0|L^2|0\rangle \langle r^{-3}\rangle}{3 m^2 c^2 E} \qquad [1.1]$$

where σ is the fraction by which the applied field is apparently shielded, e is the charge and m is the mass of the electron, c is the speed of light, E is the energy gap, $\langle r^{-3}\rangle$ refers to the distance of a 3d electron from the Cobalt nucleus, the bra and ket represent the ground electronic state and L is the angular momentum operator. Griffith and Orgel pointed out that in the strong field approximation and in O_h symmetry the only excited state that can mix in with the ground state is the T_{1g} state although this neglects the possibility of metal-ligand charge-transfer states which we will propose in Ch. 4 to also give a minor contribution to the shift. Various other modifications to this basic equation have been given including the generalization to lower symmetry (Juranic et al, 1979a), the incorporation of an orbital-reduction factor (k′) to account for covalency in the metal-ligand bond (Fujiwara et al, 1969; Betteridge and Golding, 1969) and the incorporation of a point-charge model prediction of E in the case of mixed-ligand species (Au-Yeung and Eaton, 1983). The correlation of k′ with the nephelauxetic parameter, β_{35}, has been emphasized several times by Juranic (1981, 1983, 1984) and more recently by Bramley et al (1985).

One practical application of Eq. 1.1 is the accurate determination of the magnetic moment of Co-59. This requires, among others, an accurate estimate of the diamagnetic contribution to the chemical shift which has been done in a Hartree-Fock calculation by Dickinson (1950b) who obtained $\sigma(d)$ as .00214. Then an accurate value of E must be measured from the electronic spectrum of the molecule and k′ and $\langle r^{-3} \rangle$ must be calculated theoretically. Since the latter calculation is at present rather formidable, recourse must be taken to measuring the temperature dependence of the chemical shift which when plotted against the variation of the electronic wavelength affords the product $(k')^2 . \langle r^{-3} \rangle$ from the slope and the resonating frequency of a bare Cobalt nucleus (after correcting for $\sigma(d)$) from the intercept. Alternatively, one may choose a series of compounds for which that product may be assumed to be equal and a similar plot may be made with the advantage that the extrapolation error will not be as large since relative errors in both chemical shift and wavelength will be much smaller if a larger range for both can be found. The outcome of such a study depends very much on which method and which compounds are used. Thus three of the most recent papers by Juranic (1981), by Bramley et al (1985), and by Au-Yeung and Eaton (1983) (using Fujiwara's (1969) data) all report slightly different results. The error introduced by these discrepancies is quite small considering that 200 ppm on the Co-59 chemical shift scale is essentially negligible. The inclusion by Au-Yeung and Eaton of a predictive capability using the point-charge model to simulate mixed-ligand complexes while being quite useful leads to another source of error namely the negect of inter-ligand forces. In this thesis, we discuss one type of compound where this model often works very poorly namely compounds with more than two nitrite ligands. In particular, we study hexanitrocobaltate(III) as well as some compounds formed from it by ligand exchange.

In this work, Co-59 is the most important nucleus since the coordination shifts are large, but NMR on the ligating atoms has also proved useful. In the latter case, one is typically content to simply observe a shift of reasonable magnitude upon coordination. The actual magnitude and sign of that shift is rarely easily predictable although some effort has been put into their prediction. Most theoretical studies have involved H-1 shifts in hydrides (Buckingham and Stephens, 1964) or Cobalt(III) ammines (Nakashima et al, 1975; Yoneda and Nakashima, 1974) but Juranic has shown the importance of the Cornwell-Santry effect for N-14 coordination shifts (Juranic and Lichter, 1983). Finally, just to mention some other important work on the theory of chemical shifts, Figgis et al (1962) have shown that the wavelength of the first electronic transition in simple oxy-anions correlates qualitatively at least with the O-17 shift which shows a range of over 1,000 ppm. These authors also discuss the importance of the paramagnetic shift for Co-59. Indeed, as pointed out by Ebraheem and Webb (1977) in an important article on heteronuclear shifts, the paramagnetic shift is by far the most important since the diamagnetic component usually remains relatively constant. Ab initio calculations have been carried out primarily on small molecules with varying success. We will mention only one series of articles on this subject since it represents the only attempt made on transition metals. The authors have shown inter alia that for complexes of Ag, Cd, Cu, and Zn in which the d shell is essentially filled the major contribution to the shift comes from either back-donation of electron density to the ligand producing holes in the d shell or from donation of ligand electrons to the empty metal valence p-orbital (Nakatsuji et al, 1984). On the other hand, for Mn complexes d-d excitations are by far the most important as found for Co (Kanda et al, 1984). Thus for the former set, one could say that charge-transfer transitions are important, a point we will return to later in Chapter 4.

1.5 Solid-state NMR

As mentioned previously, the area of solid-state NMR is really quite an old one but most of the work here has been carried out by solid-state physicists. Only recently with the advent of high-resolution solid-state NMR has the chemist been making substantial use of this important part of NMR (Fyfe, 1983). It is unfortunate in some ways but understandable that one of the aims of high-resolution solid-state NMR has been to produce spectra that approach those observed in the solution state with only isotropic shifts and spin-spin coupling observable. In fact with some effort a great deal more information is available from a detailed solid-state NMR study. Good reviews on this subject have been written by Wasylishen and Fyfe (1982) for chemists and Spiess (1978) has included a somewhat more rigorous introduction in his article on relaxation theory. Two recent monographs by Mehring (1976) and Haeberlen (1976) cover the subject from the solid-state physicist's point of view. A more detailed introduction to this subject is given in Chapter 5 which deals with the Co-59 NMR of polycrystalline sodium cobaltinitrite.

1.6 A Brief Summary of Coordination Chemistry

The transition metal complexes studied in this thesis can be divided into two groups: inner-sphere and outer-sphere. The first category can be further subdivided into inert or slowly exchanging and labile or rapidly exchanging. Furthermore, outer-sphere complexes can also be classified as labile complexes. Terms such as these originate from the early days of transition metal chemistry when A. Werner (1893; Morral, 1967) and his contemporaries were trying to rationalize the behaviour of certain compounds. The distinction between inner- and outer-sphere ligands was particularly important for inert complexes since it was found that the inner-sphere ligands were slow to exchange and thus presumed to be directly bonded to the metal while outer-sphere ligands being further from the metal were much more easily removed. The reason for lability of the inner-sphere of some, indeed most, metals was not as obvious although measurements of reasonably large enthalpies of formation and very small enthalpies of activation for exchange showed that lability or inertness was primarily a kinetic effect. A good rationale for the differences between the two types of complex was provided by crystal-field theory (Griffith, 1961) which showed that compounds with the largest crystal-field stabilization energies had the largest activation energies for exchange.

If we limit our discussion to Co(III) complexes, it can be shown that the imposition of a field of six ligating atoms in an octahedral disposition causes three (t_{2g}) 3d orbitals to be lowered in energy and two (e_g) to be raised. Since Co(III) has six d-electrons, these can nicely fill the bottom three orbitals and provide a large stabilization energy. Ligands which produce a large d-orbital splitting are said to exert a strong ligand-field and these form the most stable complexes. The strength of the ligand-field can be measured from the electronic spectrum arising from excitation of t_{2g} electrons to e_g orbitals (Lever, 1984). One of these excitations, labelled A_{1g}-T_{1g}, is the effective one in producing the Co-59 paramagnetic shift. The exchange lifetimes of stable molecules with relatively strong ligand fields such as hexaamminecobalt(3+) (Llewellyn et al, 1964), trisethylenediaminecobalt(3+) and hexacyanocobaltate(3-) (McDiarmid and Hall, 1954) range from a few days to so long as to be unobservable. Exchange times for other complexes particularly those with weaker field ligands such as O-bonded species or halogens exchange somewhat faster but usually in the range of several to many hours (Basolo and Pearson, 1967; Wilkins, 1974). The exceptions to this rule are few and usually involve complexes containing planar π-conjugated molecules such as salen (Tauzher et al, 1983), cobalamin (Thusius, 1971) and other macrocycles (Poon, 1973). See Table 1.1 for examples of rapid exchange rates and a comparison to Co(II) hexaaquo.

In light of the above the behaviour of Co(III) complexes containing NO_2^- as ligand is especially peculiar. Whereas molecules such as pentaamminenitrocobaltate(III), tetraamminedinitrocobaltate(III) and bis(ethylenediamine)-dinitrocobaltate(III) are extremely inert even in strong acid in the latter only (Wilkins, 1974), hexanitrocobaltate(III) exchanges with free NO_2^- in a matter of

Table 1.1

Exchange rates for Co(II) and Co(III) complexes (a)

complex	k(ex), s^{-1}	T, (°C)
$Co(H_2O)_6^{2+}$	1.10 $\times10^{6}$	25
trans-$Co(NH_3)_4SO_3(H_2O)^{+}$	1.34 $\times10^{1}$	25
$Co(HP)(H_2O)_2^{3+}$	1.70 $\times10^{1}$	25
$[Co(salen)_2O_2(H_2O)]_2$	2.00 $\times10^{-1}$	24
$Co(CN)_5(H_2O)^{2-}$	1.00 $\times10^{-3}$	40
$Co(NH_3)_5(H_2O)^{3+}$	6.00 $\times10^{-6}$	25

(a) data from Au-Yeung and Eaton (1984) and references therein minutes (Matsko, 1967) and molecules with more than three NO_2's are apparently quite unstable since few have been observed. Furthermore analysis of the spectra of the above molecules with one or two nitro ligands as well as other hexanitro metal complexes show nitrite to be a strong-field ligand second only to cyanide (Caulton and Fenske, 1967) whereas the ligand-field strength of nitrite in hexanitrocobaltate(III), while admittedly in dispute, is certainly quite a bit weaker. This was one of the factors prompting our study of this compound. See Chapter 4 for a more thorough discussion.

Surveying the entire field of coordination chemistry, we find relatively few examples of non-additive ligand fields or to put it differently such a large interligand interaction. Most of these cases refer to kinetic cis- and trans-effects which have been best documented for Pt(II) and Pd(II) (Quagliano and Schubert, 1952; Zumdahl and Drago, 1968). Similar effects in Co(III) are much more dubious in nature (Pearson and Basolo, 1956; Miyoshi et al, 1983). Some interesting references to non-additivity may be found in the literature including discussions of various kinds (Drago, 1968; Glerup et al, 1976). Nevertheless Jorgensen's rule of additivity (1962, 1969) remains an important predictive tool in mixed-ligand coordination chemistry.

In the case of outer-sphere complexes, the interactions are very much weaker but significant enough to affect rates of reactions and the rate of molecular tumbling which is of importance in NMR and dielectric relaxation. Important reviews in this field include that of J. Bjerrum (1967) and that of M.T. Beck (1968) who discussed the importance of second-sphere complexes for reaction mechanisms. A treatment of outer-sphere interactions with neutral metal complexes has appeared recently (Nekipelov and Zamarev, 1985). Important advances have also been made in the treatment of solvation by Gutmann (1978) who has defined donor-acceptor numbers which allow one to determine the average number of solvent molecules attached to a solute molecule. Since hydrogen-bonding is often involved here, one should mention the important monograph of Pimentel and McLellan (1960) who treat the subject in great detail. NMR relaxation studies relevant to this general area have been discussed by Hertz (1967) who likes to refer to the microdynamic structure of liquids, by R.G. Bryant (1978) on solute-solvent interactions and by P. Laszlo as mentioned previously.

Chapter 2

Experimental Section

2.1 Experimental Aspects of FT NMR

The primary instrumental technique used in this thesis was Nuclear Magnetic Resonance Spectroscopy. This section will outline some practical details of the NMR experiments carried out in this work. All the results reported here were obtained using Fourier Transform NMR spectrometers. Several good monographs are available discussing various practical aspects of FT NMR. Before we mention these, we should recognize the contribution of Ernst and Anderson (1966) who introduced the FT technique to magnetic resonance. A few years later, Farrar and Becker (1971) outlined the rudiments of FT NMR in a book that still offers an excellent introduction to the senior undergraduate or beginning graduate student. More recently Martin, Delpeuch and Martin (1980) have written a rather comprehensive and well organized book on the practical aspects of NMR dealing with both FT and continuous wave methods. Also Brevard and Granger (1981) give valuable advice on multinuclear methods and a book on the 'nuts and bolts' of NMR (Fukushima and Roeder, 1981) treats one to a varied menu of technical information.

In a FT NMR experiment, a strong, short radiofrequency pulse is applied to the sample at a frequency close to the resonance frequencies of the nuclei. Then the receiver is opened and the resulting free induction decay (FID) is collected. If multiple scans are required, a waiting period of 5xT_1 is required if a 90-degree pulse width has been used and accurate intensities are required. The total acquisition time is also determined by the sweep width and the resolution required (Hz/pt).

Measurement of T_1 can be done in various ways, the simplest and most popular of which is the inversion-recovery method (Levy and Peat, 1975; Martin, Delpeuch and Martin, 1980). In this method, which is the only one used in this thesis, a 180 degree pulse is applied to invert the equilibrium z-axis magnetization. Then a variable delay time, τ, is introduced after which the magnetization is sampled usually with a 90 degree pulse. An analysis of the intensity vs. time data yields a value of T_1 either by a three-parameter fit where the three parameters are T_1, M_o, the magnetization at τ=0, and M_∞ or by a straight-line fit where M_∞ is first estimated. In the latter stages of this work, T_1's were calculated directly after data acquisition using the Bruker T_1 calculation routine. T_2 measurements were made using either the unmodified Hahn spin-echo method (Hahn, 1950) or the method of half-widths. In the latter case instrumental inhomogeneity, if appreciable, was estimated from other peaks in the spectrum. As suggested by Rabenstein and Nakashima (1979), the Hahn spin-echo method was also used in Chapter 6 as a T_2-sorting multiple-pulse technique (SEFT) to clearly distinguish the N-15 satellites of thiourea from the much more intense and much broader N-14-coupled peak.

Error estimates for T_1 were calculated from the least-squares covariance matrix (Leipert and Marquardt, 1976). In those cases where more than one T_1 was measured on the same sample, the error was taken to be the larger of the least-squares error and the deviation between the two measurements. The errors in T_1 only affect the conclusions of Ch. 3 where a very large uncertainty in T_1 values would obviously make any conclusions meaningless. The errors in the T_1 values of Ch. 5 have only a minor effect on the resulting calculations based on the $T_{1\rho}$ results since most $1/T_1$ values were much smaller than $1/T_{1\rho}$. Generally speaking, unless stated otherwise, the errors in T_1 and T_2 are estimated to be 10%. It should be noted here that errors due to incorrect pulse lengths or B_1 inhomogeneity which result in the creation of some x-y magnetization after the 180 degree pulse can be eliminated with a simple 180° phase shift in B_1 on alternate scans (Pegg et al, 1976). Errors in $T_{1\rho}$ values were not usually calculated but most of the H-1 experiments gave almost perfect exponential decays as could be observed using the Bruker T_2 routine. The results for Co-59 $T_{1\rho}$'s were much poorer and the error may be estimated as at least 10%. The covariance error estimates were calculated using one of two BASIC programs implemented on an Osborne microcomputer. The code for these programs, GRAPTECH and RLENKT1, is reproduced in Appendix 1. The first was written by the author and is based on a method of Draper and Smith (1981). The author is grateful to R. Lenkinski for giving permission to use the second program which iterates from initial estimates and is based on a routine derived by J.C. MacDonald (1980).

The NMR spectrometers (all Bruker manufactured) used in this work are tabulated below along with the nuclei run, the type of experiment for each nucleus, the magnetic field, and the ambient temperature. All except the first two spectrometers have superconducting magnets so the D-2 lock was not used except for variable temperature (V.T.) work. An advantage of this was that deuterated solvents were not required. V.T. work was carried out only on the WM-250. Errors in temperatures are not expected to exceed ± 1K.

Chemical shift references used were TMS (H-1), aqueous 1M potassium cobalticyanide (Co-59), the nitrate resonance in saturated aqueous ammonium nitrate (N-14) and distilled water at neutral pH (O-17). In all cases, the currently approved sign convention in which high frequency

Table 2.1

Description of NMR spectrometers

Spectrometer	Nuclei	Experiment	Field (Tesla)	Ambient Temp. (K)
WP-80	H-1, C-13	T_1	1.879	303
WH-90	Co-59	liquid (*)	2.114	300
CXP-200	N-14 Co-59	liquid, T_1 liquid, T_1, solid, $T_{1\rho}$	4.698	293
WM-250	H-1 N-14, O-17 Co-59	$T_{1\rho}$ liquid liquid, solid	5.874	294
AM-300	Co-59	solid	7.047	294
WM-400	Co-59 O-17	liquid, solid liquid	9.396	294
AM-500	Co-59	solid	11.744	294

(*) refers to routine spectra run in the liquid state is positive is used (IUPAC, 1976). Except where internal secondary references were available (e.g. acetone-d^6 for H-1) external references were always used. Except for H-1, the errors in chemical shift due to field drift, diamagnetic susceptibility effects or temperature variation are virtually negligible considering the large chemical shift ranges encoutered here. In particular, relative chemical shifts in a given spectrum can be considered accurate to 1-2 ppm even for broad lines with a maximum error of 10% of the line-width. It should be noted that for Co-59 particularly, care must be taken to use the correct spectral frequency (SF) when calculating chemical shifts. This can be a problem when SY is changed on instruments such as the WM-250 or the WH-400 since SF will change also to an incorrect value. A simple correction is to change the original SR value (Hz) to the new value, SR', appropriate to the new SY' (MHz) by the use of the formula:

$$SR' = SR + A \times (SY' - SY) \times 10^6$$

where A=2 (WM-250) or 4 (WH-400).

The use of high-resolution instruments to do broad-line NMR creates several problems which limit the usefulness of multinuclear NMR on such instruments. One of the problems is that the 90 degree pulse widths particularly for low-gamma nuclei such as N-14 and O-17 can be as long as 100 µs or more with the result that very broad lines with

$T_2 < 200$ μs are virtually unobservable due to relaxation during the pulse. To make matters worse, acoustic ringing can take away another 100 μs or so from the FID causing further intensity loss. Another problem with long pulses is that the effective excitation width decreases with increasing pulse width which may necessitate scanning spectral areas as small as 30 kHz at a time to even see the signals and also obtain accurate intensities. This latter problem especially hurts because it really inhibits the use of pulse sequences requiring 180 degree pulses (Patt, 1982) designed to reduce acoustic ringing. Acoustic ringing and pulse breakthrough combine to produce irregularly rolling baselines which render broad lines difficult to observe and especially create havoc with linewidth measurements. Especially when several lines overlap, phasing of the spectrum becomes very difficult (Canet et al, 1976) and line-fitting requires some inspired guesswork as to which way the baseline curves beneath the signals. On top of that, one usually has to cope with a distortion of the signal which worsens as the linewidth increases. This distortion, which results in spectra such as that shown in Figure 2.1, is caused by the response of the Butterworth filters to the actual signal itself as shown by Hoult et al (1983). Unfortunately this effect is quite difficult to eliminate and can only be done at the cost of S/N.

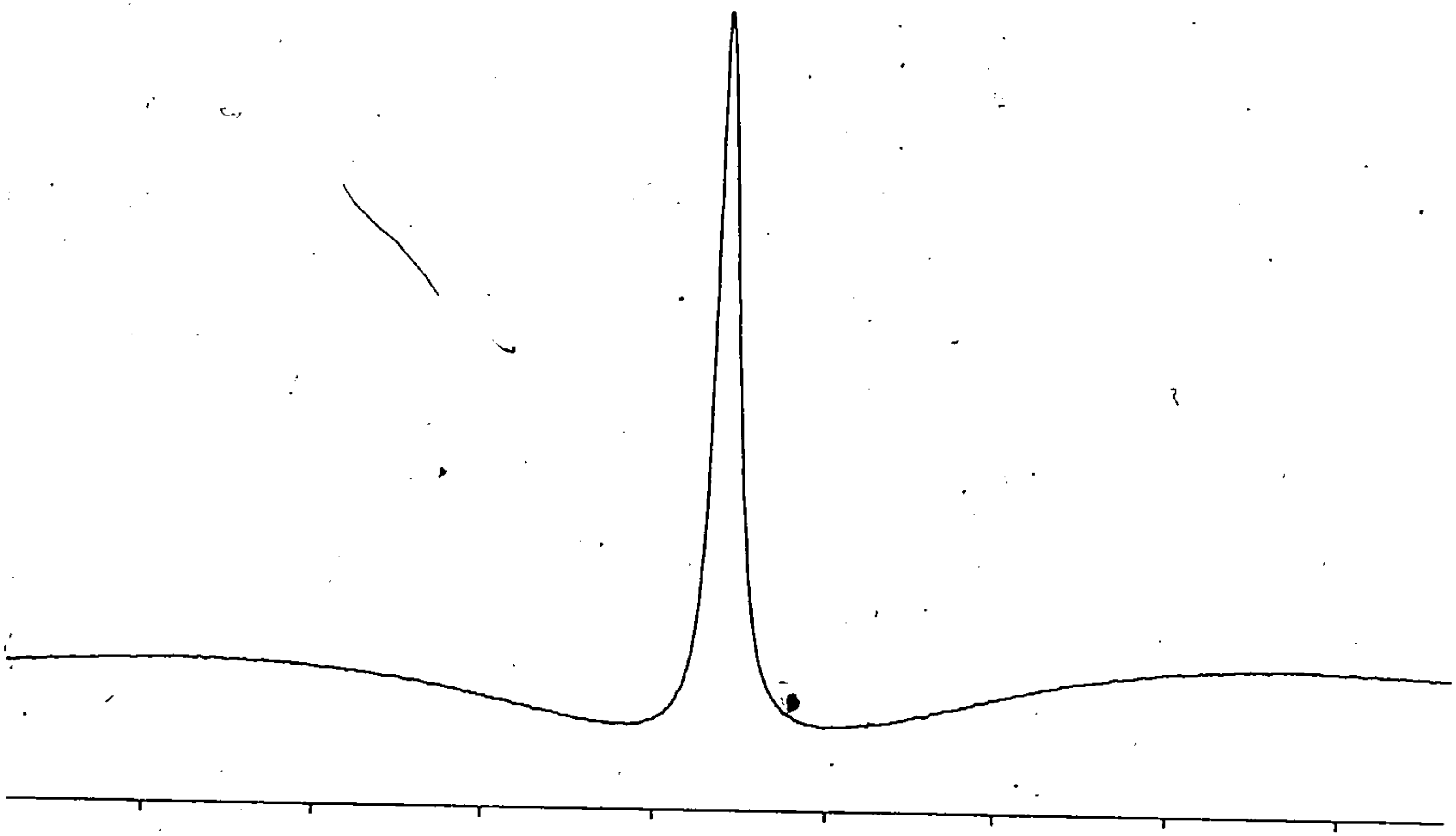

Figure 2.1 WM-250 Co-59 NMR spectrum of trans-Co(en)$_2$(NO$_2$)$_2$ illustrating the spectral distortion caused by Butterworth Filters. Scale markers are spaced 10 kHz. 800 transients, 100 kHz sweep width.

In this thesis attempts to improve on the quality of some spectra to allow a more quantitative analysis have been sacrificed in favor of making use of instrument time to run as many spectra as possible. In any case, we have bypassed the worst situations by taking advantage of isotopic enrichment to obtain excellent O-17 spectra with very high S/N (729 for 8 scans on the original 18% enriched H_2O sample) allowing easy observation of coordinated water (about 0.1M). For the N-14 measurements on cobaltinitrite samples, use of the CXP-200 spectrometer was a definite asset because of the greatly reduced rolling baseline problems and much shorter pulse widths (5 - 10 µs even for N-14). Also sweep widths of up to 200 kHz could be used which was a definite boon for Co-59 spectra with signals covering a few thousand ppm since a pulse width of 5 µs just about covers that range and the problem of signals folding in from outside the sweep range is also reduced. With such large sweep widths very rapid scanning is also possible if quantitative information on relatively narrow lines is not important and zero-filling helps to reduce errors in chemical shifts and linewidths. Quantitative measurements on narrow lines are also improved considerably by exponential multiplication of the order of the linewidth which not only improves the S/N but also improves spectral definition.

2.2 Some Details on the $T_{1\rho}$ Experiment

Since the $T_{1\rho}$ experiment is not routinely run on commercial instruments, we will now give some details on its operation. The CXP-200 instrument is best equipped for this type of experiment since the broad-band transmittter power is directly attenuable from the console. This means that $T_{1\rho}$'s can be run on any nucleus observable on this instrument. For H-1 the high-power decoupler was used to provide the variable strength spin-locking field. Since the attentuation available directly on the decoupler unit was limited to about 10dB, additional attentuation was attained by manually inserting into the decoupler line a variable attentuator with settings ranging from 3dB to 100dB. Excessive sample heating was not found to be a problem if spin-locking times were kept below 2 s and if 30 s cooling time was allowed between experiments. On the WM-250 cooling air was also passed over the sample. On this instrument the spin-locking field was applied through the decoupler channel with the decoupler and receiver leads on the computer connected together to ensure a constant phase relationship between the two. Except for a few Co-59 runs, all measurements on both instruments were taken with one scan to reduce instrument time. The decoupler power was measured by finding the 180 degree null or averaging the results obtained from a 180 degree null with that from a 360 degree null. Other methods of calibrating the spin-locking field were not used extensively since they required substantially more time and effort. Setting up the $T_{1\rho}$ experiment on the CXP-200 is fairly straightforward since the pulse program required is described in the instrument manual. $T_{1\rho}$'s on the WM-250 were run with the following microprogram:

```
1. ZE             ; erase memory
2. D1 D0          ; wait 5xT1, turn decoupler on
3. P1:D B1        ; 90° pulse from decoupler along +x
4. D2             ; delay time 1-2 ms for phase
                     switching
5. VD HG B0       ; 90° phase shift, turn on decoupler
                     for variable time, τ
6. GO= 2 A0       ; open receiver and cycle back to 2.
                     NS times
7. WR #1          ; store data
8. IF #1
9. IN= 1          ; cycle back to 1. NE times
```

$T_{1\rho}$'s were either calculated with a log(I) vs. time plot or mostly using the Bruker T_2 calculation routine on the instrument.

2.3 Miscellaneous

Other instruments used in this thesis play a role only in Chapter 4. Here some fairly important UV-vis results could be obtained on a Tracor-Northern 6050 instrument which, thanks to a diode detector array, allows full spectral scanning as fast as once per second. The spectra of Figure 4.1 were obtained on this instrument.

IR spectra were run on KBr discs using a Perkin-Elmer 283 instrument calibrated with polystyrene. Raman spectra were obtained using a Spex 14018 spectrometer equipped with a He-Ne laser and the calibrant was CCl_4. pH measurements were made using a Radiometer PHM82 pH meter and are uncorrected for ionic strength.

The phenols used in Chapter 3 were of analytical purity and were used without further purification. The solubility of $K_3Co(CN)_6$ (BDH) in DMSO was enhanced by the addition of cyclohexyl-18-crown-6 ether (Parish). Deuterated DMSO (99.5% D) was used as purchased from Stohler in 5 gram quantities. Dissolution of cobalticyanide in DMSO containing crown ether was quite slow and required several hours stirring in a small flask covered with paraffin. Molecular sieves (Fisher, 8 - 12 mesh) were added to the solutions if they contained an appreciable amount of water. Deuterated acetone (Stohler, 99.7% D) used in Ch. 5 was purchased in 1 gram sealed ampoules. The amount of water in the sealed ampoules is very small indeed and by thoroughly drying all materials before usage the amount of water in most samples could be kept to a minimum. Since most of the T_1's and $T_{1\rho}$'s measured were less than 2s, no attempt was made to remove O_2 from the solutions. Since the contribution to relaxation by the paramagnetic O_2 is quite small this should not result in significantly large errors.

$Na_3Co(NO_2)_6$ was used as purchased from Fisher (reagent grade). All studies in aqueous solution were carried out in distilled H_2O. The use of buffers to control the pH of solutions was not attempted since most simple buffers have the capacity to coordinate to Cobalt(III). Except where indicated the pH of aqueous solutions was unadjusted so that solutions of cobaltinitrite with excess cyanide or ethylendiamine were strongly basic. On the other hand, aqueous solutions of cobaltinitrite typically reached pH values of 4.3 - 4.5 within half an hour. The synthetic procedure for trans-$Co(NH_3)_4(NO_2)_2$ was taken from Inorganic Synthesis (Kauffman et al, 1978) and the mother liquor used to obtain the Co-59 NMR spectrum in Figure 4.7 was used several days after the synthesis without adjusting the pH. 1 gram of water enriched to 18.2% in O-17 was purchased from MSD Isotopes. Thiourea (Baker Analyzed Reagent) was used unpurified while the Zn complexes were synthesized in a previous study in this lab (Eaton, Majid and Tong, 1982).

Chapter 3

Outer-sphere complexes of the cobalticyanide anion with phenols, anilines and benzoic acids

3.1 Introduction

The interaction of potassium cobalticyanide with molecules capable of hydrogen-bonding has been the subject of several recent studies in this laboratory (Eaton, Rogerson and Sandercock, 1982; Eaton and Sandercock, 1982; Eaton, Buist and Rogerson, 1983). The primary probe used was Co-59 NMR which in a very sensitive manner shows evidence of interaction through easily measured chemical shift and linewidth changes. Similar studies have been carried out by Laszlo and co-workers (Laszlo and Stockis, 1980; Delville et al, 1981; Laszlo, 1983b). Analysis of chemical shift and linewidth data can lead to valuable information on the thermodynamics and kinetics of second-sphere coordination. Furthermore DNMR-II measurements of the type described in Chapter 1 have been used to confirm hypotheses about the lifetime of p-NO_2-phenol in the second coordination sphere. The importance of the second coordination sphere in transition metal complexes has been reviewed in Ch. 1.

The work described in this chapter was carried out in DMSO since this aprotic molecule should have only very weak interactions with the H-bond-accepting cobalticyanide ion. In fact, the potassium salt is sparingly soluble in DMSO as one might expect. However, concentrations of 0.05M in $Co(CN)_6^{3-}$ could be attained by addition of at least 0.15M of 18-cyclohexyl-crown-6 ether which binds strongly to the K^+ ion in a 1:1 complex which is moderately soluble in DMSO (Pedersen, 1967). In a previous study, Eaton, Rogerson and Sandercock (1983) have shown that the Co-59 shift of cobalticyanide is unaffected by the presence of the crown ether. The object of the present work, then, was to study the behaviour of weak to moderate strength H-donors which were soluble enough in DMSO to allow the preparation of solutions with a large excess of second-sphere ligand. The molecules used were a series of substituted phenols, anilines and benzoic acids. The complete set of data of Co-59 chemical shifts and linewidths measured for a series of concentrations is given in Appendix 2.

3.2 Results and Discussion

3.2.1 Studies of phenol coordination

To begin with, the results obtained for the phenols with the use of Co-59 NMR will be discussed. In all, ten substituted phenols have been examined with substituents ranging from the electron-withdrawing nitro group to the electron-donating amino and methoxy groups. In all cases shifts to high field are observed with values at the highest phenol concentrations as high as 120-130 ppm. As Eaton, Rogerson and Sandercock (1982) have pointed out in their discussion of the effect of hydrogen bonding on the Co-59 chemical shift of cobalticyanide, the direction of these shifts is consistent with the formation of a hydrogen bond between the phenolic proton and the cyanide nitrogen. Dramatic increases in linewidth of up to more than 1 kHz are also observed. A likely origin for this effect will be discussed later. The limiting Co-59 chemical shifts and linewidths are shown in Table 3.1 along with the calculated apparent equilibrium constants for second-sphere complexation. The calculation of equilibrium constants and the limiting shifts is based on the simplest possible model of a 1:1 complex between the phenol and the cobalticyanide. It can be shown that the concentration of free phenol (P) and the observed chemical shift ($\delta\nu$) are related by the equation:

$$\frac{P}{\delta\nu} = \frac{1}{K\delta\kappa} + \frac{P}{\delta\nu_{\infty}} \qquad [3.1]$$

where K is the association constant and $\delta\nu_{\infty}$ is the chemical shift of the hydrogen-bonded adduct. Computerized fitting of the data to this equation by an iterative method was carried out on an Osborne microcomputer with the result that

Table 3.1

Equilibrium constants, chemical shifts and linewidths of second sphere complexes with phenols

Substituent	K_{eff}	$\delta\nu_{c}$ (ppm)	Correlation Coefficient	Linewidth (Hz)
p-NO_2	2.726	164	0.990	2408
H	0.584	168	0.998	2453
m-NO_2	1.252	159	0.999	2331
p-NH_2	0.231	228	0.962	3327
m-NH_2	1.208	126	0.999	1841
p-F	0.970	167	0.999	2441
p-CN	2.176	163	0.999	2385
p-OCH_3	0.596	181	0.996	2648
p-C_6H_5	1.014	155	0.994	2273
p-COOH	1.626	145	0.980	2129

excellent fits were obtained yielding correlation coefficients in the range 0.962 - 0.999. The degree of association of the cobalticyanide for a given concentration of phenol is readily obtained as $\delta\nu/\delta\nu_{-}$. Plots of this function versus the observed linewidth are also satisfactorily linear as shown in Figure 3.1 and yield the linewidth values in Table 3.1.

The above analysis neglects, of course, the possibility of complexes being formed with stoichiometries higher than 1:1. Although one might expect the H-bonds of successive ligands to become weaker as the electron-acceptability of the cobalticyanide decreases due to increasing charge-transfer, one cannot exclude the possibility of 2:1 or 3:1 complexes with successive association constants approximately equal or slightly less than the first. Kitaigorodski et al (1979) have derived suitable expressions which allow for these other equilibria. We have carried out calculations in the case where two molecules are complexed. If the equilibrium constants for successive degrees of association are similar then one cannot distinguish with our data between a 1:1 complex and a 2:1 complex. This agrees with the findings of Kitaigorodski et al. Nevertheless, even if this is true one might expect such behaviour to be similar for all the members of this particular series and thus the calculated effective K's provide a reasonably accurate measure of the

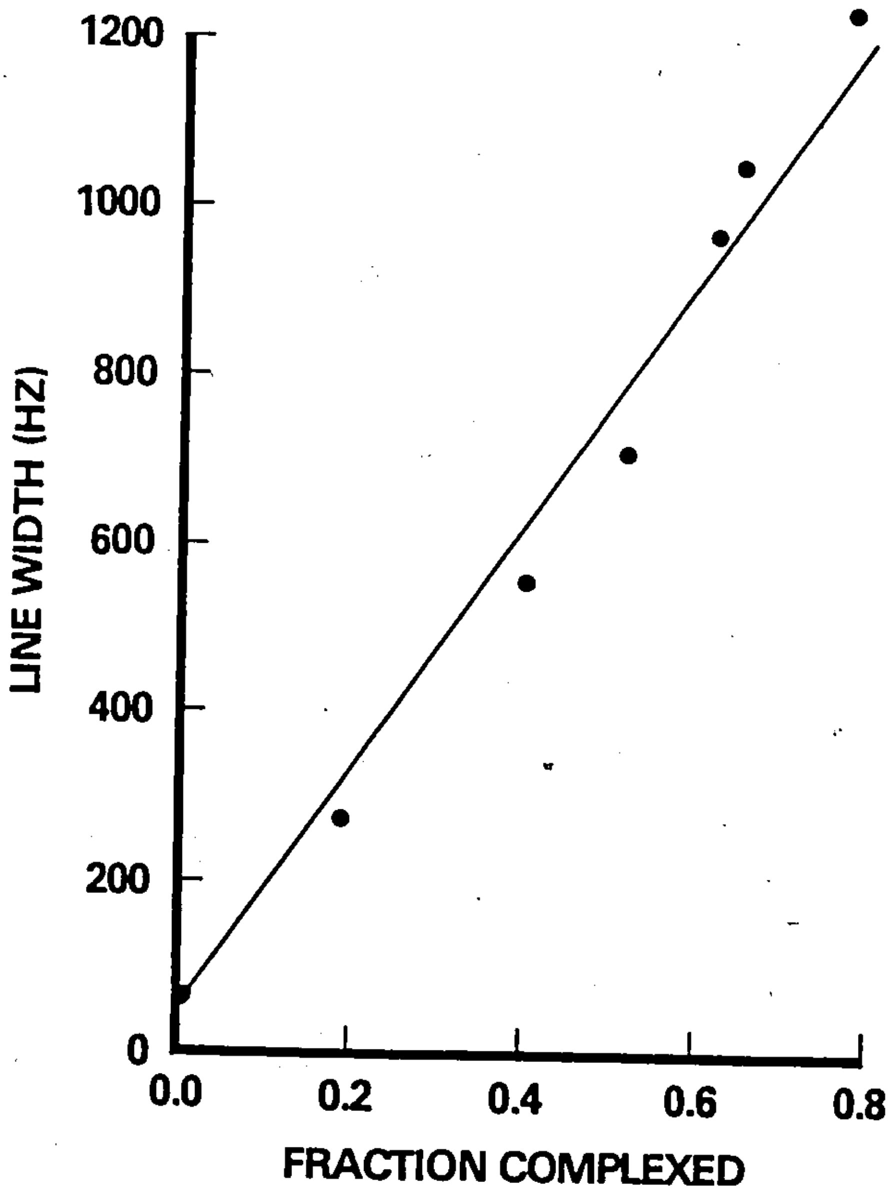

Figure 3.1 Variation of linewidth with degree of association for para-nitrophenol.

relative stability of the second-sphere complexes. In fact, Kitaigorodskii et al have shown, in the same paper, that the values of K_{eff} obtained by neglecting complexes of higher stoichiometry are only slightly less than the values of the true equilibrium constant. Thus the absolute errors in the calculated limiting linewidths and chemical shifts due to this assumption should also be small.

It is interesting to note that, with the exception of the two amino phenols, the chemical shift and linewidth are almost independent of substituent although the K_{eff}'s vary by over a factor of five. The amino phenols can H-bond either through the hydroxyl or the amino group and this is the most likely explanation for their anomalous behaviour. The apparent equilibrium constants of the others correlate well with electron-withdrawing ability as measured by pKa and by Hammett and other substituent parameters. Fig. 3.2 shows a plot of log(K_{eff}) vs. H-1 hydroxyl chemical shifts. This plot is reasonably linear as might be expected from the work of Eyman and Drago (1966) who have related the proton shifts to hydrogen bond strengths. Fujio et al (1975) have used these shifts to derive substituent parameters and have discussed their relationship to the electronic structure of the phenols.

Although the magnitude of the shifts and linewidths shows there is a definite interaction, the small size of the equilibrium constants has to make one wary about concluding

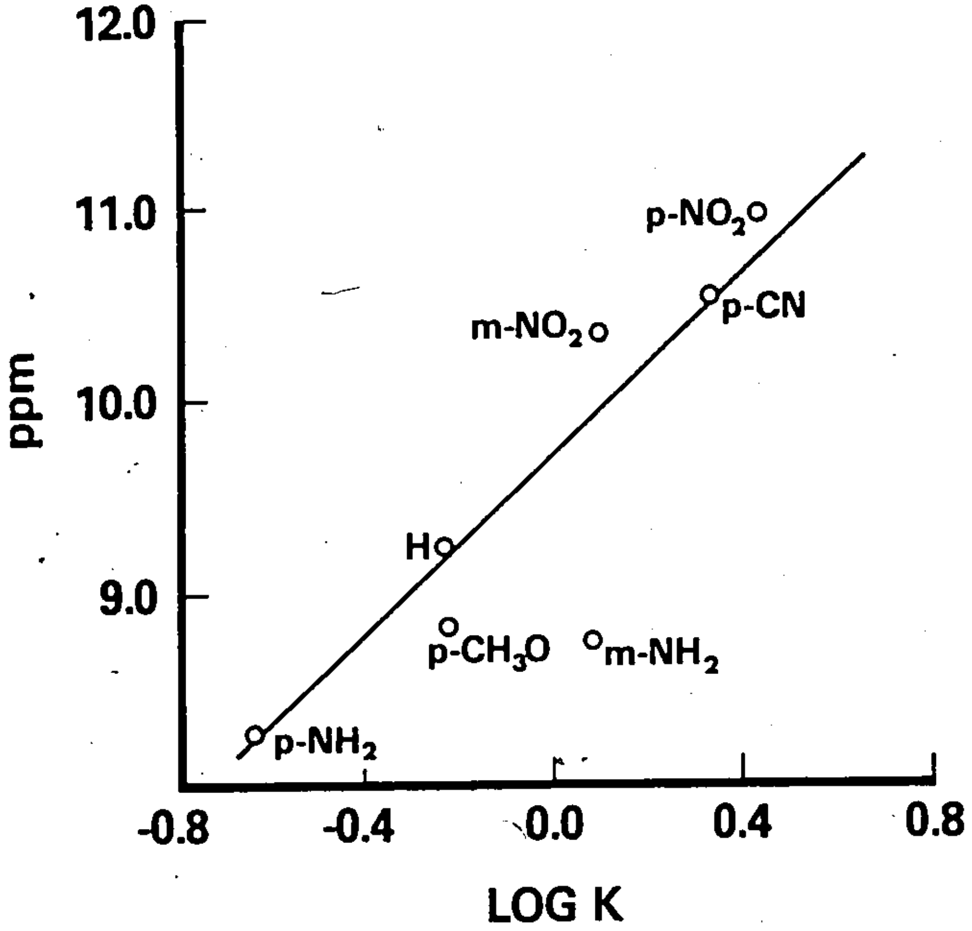

Figure 3.2 log K(-++) vs. proton hydroxyl chemical shifts.

that a true complex as defined in Chapter 1 is being formed here. To confirm that, C-13 and H-1 T_1 measurements were carried out on one of the phenols (p-nitro) and analyzed by the method of Anderson and Fryer (1969) for the case of dipolar relaxation in the extreme narrowing condition. These authors have shown that if the two interacting molecules are rotating as a unit then, when rapid exchange with free phenol is also taking place such that only one peak is observed, the T_1 of that peak is obtained by taking the weighted average of the relaxation rates as per Equation 3.2:

$$\frac{1}{T_1} = \frac{P_c}{T_{1c}} + \frac{P_f}{T_{1f}} \qquad [3.2]$$

where P_c refers to the fraction complexed and P_f to the fraction free. On the other hand, if the lifetime of the complex is shorter than the largest rotational correlation time, then a similar equation [3.3] is obtained except that the relaxation times are averaged:

$$T_1 = P_f.T_{1f} + P_c.T_{1c}. \qquad [3.3]$$

For intermediate cases a complex equation is necessary. Tables 3.2 and 3.3 show the T_1 results obtained for H-1 and for C-13 respectively. It is apparent that the T_1's are not only dependent on the presence of cobalticyanide but also

Table 3.2

Proton spin-lattice relaxation times of p-nitrophenol.

PNO_2phenol (M)	Crown ether (M)	KCl (M)	$K_3Co(CN)_6$ (M)	T1(s)	
				7.7ppm	6.6ppm
0.044	--	--	--	3.37	2.53
0.538	--	--	--	2.71	1.58
1.37	--	--	--	2.02	1.13
2.00	--	--	--	1.79	1.07
0.050	0.229	0.15	--	2.99	2.15
0.462	0.164	0.15	--	3.26	2.28
1.32	0.145	0.13	--	1.15	0.63
2.23	0.168	0.00	--	1.43	0.74
0.047	0.167	--	0.060	1.96	1.00
0.470	0.163	--	0.050	2.42	1.57
1.27	0.124	--	0.041	1.84	1.38
2.19	0.165	--	0.050	0.67	0.38

Table 3.3

C-13 spin-lattice relaxation times of p-nitrophenol

Crown ether (M)	KCl (M)	$K_3Co(CN)_6$ (M)	PNO_2phenol (M)	T1(s)	
				129ppm	119ppm
--	--	--	2.55	1.01 ±.09	1.11 ±.05
0.166	--	0.035	0.40	1.04 ±.02	1.04 ±.02
0.123	--	--	0.462	2.52 ±.09	2.20 ±.11
0.130	--	--	0.475	1.17 ±.02	1.09 ±.02
0.126	0.135	--	0.450	1.93 ±.02	1.94 ±.04

change with p-nitrophenol concentration and with the addition of the potassium complex of the crown ether presumably due to H-bonding of p-nitrophenol to itself (Tsuno et al, 1972; Fujio et al, 1975) or to the crown ether (Virtanen and Viiret., 1978). Comparisons between measurements with and without cobalticyanide were therefore made at constant p-nitrophenol and crown ether concentration. The mechanism of relaxation of C-13 and probably of H-1 may be assumed to be purely intramolecular dipolar. This was confirmed for C-13 by an NOE measurement of 1.83 ± 0.20 comparable to the theoretical maximum of 2.0. Thus any changes in relaxation time may be directly linked to changes in correlation time and the analysis of Anderson and Fryer holds.

Using the effective equilibrium constant from Table 3.1, it is easy to calculate the fraction of p-nitrophenol free and complexed given the initial concentrations of phenol and cobalticyanide. Since the relaxation time of the free phenol was measured separately under equivalent conditions to that in which the cobalticyanide was present, the only unknown remaining in Equations 3.2 and 3.3, namely T_{1c} could be calculated. Calculations based on both 'fast exchange' (Eq. 3.2) and 'slow exchange' (Eq. 3.3) for three sets of H-1 measurements are shown in Table 3.4. In all cases, the T_1's calculated for the case of fast exchange are less than zero showing that this hypothesis is clearly

Table 3.4

Calculated H-1 relaxation times of complexed p-nitrophenol

			7.7 ppm				6.6 ppm			
					T_{1c}				T_{1c}	
PNO_2phenol	$K_3Co(CN)_6$	α	T_1(obs)	T_{1f}	Fast Exchange	Slow Exchange	T_1(obs)	T_{1f}	Fast Exchange	Slow Exchange
0.047	0.060	0.1273	1.96 ±.14	2.59 ±.08	<0	0.74 ±.25	1.00 ±.12	2.15 ±.07	<0	0.21 ±.05
0.470	0.050	0.0579	2.42 ±.03	3.26 ±.19	<0	0.47 ±.10	1.57 ±.10	2.28 ±.14	<0	0.26 ±.10
2.19	0.050	0.0195	0.67 ±.02	1.43 ±.13	<0	0.024 ±.004	0.38 ±.01	0.74 ±.02	<0	0.015 ±.001

invalid. Thus we have shown unequivocally by H-1 T_1's and confirmed by C-13 measurements that the p-nitrophenol-cobalticyanide complex rotates as a unit and does not constitute a mere collision complex. The results for T_{1c} obtained in the H-1 case for p-nitrophenol concentration of 2.19M are considerably lower than those obtained from lower concentrations. This suggests that the fraction complexed calculated on the basis of a 1:1 complex is probably too low and that substantial amounts of higher complexes have been formed. It should also be kept in mind that relatively small errors in the T_1 values will produce quite large changes in the calculations so the conclusions should be regarded as qualitative in nature.

The C-13 T_1's can be used to calculate a rotational correlation time since the NOE measurement confirms exclusive intramolecular dipolar relaxation. The equation is (Martin, Delpeuch and Martin, 1980):

$$\frac{1}{T_1} = \frac{\mu_o^2 \, \gamma_H^2 \, \gamma_C^2 \, h^2 \, I(I+1) \, \tau_c}{12\pi^2 \, r^6} \qquad [3.4]$$

For 0.40M p-nitrophenol, we measure 0.16 and 0.14s as C-13 T_1's for the aromatic carbons of complexed p-nitrophenol. Using an average value of 0.15s leads to a rotational correlation time of 2.8×10^{-10}s. The corresponding value for free phenol is 2.2×10^{-11}s and, as reported by Ader and Loewenstein (1971), 1.8×10^{-11}s for cobalticyanide. The correlation time is proportional to the cube of the molecular radius which is 3.9 A for $Co(CN)_6^{3-}$. The increase in correlation time for cobalticyanide is remarkably consistent with a model for the complexed molecule in which the C-N ... H-O bond is linear and all other bond distances and bond angles assume normal values. In this model the distance between the Co atom and the average postion of the oxygen atoms of the nitro group is 9.8 A which is very close to the value of 9.75 A which is obtained as the product of 3.9 A with the cube root of the ratio of the correlation times for complexed and free. This indicates that the proposition of a hydrogen-bonded adduct between p-nitrophenol and cobalticyanide is quite reasonable.

The analysis of Co-59 linewidths is not clear-cut since the relaxation mechanism is not unambiguously known. Although quadrupolar relaxation usually dominates in asymmetrical complexes at low fields, contributions from shielding anisotropy (SA) cannot be neglected. Since field-dependent measurements were not carried out, one can only assume that SA effects are small here. In that case, the combination of the linewidth of 2408 Hz and the above correlation time yields a quadrupole coupling constant using Equation 3.5:

$$\frac{1}{T_1} = \frac{3}{40}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\eta_Q^2}{3}\right)\frac{2I+3}{I^2(2I-1)}\tau_c \qquad [3.5]$$

of 8.3 MHz which is similar to that obtained from solid-state measurements on octahedral complexes where small second-sphere electric field gradients are created by proximate counter-ions as also observed in the following chapter in the case of sodium cobaltinitrite where a value of 8.1 MHz is obtained. It should be kept in mind that this value is only correct if the assumption of a 1:1 complex holds. If other complexes are also present the calculated quadrupole coupling constant would be overestimated by as much as a factor of two. Another assumption is that the asymmetry parameter is zero. This would probably be true for a 1:1 complex since axial symmetry would be preserved.

3.2.2 Complexing with anilines and benzoic acids

Analysis of the data obtained for the six anilines and eight benzoic acids is much more limited than that obtained for the phenols. In the case of the anilines the equilibrium constants are too small to allow a calculation of both K and $\delta\nu_{\infty}$. Instead, only the product of K x $\delta\nu_{\infty}$ can be obtained. This product is easiest to obtain from the slope of a plot of $\delta\nu$ versus free aniline concentration, [An]. The appropriate formula rearranged from Eq. 3.1 is:

$$\delta\nu = \frac{K[An]}{1 + K[An]} \delta\nu_{\infty} \qquad [3.6]$$

where the denominator simplifies to 1 when K[An] << 1. Table 3.5 gives K x $\delta\nu_{\infty}$ values for the anilines and, for

Table 3.5

$K\delta\nu$- values for anilines, benzoic acids and phenols

Substituent	Benzoic acid	Phenol	Aniline	r(*)
H	69	98	9	0.9921
m-NO_2		199	21	0.9975
p-NO_2	135	447	36	0.9962
p-Cl	91		14	0.9992
p-F	98	162		
m-NH_2	90	152		
p-NH_2	43	53		
p-OH	208			
o-Cl	108			
p-CN		355		
p-OCH_3		108	9	0.9978
p-C_6H_5		157		
p-Br			16	0.9942

(*) correlation coefficient for aniline plots comparison, also those obtained for the benzoic acids and phenols. These data show that the interaction of the anilines with cobalticyanide is a lot weaker than that observed with the phenols. The linewidth increases for the anilines are also much smaller.

As shown in Table 3.5, the benzoic acids show considerably stronger interactions than the anilines but somewhat weaker than the phenols even though the phenols are weaker acids. The analysis of the benzoic acid data is again not as simple as that for the phenols. As shown in Figure 3.3 for the para-nitro and ortho-chloro benzoic acids, the plots of Eq. 3.1 are not strictly linear but show a slight upward curvature. The reason for this deviation is most likely the formation of benzoic acid dimers. Unfortunately the formation constant for such a dimer is not known for DMSO although values have been obtained in many solvents (Muller and Rose, 1965; Muller and Hughes, 1966; Yoon et al; 1976). Although, in principle, analysis of the data could be modified to include the dimer equilibrium, in practice the limited accuracy and number of measurements precludes such an analysis. However, at low concentrations of benzoic acid dimer formation is negligible, so that the intercept may be considered to be reliable in terms of an analysis based on Eq. 3.1. From the intercepts values of $K \times \delta\nu_{\infty}$ can be calculated and these have been included in Table 3.5.

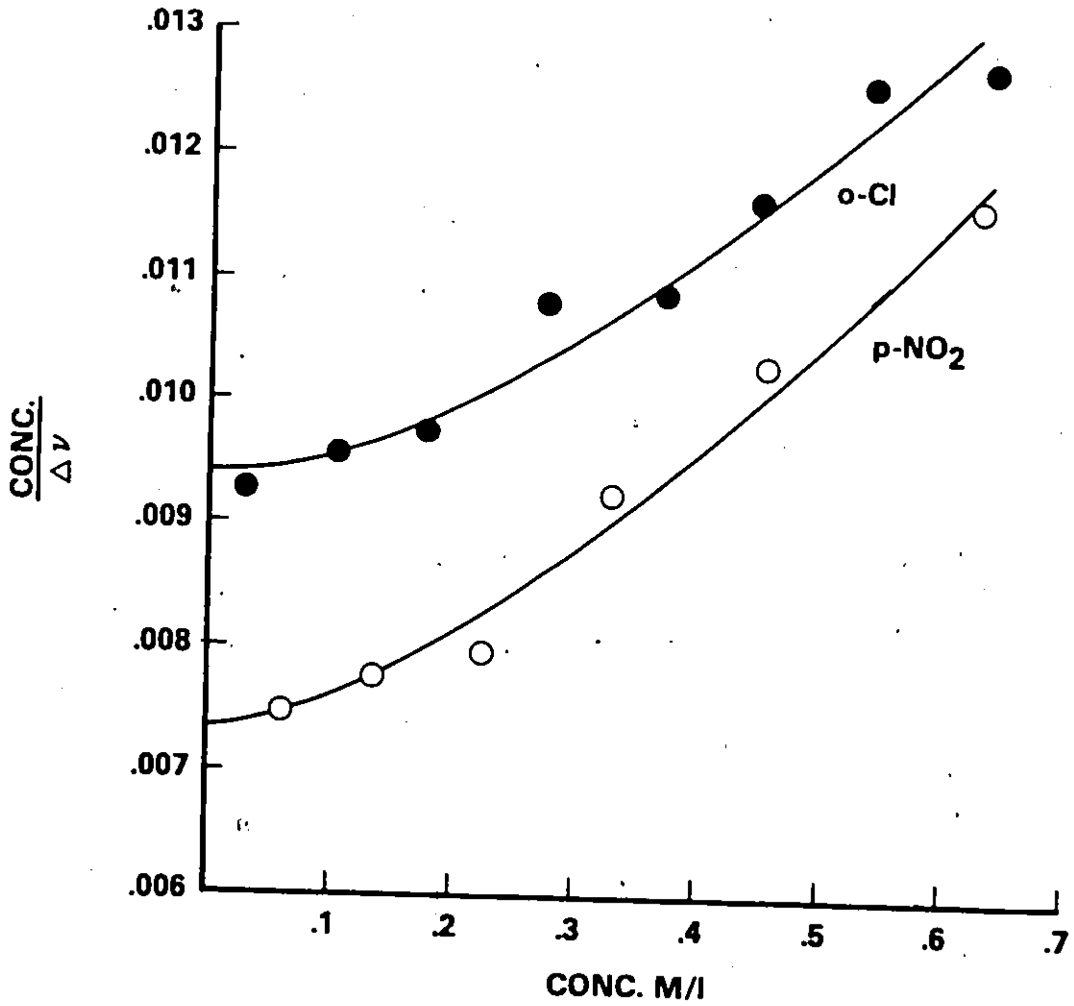

Figure 3.3 Plots of [B]/δν vs [B] for benzoic acids.

3.2.3 Further comparison of the data for anilines, benzoic acids and phenols

The K × $\delta\nu_-$ values of Table 3-5 show some interesting trends. The substituent effect is at least qualitatively similar for all three sets of data. In all cases the larger effects are observed for electron withdrawing substituents and the smaller effects for electron donating. We have clearly shown for the phenols that the variation with substituent is almost entirely due to changes in the K values. Similarly the Co-59 chemical shifts observed relative to DMSO for a wide range of H-bonding solvents are remarkably constant. They range from about 350 ppm in formic acid, to 280 ppm in water and 200 ppm in methanol. If we assume then that the chemical shifts for the aniline and benzoic acid complexes are the same as that for the phenols within a factor of two, then it is clear that the equilibrium constants for the anilines are at least an order of magnitude smaller than those for the phenols while the benzoic acid K's are perhaps a factor of two or three smaller than those for the phenols.

Finally, we should compare the lifetimes of the complexes of cobalticyanide with each of the three types of complexing molecule. We have already shown by the use of H-1 and C-13 relaxation times that the exchange lifetime of p-nitrophenol is longer than the rotational correlation time. An upper limit on the exchange lifetime can be inferred from the apparent lack of exchange broadening observed in similar situations (Eaton, Rogerson and Sandercock, 1982). Since the chemical shift difference between free and complexed cobalticyanide is 150 ppm (3200 Hz at the field of the present experiments), the lifetime must then be greater than 10^{-4} s. The latter limit applies also to the anilines and benzoic acids. However, for these molecules the absolute equilibrium constant cannot be obtained and therefore no quantitative analysis of the lifetimes can be made in the same way as for the phenols.

Nevertheless, the Co-59 linewidth changes may be used to make some tentative conclusions about the lifetimes of the aniline and benzoic acid complexes. As explained earlier, the relaxation mechanism for Co-59 is not easily determined. However, a reasonable proposition is that the predominant mechanism for the complexed molecule is purely quadrupolar. Assuming this, the effectiveness of this mechanism will be primarily dependent on the size of the quadrupole coupling constant or, in other words, the strength of the H-bonding interaction creating the electric field gradient. As well, the relative magnitudes of the exchange lifetime and the rotational correlation time will be crucial since if the latter is larger than the former then the relaxation times will be averaged rather than the rates as is the case for p-nitrophenol. As a simple calculation based on Eq. 3.4a will show, averaging relaxation times favors the longer relaxation time so that, in this case, for approximately equal concentrations of complexed and free cobalticyanide, a very small change in the relaxation rate will occur. On the other hand, averaging relaxation rates under similar conditions will produce a much larger change. Furthermore, the linewidth might be anticipated to be proportional to the concentration of the complexed molecule with the short relaxation rate. As has been illustrated already in Fig. 3.1 such a plot is indeed linear for p-nitrophenol.

Since the degree of assocation is proportional to the observed chemical shift, a qualitative examination of the aniline and benzoic acid behaviour can also be made using this criterion. In Table 3.6 we show the slopes of the plots of linewidth versus chemical shift obtained for all the molecules studied in this section. The correlation coefficients for the phenol and benzoic acid plots are all greater than 0.98 and most are greater than 0.99 indicating that the rates are averaged. The anilines behave quite differently. First of all, the increases in linewidths are much smaller. Furthermore, the correlation with chemical shift is fairly poor primarily due to the relatively large errors involved due to changes in inhomogeneity from sample to sample. The small size of the linewidth effects for the anilines is quite possibly due to the fact that the

Table 3.6

Dependence of linewidths on chemical shifts (*)

Substituent	Aniline	Phenol	Benzoic acid
H	0.8	6.0	16.1
m-NO_2	0.2	11.5	
p-NO_2	2.0	9.3	25.4
p-Cl	1.6		24.5
p-F		5.9	18.8
m-NH_2		7.4	16.5
p-NH_2		9.9	14.3
p-OH			14.6
o-Cl			16.5
p-CN		8.9	
p-OCH_3	1.2	7.5	
p-C_4H_9		11.4	
p-Br	1.1		

(*) Increase in linewidth/chemical shift (Hz/ppm) lifetimes of the aniline complexes are less than the rotational correlation times. Alternatively, one might suppose that the strength of the H-bonds is considerably weaker due to the very weak acidity of these molecules. The large errors involved make it impossible to make any definite conclusions. Turning to a comparison of the phenols with the benzoic acids, it is interesting to note that the benzoic acids have consistently larger linewidth changes. This supports the notion that an important component of the rationalization of the magnitude of the linewidth effects must be the size of the quadrupole coupling constant which would be expected to be proportional to the acidity of the complexing protic group. A similar effect has been observed by Eaton, Rogerson and Sandercock (1982) with the addition of a very strong acid, trifluoroacetic acid, to cobalticyanide which produced linewidth changes of 3450 Hz for a mole fraction of only 0.0225. Thus, although the equilibrium constants for benzoic acid complexation are apparently smaller than those of phenols, the Co-59 linewidth data shows that the electronic changes induced by benzoic acid complexation are larger. On the other hand, the interaction of anilines is considerably weaker.

Chapter 4

Spectroscopic Studies on Sodium Cobaltinitrite

4.1 Introduction

More than 150 years ago, the formation of the cobaltinitrite ion in the reaction of cobaltous ion with nitrous acid was reported (Fischer, 1830). Soon afterward the relative insolubility of the potassium salt was realized and the much more soluble trisodium salt soon became a popular precipitation agent for potassium ions. This analytical technique is still extant today. Nevertheless certain properties of this compound are anomalous as noted in Chapter 1. These properties have been discussed by a number of groups but are as yet incompletely explained. In particular what seems to be lacking is a comprehensive discussion in which all the evidence, spectroscopic and chemical, is considered. In this chapter we first undertake a fairly extensive literature review on cobaltinitrite and other nitro-containing compounds and then describe some new evidence gathered in this lab primarily from NMR experiments. Some of the outstanding questions we attempt to answer concern the ligand-field strength of the nitro ligand in Co(III) complexes, the type of coordination of nitrite in solid and dissolved cobaltinitrite, and the rate and nature of the decomposition processes affecting cobaltinitrite particularly in aqueous solution. Most of our research presented in this chapter has been published recently (Buist, Au-Yeung and Eaton, 1985).

4.2 Literature Review

4.2.1 On the instability of aqueous cobaltinitrite

The decomposition of cobaltinitrite in aqueous solutions has been noted by many authors. An early report (Bhagwat and Dhar, 1931) claims the following stoichiometry for the decomposition reaction:

$$2[Co(NO_2)_6]^{3-} + H_2O = 6NaNO_2 + 2Co(NO_2)_2 + HNO_2 + O$$

This equation is clearly incorrect since a molecule of HNO_2 is missing from the right hand side. It seems likely that HNO_3 is actually formed as noted by Brauer (1962). Very little is known about the intermediates involved although presumably aquated species play a role. Some of these compounds containing up to three aqua ligands have been identified by Carunchio and Gerardi (1967) who separated them chromatographically from a preparation of cobaltinitrite from Co^{2+}, nitrous acid and excess nitrite. The preparative reaction in which the typical Co(II)/Co(III) redox couple is used has also not been analyzed nearly as thoroughly as the corresponding preparations of hexaamminecobalt(III), hexacyanocobaltate(III) or others. What has been established is that the oxidizing agent is HNO_2 which acts both as an oxidizing and reducing agent and normally decomposes itself quite rapidly as a result by the following reaction (Bailar et al, 1973):

$$3HNO_2 = H_3O^+ + NO_3^- + 2NO$$

which combines the following half-reactions:

$$HNO_2 + H_2O = NO_3^- + 3H^+ + 2e^- \qquad E^\circ = -.94V$$
$$2HNO_2 + 2H^+ + 2e^- = 2NO + 2H_2O \qquad E^\circ = 0.99V$$

The reverse reaction, the reduction of cobaltinitrite to Co^{2+} has been studied polarographically but the analysis of the resulting polarograph is complicated by accompanying reduction of the ligand as one might expect (Willis et al, 1945). As a result, little is known about the reduction potential for the couple $Co(II)(NO_2)_6/Co(III)(NO_2)_6$ nor has a formation constant for cobaltinitrite been determined. In fact even less seems to be known about the solution chemistry of cobalt(II) nitrite complexes.

In any case the relative instability of cobaltinitrite particularly in acidic conditions has been utilized in many synthetic preparations particularly those leading to dinitro- or tetranitro- species (Charalambous et al, 1982; Muto et al, 1982). In one case the kinetics of the substitution of nitro groups by amino-acids has been studied and found to be quite rapid (Celap et al, 1973). The lifetimes for these reactions are quite similar to the rate of isotopic exchange between N-15 labelled nitrite and cobaltinitrite. The latter reaction, studied by Matsko et al (1967), was found to have a half-life of 15 min at 25°C, cobaltinitrite concentration of 0.3M and free nitrite concentration of 0.15M. The decrease in rate with added nitrite and increasing cobaltinitrite concentration led the authors to propose a dissociative mechanism involving $Co(NO_2)_5(H_2O)^{2-}$ as intermediate. One other rate study studying the catalytic effect of charcoal on the decomposition of cobaltinitrite reported rate enhancements of about a factor of 5 (Tomita and Tamai, 1971) but unfortunately they followed the reaction by measuring the disappearance of the 480nm absorption band which we have now shown to be due not to cobaltinitrite itself but to a secondary decomposition product.

4.2.2 On the spectroscopy of cobaltinitrite

The spectroscopy of cobaltinitrite has been studied much more thoroughly than the chemistry but the interpretations do not always agree. We will review here the results of NMR spectroscopy involving the Co-59 and N-14 nuclei, the UV-vis spectrum and IR and Raman results. To begin with the Co-59 results, the first report of the chemical shift of cobaltinitrite was given in the historic paper of Proctor and Yu (1951) which was the first to note the presence of an additional weak signal a few hundred ppm downfield. Interestingly this was the first report of two resonances in an NMR spectrum. Many subsequent reports also note the puzzling presence of two peaks in the Co-59 spectrum even from highly purified samples (Kidd and Goodfellow, 1978). The chemical shifts reported for these peaks varies over a healthy range but average to about δ 7450 ppm for the strongest and δ 8050 ppm for the other. For a discussion of how these shifts correlate with the observed UV-vis maxima vide infra. Although the linewidths reported for these peaks are not too accurate it has generally been recognized that the δ 7450 ppm peak was quite narrow and therefore probably corresponded to a species of high symmetry in agreement with the generally accepted structure of cobaltinitrite. Several authors report that the intensity of both peaks decrease with time but no kinetic analysis was attempted. Gasser and Richards (1960) were the first to suggest that the peak at δ 8050 ppm actually consisted of two overlapping peaks arising from an aquated species and a species with one nitro group bonded through O instead of N. They concluded this from measurements of the temperature and nitrite ion concentration dependence of the relative intensities of the two peaks. Recent T_1 and T_2 measurements have shown that T_1 is substantially longer than T_2 and assigning this difference entirely to scalar relaxation of the second kind Rose and Bryant (1979b) have calculated J(Co-59 - N-14) as 54 Hz. However as we will discuss shortly, the N-14 T_1 they use is incorrect. Yamasaki and Nakamura (1978) and Doddrell et al (1979b) also point out the difference in T_1 and T_2 and assign it to scalar relaxation of the second kind. The mechanism of spin-lattice relaxation for O_h or pseudo-O_h cobalt complexes is still in dispute (Laszlo, 1983b).

Reports of NMR spectroscopy on the other two nuclei in the cobaltinitrite ion are sparse. O-17 NMR on cobaltinitrite itself has not been reported at all prior to this work and the only data reported on related compounds has been that of Jackson et al (1982) who studied the nitro-nitrito conversion in $Co(NH_3)_5ONO$. They obtained chemical shifts of δ 670 ppm for N-bonded nitro and δ 640 and δ 470 ppm for $Co(NH_3)_5{}^{17}ONO$ and $-ON^{17}O$ respectively. O-17 chemical shifts for coordinated water have been reported recently for several diamagnetic complexes and are listed in Table 4.4 in the Results and Discussion. Nitrogen NMR of nitrite coordinated to cobalt has not been particularly fruitful either. Bramley et al (1967) reported three coordinated nitro resonances all with exactly the same shift as nitrate. One of these compounds was, of course, cobaltinitrite which probably had decomposed extensively during the course of running the NMR spectrum yielding a large, narrow nitrate resonance as observed also by Rose and

Bryant (1979b). The latter authors were also unsuccessful since they observed a large free nitrite signal around δ 230 ppm. This signal shifted with aging which they attributed correctly to the production of paramagnetic Co^{2+}. However they were forced to propose rapid exchange between free and coordinated nitrite to explain why they only observed one peak which shifted downfield with the addition of Co^{2+} and back upfield with the addition of sodium nitrite. This is quite unlikely in view of the above quoted results by Matsko regarding isotopic exchange. The only other N-14 NMR work prior to this thesis was carried out by Hartmann and Sillescu (1964) who report two peaks at δ 60 and δ 200 ppm but made no definitive assignments. These authors did not report a nitro signal in pentaamminenitrocobalt(III) but did observe a signal at δ 120 ppm (700 ± 150 Hz) for trans-diamminetetranitrocobaltate(III). To our knowledge the only example of an N-15 signal due to coordinated NO_2 has been reported recently by Bell et al (1983) who observed N-15 signals in the range of δ 43-46 ppm for a series of square-pyramidal Rh compounds with the formula $[Rh(Cl(NO)(NO_2)(PR_3)_2]$. Considering the 'coordination shift' for nitromethane, 230 ppm to high field of NO_2^-, this shift is much more reasonable than that observed by Rose and Bryant. The magnitude of the coordination shift for N-bonded nitro can be rationalized on the basis of the fact that the large paramagnetic shift for

NO_2^- arises primarily from low-energy lone pair excitations (Jallali-Heravi and Webb, 1978) and this contribution is greatly reduced when the lone pair interacts with the metal to form a coordinate bond. A similar effect presumably operates to create the large upfield coordination shift noted above in the O-17 NMR of the nitrite oxygen bound to cobalt. A nitrogen NMR signal has yet to be observed from O-bonded nitrite but the coordination shift would likely be substantially smaller and might even be in the opposite direction as observed in the O-17 NMR of N-bonded nitrite and in the N-14 NMR of S-bonded thiocyanates (Howarth et al, 1964).

The interpretation of the UV-vis spectrum of cobaltinitrite has provoked considerable controversy particularly as to the assignment and authenticity of the purported shoulder at 460-480 nm. This controversy seems to have escaped the notice of Co-59 NMR spectroscopists who have considered this shoulder to be the A_{1g}-T_{1g} transition for cobaltinitrite. As the calculations of Dharmatti and Kanekar (1959) indicate this wavelength does not correlate particularly well with the Co-59 shift at δ 7450 ppm but rather with the peak at δ 8050 ppm. For the rest this anomaly has provoked little comment except that by Jorgensen (1963) who suggests that the cobalt NMR result shows that the ligand-field strength of nitrite in cobaltinitrite is stronger than appears from the electronic spectrum. Other authors suggest that the 480 nm shoulder is a charge-transfer band (Caulton and Fenske, 1967) or do not consider it to be genuine at all. Certainly the peak does not show clearly in the solid-state reflectance spectrum although the quality of such spectra is seldom as good as those obtained on clear solutions. Garnier (1970) does not see this band, even in aged solutions and instead claims to have located the much sought-after A_{1g}-T_{1g} transition at 394 nm underneath the intense 355 nm charge-transfer band but gives no details as to the statistical validity of this calculation which, considering that the intensity of the ligand-field transition is likely to be almost two orders of magnitude smaller than that of the charge-transfer band, has to be quite low.

As pointed out by Caulton and Fenske, the suggestion that the UV-vis spectrum is anomalous because of nitro-nitrito conversion is disproved by the solid-state IR spectrum which lacks any peaks in the region expected for nitrito species 1000 - 1200 cm^{-1} (Hitchman and Rowbottom, 1982). There is of course the possibility that the isomerization occurs only in solution but Garnier has run the IR of aqueous cobaltinitrite and observes nothing in that region in aqueous solutions although peaks at 1350, 1240 and 1185 cm^{-1} appear upon aging. Raman studies on fresh solutions and the solid-state also do not give evidence for nitrito formation (Krasser, 1969; Kanamori et al, 1980). It should be noted here as well that the X-ray structure performed recently (Ohba et al, 1978) on the monosodium dipotassium salt shows unambiguously that the solid-state structure has all six ligands N-bonded. Although the symmetry about Co in this particular salt is T_h, which is essentially the highest possible, the symmetry in the trisodium salt is substantially lower as shown by the splitting of the NO_2 asymmetric stretching band at 1435 cm^{-1}. The observation of five bands (Caulton and Fenske, 1967) there suggests that the symmetry has been lowered to D_2 presumably by rotations of the NO_2's either to maximize ionic interactions with the sodiums or conversely to create larger holes for them to occupy. This observation of symmetry lowering helps also to explain the observation of a modestly large quadrupole coupling constant (8 MHz) in the Co-59 solid-state NMR of sodium cobaltinitrite as reported by Saraswati and Vijayaraghavan (1967) and in this thesis.

4.3 Results and Discussion

4.3.1 Comparison of the solid-state and solution structures of cobaltinitrite

The first aim of this research was to show as decisively as possible that the primary species in fresh, aqueous solutions of cobaltinitrite truly contained six N-bonded nitrites and had not undergone rapid conversion to a partially O-bonded species. As well we wished to confirm that the Co-59 chemical shift of the fully N-bonded species was, in fact, δ 7450 ppm. Certainly the X-ray structure confirmed the first point but the possibility remained that the N-bonded species crystallized out preferentially from a solution containing primarily other species. A comparison of IR and Raman data for the two phases indicates that apart from slight solvation frequency shifts and the expected absence in solution of low-frequency solid-state bands, the vibrational data are consistent only with a fully N-bonded species both in the solid-state as well as in solution. Table 4.1 lists the frequencies observed in this lab in the IR and Raman spectra of solid cobaltinitrite and the Raman of aqueous cobaltinitrite along with some data from the literature. Apart from one extra peak at 1050 cm^{-1} in our Raman spectra of both phases the data we obtain agrees well with the literature and a comparison of spectra from both phases shows that no isomerization has apparently occurred. In particular, the suggestion of several authors in the past of isomerization to a nitrito species seems to be unfounded. Of course, the disadvantage of such vibrational spectra is that species in low abundance can easily go undetected.

Although solid-state Co-59 NMR also would not readily show the presence of impurities, the fact that Saraswati et al (1967) had observed a peak from

Table 4.1

IR and Raman vibrational spectra on sodium cobaltinitrite in the solid and solution phases

Raman bands (cm^{-1})		IR bands (cm^{-1})	
solid	aqueous(1M)	solid	aqueous (*)
1470w		1470sh	
		1440s	
1410w		1420s	1402
1325s	1316s	1330s	1315
994w	982m		
859m	843s	837s	833
837s	827s	820w	
		608m	
		447m	
		365s	
304m	292s		
271w	270sh	262m	
248m			
213w			
174m			
139w			

(*) data from Garnier (1970)

polycrystalline sodium cobaltinitrite suggested to us that at least species of pseudo-octahedral symmetry would be easily observed. Further, since Saraswati had not reported an accurate chemical shift (the shift they show is apparently from aqueous solution) we thought that perhaps the shift would turn out to be substantially to lower field than the aqueous value which we have determined to be δ 7470 ± 5 ppm. In fact, the value we determined (see Ch. 5 for a more thorough discussion) was δ 7601 ± 5 ppm indicating that H-bonding of the nitrite ligands to the solvent actually increases the ligand-field strength of the nitro group in the same manner as noted in Chapter 3 for cobalticyanide. A detailed analysis of the field dependence of the quadrupole splitting of the central line led us to a value of 8.1 ± .3 MHz for the quadrupole coupling constant which is consistent with a small second-sphere perturbation of an otherwise highly symmetrical first coordination sphere. The apparent lack of an appreciable shielding anisotropy also confirms that the perturbation does not arise from an asymmetric ligand field as might result from isomerization of the N-bonded species since, as Spiess et al (1969) have shown, shielding anisotropy of about 300 ppm accompanies a quadrupole coupling constant of such magnitude in the case of an asymmetric ligand field, although admittedly the correlation of Spiess is based on just a few compounds.

The large solvent effect observed for the chemical shift of aqueous cobaltinitrite prompted an attempt to obtain Co-59 spectra in other non-hydrogen bonding solvents. Unfortunately, these efforts were not too successful since the solubility in these solvents was predictably far too low to allow any signals to be observed. The technique of using crown ether to aid dissolution in DMSO failed since, during the overnight stirring required to dissolve the equivalent of 0.05M cobaltinitrite, the compound decomposed to produce a species with one or more DMSO ligands and a dark-brown solution was obtained with a chemical shift of 8685 ppm (half-width = 2600 Hz). As an alternative approach, mixtures of several solvents with water could be used to produce modestly concentrated solutions and since the linewidth typically stayed less than 200 Hz the spectra could be obtained quite rapidly before isomerization or decomposition occurred. In fact, some of these samples were found to persist quite long without complete decomposition to Co^{2+} as occurs for dilute aqueous solutions. For the three solvents used, DMSO, acetonitrile and methanol, an increase in chemical shift with increasing amounts of nonaqueous solvent was qualitatively observed. The shifts observed for the highest ratio of nonaqueous/aqueous attained are given in Table 4.2. The trend observed for these shifts suggests that the solid-state value reflects a value observed under the

Table 4.2

Cobalt-59 NMR chemical shifts of cobaltinitrite in nonaqueous/aqueous solvent mixtures

Nonaqueous solvent	w/w ratio nonaqueous/aqueous	δ (ppm)
methanol	1/1	7546
acetonitrile	2.5/1	7589
dimethyl sulfoxide	1/1.5	7584

conditions of weak H-bonding and that H-bonding actually strengthens the nitrite ligand field.. While the behaviour of solvent mixtures is a subject in itself and cannot be discussed in detail here, one interesting aspect of these experiments should be noted. The result for CH_3CN shown in the table was in fact obtained from a solution of 0.05M cobaltinitrite in a 2/1 (v/v) mixture of CH_3CN and H_2O which disproportionated into two phases, one rich in H_2O and cobaltinitrite (δ 7518 ppm) and the other rich in CH_3CN as shown by H-1 NMR quantitative analysis. This phenomenon has been observed previously in solutions of simple ionic salts in mixtures of otherwise fully miscible liquids (Schneider, 1973).

So far the evidence points quite strongly toward the conclusion that the primary species in aqueous solution is fully N-bonded and its true Co-59 chemical shift is even further downfield than expected. Further confirmation for the former conclusion comes from measurements of Co-59 T_1 and T_2. The linewidth of aqueous cobaltinitrite is about 55 Hz which corresponds to a T_2 of 5.6 ms. However, the T_1 is much longer at 37.5 ms according to our measurements. This is one of the longest Co-59 T_1's reported at ambient temperature and can only be explained by invoking spherical symmetry about cobalt. This is also strong evidence for complete N-bonding. The difference between T_1 and T_2 is primarily due to scalar relaxation of the second kind caused by the six nitrogens. This matter will be discussed more fully in Ch. 5. As mentioned previously, the coordination shifts observed for N-14 and O-17 NMR spectroscopies can also give information about the mode of coordination of the nitrite ion. These spectra will be more fully discussed shortly but suffice it to say now that the large shift observed for N-14 and the small shift observed for O-17 also confirm coordination through nitrogen. All this evidence leaves little doubt about the nature of coordination but of course raises serious questions about the ligand-field strength of the nitrite ligand as well as the unusual instability of cobaltinitrite in aqueous solution.

4.3.2 Studies on the mechanism of decomposition of cobaltinitrite

A careful study of the time-dependence of the electronic spectra of aqueous cobaltinitrite solutions has provided us with information relevant to both those problems. This experiment was prompted by the observation that the δ 7470 ppm signal in the Co-59 spectrum of 0.1M cobaltintrite solutions decayed rapidly immediately after dissolution. This had not been observed previously. The ability to obtain entire electronic spectra in one second allowed us to easily follow changes in the spectrum of 2.7 mM cobaltinitrite as shown in Figure 4.1. At this concentration the band at 355 nm is off-scale in the first spectrum taken after 2 min. so that only its tail-end can be observed stretching into the visible region. As reported already by Garnier (1970) the shoulder at 480 nm is absent and only appears clearly 6 min. after dissolution. Concurrently, the peak at 355 nm decreases in intensity. This suggests, then, that a dissociative process such as aquation occurs extensively at the low concentrations necessary for observing the intense peaks present in the spectrum. Thus we have shown conclusively that the peak at 480 nm does not arise from $Co(NO_2)_6{}^{3-}$ but from a decomposition product. Similar experiments carried out at much lower concentrations suggest that the wavelengths usually quoted for the intense charge-transfer bands in the

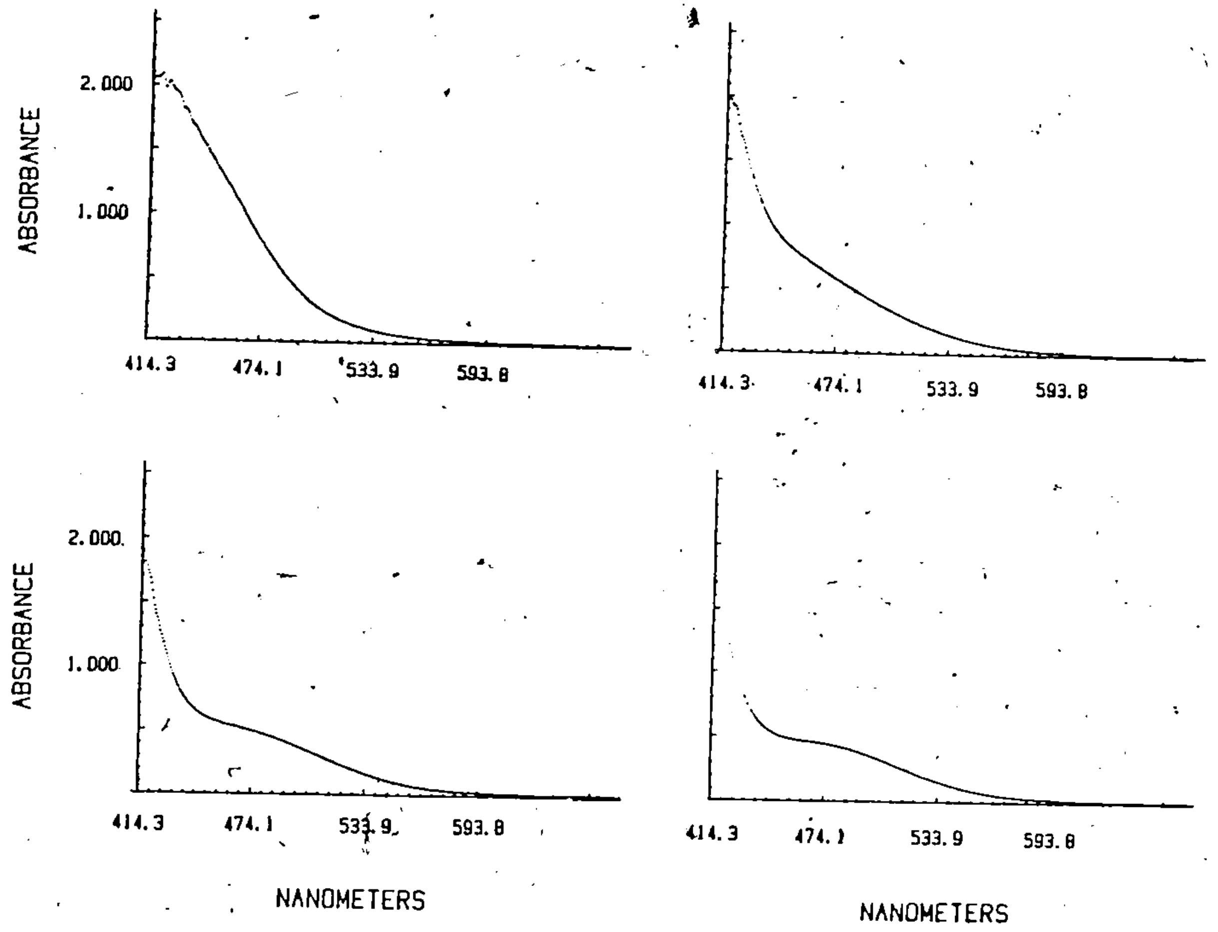

Figure 4.1 Electronic spectra of aqueous cobaltinitrite (2.7 mM; l = 1cm) for varying lengths of time after dissolution. (A) t = 2 min. (B) 4 min. (C) 6 min. (D) 9 min.

UV region (Caulton and Fenske, 1967) are somewhat in error. The first CT band is located at 365 nm immediately after solution and decreases in intensity somewhat while shifting to 355 nm. The second intense peak also shifts slightly with time. On the other hand, addition of 1.0 M sodium nitrite to 2 mM solutions prevents the formation of the 480 nm band confirming that it belongs to an aqua species.

Similar results are obtained in the Co-59 spectrum of cobaltinitrite. While the δ 7470 ppm peak predominates in concentrated solutions (> 1M) and decreases only slowly with time, quite a different picture emerges at lower concentrations. Figure 4.2 shows a plot of Co-59 intensity vs. time for a 0.1 M solution and here is clearly indicated that the δ 7470 ppm peak undergoes rapid decay with a half-life of about 180 s while the intensity of the peak at δ 8052 ppm grows in at approximately the same rate. Furthermore we have shown that at least seven other peaks can be observed before the solutions are more than a few hours old. The entire spectrum of cobaltinitrite and its decomposition products is shown in Figure 4.3 and Table 4.3 lists the chemical shifts and linewidths. Not all these peaks are visible at a given time and concentration and the relative concentrations of these species vary in a rather complex manner with time, concentration and pH. However, as shown in Table 4.3, we have determined that the ratio of the δ 7470 peak to that at δ 8050 ppm decreases with decreasing

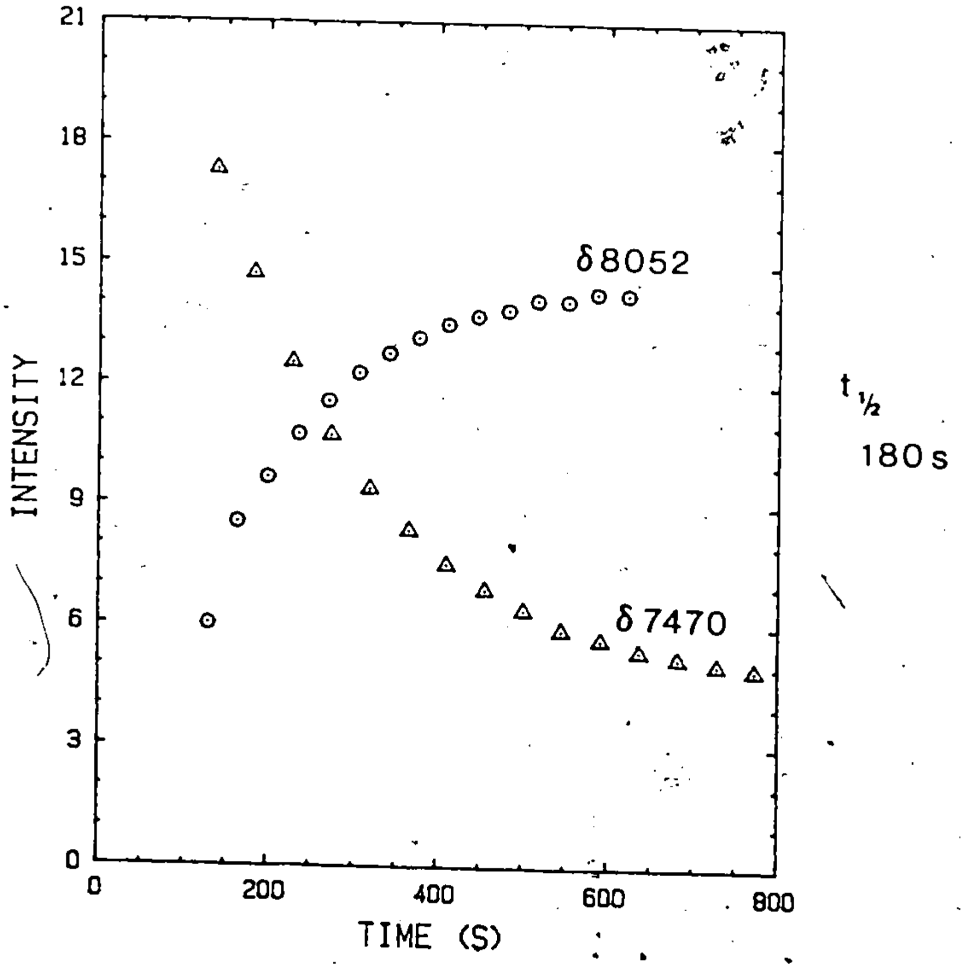

Figure 4.2 Co-59 NMR intensity as a function of time after dissolution. Initial [cobaltinitrite] = 0.1 M. Time required for complete dissolution was about 90 s in each case.

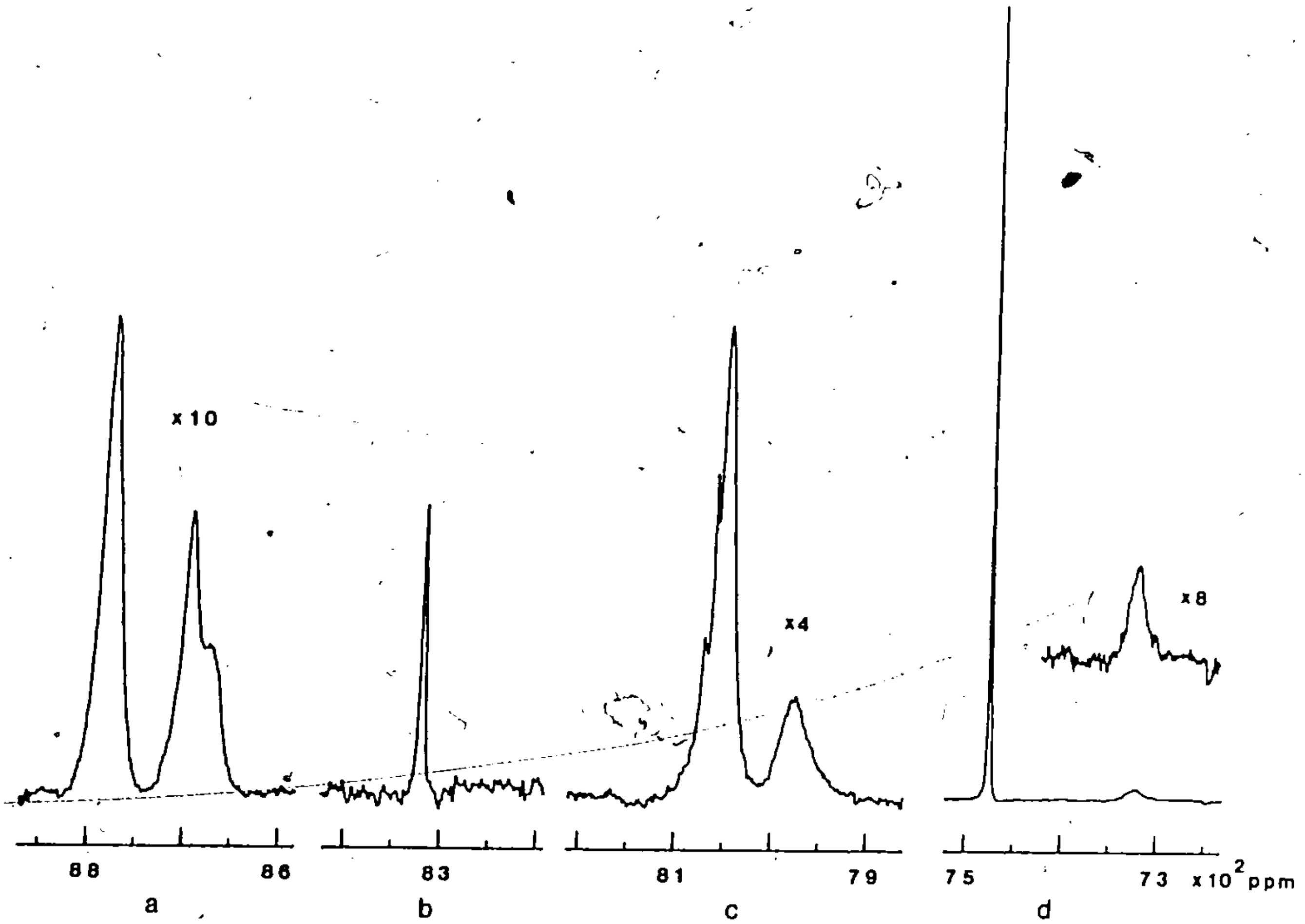

Figure 4.3 Co-59 NMR spectrum of aged aqueous cobaltinitrite. Spectra (a), (c) and (d) were obtained at 9.7 T on a 0.1 M solution. (a) 16,000 scans, aged 95 min. (c) 800 scans, aged 160 min. (d) 800 scans, aged 80 min. Spectrum (b) was obtained at 5.9 T on a 0.9 M solution. (b) 800 scans, aged 35 min.

Table 4.3

Cobalt-59 NMR spectrum of aqueous cobaltinitrite

Observed δ (ppm)	Linewidth (Hz)	Assignment	Calc. δ (ppm)
7318	1650	$Co(NO_2)_5(ONO)^{3-}$	7573
7470	55	$Co(NO_2)_6^{3-}$	7511
7970	3300	c-$Co(NO_2)_4(ONO)_2^{3-}$	7816
		t-$Co(NO_2)_4(ONO)_2^{3-}$	7811
8052	1550	$Co(NO_2)_5(H_2O)^{2-}$	8108
8065	220	or $Co(NO_2)_5(OH)^{3-}$	8092
8074	300		
8315	175	c-$Co(NO_2)_4(H_2O)(ONO)^{2-}$	8331
8693	(*)		
8670	(*)	c-$Co(NO_2)_4(H_2O)_2^{2-}$	8846
8790	2100		

[$Co(NO_2)_6^{3-}$] (M)	[NO_2^-] (M)	Intensity Ratio δ8052 : δ7470
0.9	0.0	0.389
0.5	0.0	0.418
0.1	0.0	3.19
0.1	1.0	0.329

(*) broad, overlapping lines

concentration approximately as expected for the dissociative equilibrium:

$$Co(NO_2)_6^{3-} + H_2O - Co(NO_2)_5(H_2O)^{2-} + NO_2^-$$

with an equilibrium dissociation constant of about 0.1 M. Addition of excess NO_2^- drives the equilibrium back towards $Co(NO_2)_6^{3-}$ as expected. The assignment of the other lines in the Co-59 spectrum will be discussed later.

The observation that free nitrite suppresses the decomposition of cobaltinitrite solutions prompted an N-14 NMR study since previous N-14 work was not too successful apparently due to instrumental limitations. Although we could obtain N-14 spectra readily on the WM-400, the quality of the spectra left something to be desired due to the large linewidth of the coordinated nitrite signal which was nevertheless detected for the first time at δ 95 ppm. A signal due to free nitrite was readily apparent appearing at δ 240 ppm in a fresh solution. In samples aged for a few days, an intense nitrate signal was the only signal observed. Much better spectra could be obtained in a shorter time on the high-power CXP-200 as shown in Fig. 4.4 and they confirmed that in fresh solutions the relative concentration of free nitrite increases with decreasing concentration again as expected from a dissociative process. The amount of free nitrite increases with time as does the concentration of nitrate ion. Both these signals

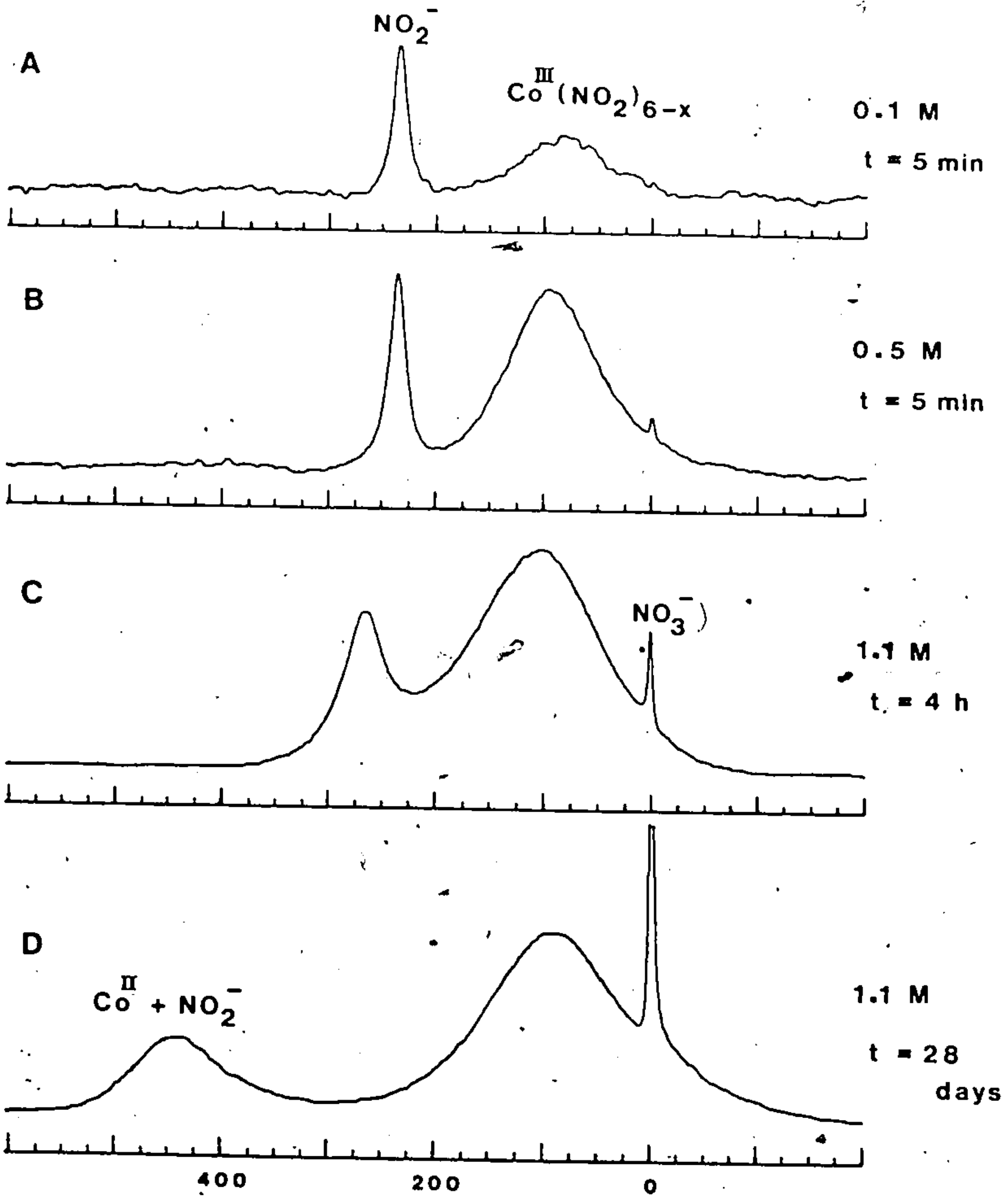

Figure 4.4 N-14 NMR spectra of cobaltinitrite obtained at 4.7 T. Concentrations shown at right are initial conc'ns. Times shown are average times of aging.

shift downfield and broaden with time due to the presence of paramagnetic Co^{2+}. The nitrate signal shifts only 6 ppm in highly decomposed samples whereas a shift difference of 200 ppm is observed for free nitrite in a month-old solution of 0[illegible]9 M cobaltinitrite (Fig. 4.4D). In a separate experiment, addition of 0.01M Co^{2+} to 1.0 M NO_2^- caused a shift of 12 ppm and the nitrite line broadened from 170 Hz to 250 Hz while approximately twice as large an effect was observed for 0.02M Co^{2+}. We have also observed that the intensity of the nitrate peak could be greatly reduced by addition of free nitrite indicating that dissociation is an essential intermediate step in the eventual reduction to Co(II) which presumably occurs through oxidation of nitrite to nitrate perhaps with the involvement of nitrous acid. As noted earlier the magnitude of the coordination shift shows N-bonding beyond a doubt. There is however no indication that more than one cobalt species is present as only one peak for coordinated nitrite is observed. Presumably the chemical shifts and linewidths of all the different types of coordinated nitrite there must be especially in dilute solutions are all very similar. There is also no sign of a signal from nitrito species although this is not surprising considering that the concentration of such species is probably quite low and this peak would severely overlap with the other signals.

Natural abundance (.037%) O-17 spectra were difficult to obtain but we did observe a weak signal at δ 690 ppm which we attributed to coordinated NO_2^- based on the observation of Jackson et al (1982). What we could observe readily was the solvent signal which shifted downfield and broadened with time as might be expected in a solution producing Co^{2+} ions. Also a surprisingly strong signal was observed at δ 168 ppm (250 Hz) the origin of which still remains a mystery. Presumably this species is not derived from cobaltinitrite since it is not observed in an enriched sample prepared by dissolving 0.9 M cobaltinitrite in water 18.2% enriched in O-17. In this sample, exchange with the solvent occurred readily allowing confirmation of the coordinated nitro shift at δ 690 ppm and an accurate measurement of the linewidth (1550 Hz). The intensity of the δ 690 ppm signal is plotted versus time in Figure 4.5 and some of the spectra shown in Figure 4.6. The initial spectrum in which the coordinated nitrite is observed shows a definite shoulder which is probably due to free nitrite. A mechanism for exchange which therefore suggests itself consists of initial enrichment of free nitrite which then is incorporated into the complex. As can be seen in the plot of Fig. 4.5 there is first an initiation period which is primarily due to the drop in pH to a value of 4.3 during that period as observed separately in another sample of the same concentration. The subsequent rate of exchange at that pH corresponds quite well with that

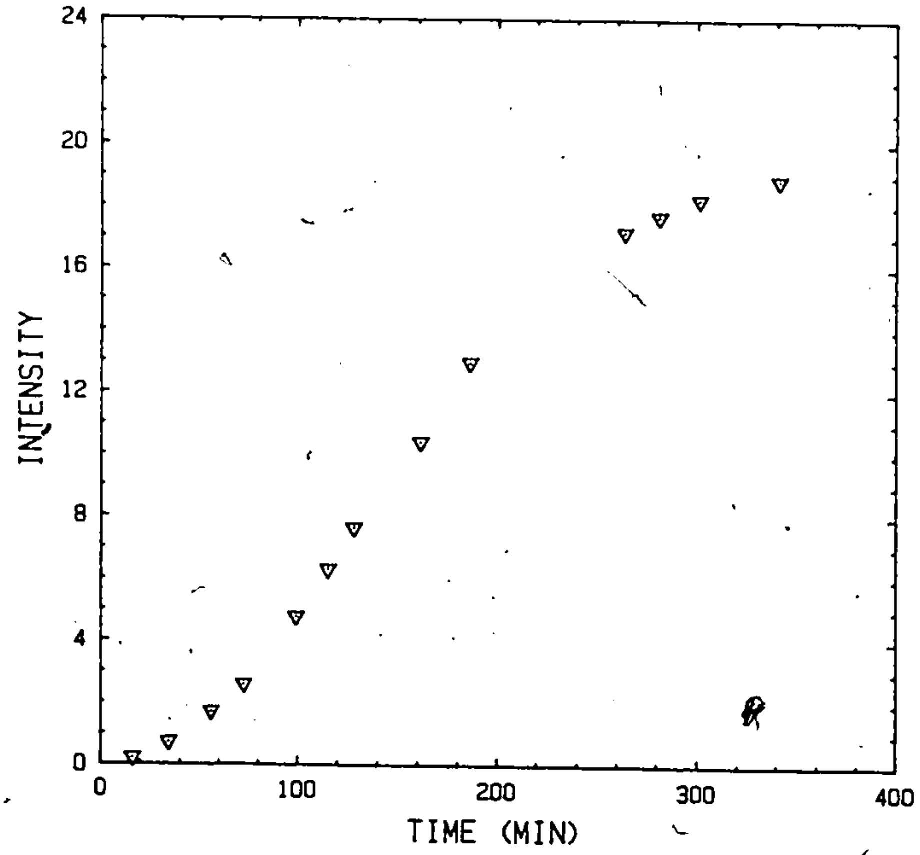

Figure 4.5 O-17 NMR (9.7 T) intensity as a function of time after dissolution. See also Fig. 4.6.

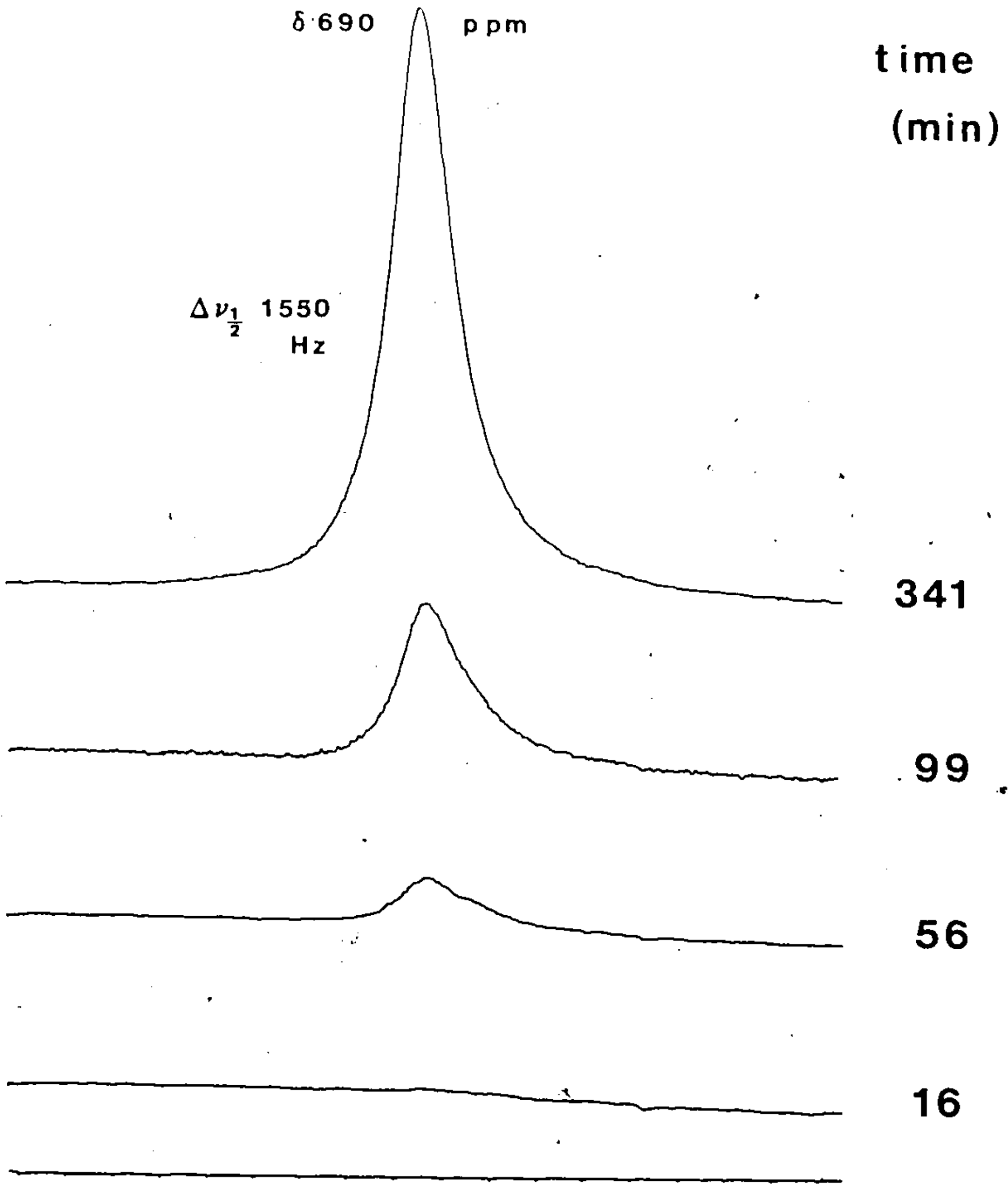

Figure 4.6 O-17 NMR (9.7 T) spectra of cobaltinitrite. Times shown are times after dissolution of 0.9 M cobaltinitrite in 18.2% O-17 enriched water. 4,000 scans.

Table 4.4

O-17 NMR chemical shifts for coordinated water

complex	O-17 shift (ppm)	Ref.
$Co(NH_3)_5(H_2O)^{3+}$	-127	Jones et al (1983)
$Co(NH_3)_5(OH)^{2+}$	-214	" "
$Co(en)_2(H_2O)PO_4H^+$	-122	" "
$Co(en)_2(H_2O)_2^{2+}$	-126	Aygen et al (1985)
$Pt(H_2O)_4^{2+}$	-124.3	Helm et al (1985)
$Pd(H_2O)_4^{2+}$	-131.8	" "
$Ru(H_2O)_6^{3+}$	-198	Bernhard et al (1985)
$Co(NO_2)_5(H_2O)^{2-}$	-70	this work

calculated on the basis of a rate law for nitrite/water O-exchange proposed by Bunton et al (1959). It should be noted here that the drop in pH is most likely due to the partial deprotonation of the aqua ligand. A small signal for coordinated water was also observed in these spectra at δ -70 ppm (300 Hz). This shift adds to a growing number of O-17 signals for coordinated water as listed in Table 4.4.

Thus fairly strong evidence has been accumulated in this thesis that the initial step in the decomposition of aqueous cobaltinitrite involves replacement of one nitrite by water with a rate considerably faster than normally observed for cobalt(III) ligand exchange processes. The rates and nature of subsequent reactions are not nearly as easily to determine. However, the drop in pH noted earlier certainly helps to catalyze decomposition since the nitrous acid which must be produced eventually decomposes to nitrate and nitrogen oxide and also acts to reduce any cobalt species which has lost enough nitrite to render itself easily reducible. The decomposition of nitrous acid is supported by the observation of a strongly acidic liquid which condenses above closed containers of concentrated cobaltinitrite solutions. This is presumably due to the formation of nitric acid from the reaction of NO with O_2 to produce NO_2 which combines with water vapour to form the acidic liquid. Nitrate has been shown to be present in this liquid by UV-vis spectroscopy (300 nm). Another possiblity is the direct production of NO_2 by the reaction:

$$Co^{(III)}(NO_2)_6^{3-} \rightleftharpoons Co^{(II)}(NO_2)_5^{3-} + NO_2$$

which forms an important step in one of the mechanisms to be discussed in the next paragraphs. It should be noted here that the five-coordinate Co(II) nitro species has been reported by Dwyer in a private communication to Gillespie and Nyholm (1957).

At least two mechanisms may be postulated for the rapid aquation of cobaltinitrite. The simplest would be to invoke as intermediate a nitrito species which would presumably aquate quite readily. This seems fairly unlikely considering that all known equilibrium constants for equilibria of the type:

$$Co(X)_5NO_2 \rightleftharpoons Co(X)_5ONO$$

are quite small. However the case may be quite different for a complex with a high degree of electron donation from the ligands to the metal which may change the character of the metal sufficiently that it no longer prefers ligation through N (Gp. V) over O, S (Gp. VI). A good example of this is the $Co(CN)_5SCN$ molecule which has been found with the thiocyanate S-bonded although it is otherwise typically N-bonded (Gutterman and Gray, 1969). In this case the π back-bonding of the five cyanides evidently changes the character of the metal significantly. Although π-

interactions may not be important in cobaltinitrite, evidence for extensive delocalization in cobaltinitrite has been obtained from careful electron density maps measured by Ohba et al (1978) who found that the cobalt atom had essentially zero charge. Other evidence for this mechanism may be derived from peaks in the Co-59 spectrum which we have plausibly assigned to nitrito species.

Another mechanism we have proposed involves a rate determining step of electron transfer from NO_2^- to cobalt, followed by rapid ligand exchange of the resulting labile Co^{2+} complex, with the reaction being completed by rapid reverse electron transfer from Co^{2+} to NO_2. The resulting sequence of steps is shown below:

$$LCo^{3+}NO_2^- = LCo^{2+} + NO_2 \quad (1) \text{ slow}$$

$$LCo^{2+} + L' = L'Co^{2+} + L \quad (2) \text{ fast}$$

$$L'Co^{2+} + NO_2 = L'Co^{3+}NO_2^- \quad (3) \text{ fast}$$

$$NO_2 + NO_2 + H_2O = NO_3^- + NO_2^- + 2H^+ \quad (4) \text{ slow}$$

A very similar mechanism has been recently proposed by Sasaki et al (1982) for ligand substitution reactions of cobalt(III) oxygen complexes in which electron transfer from the peroxide ligand to the metal is suggested to occur. Such an electron transfer step can only take place with an oxidizable ligand such as peroxide or nitrite and thus cannot occur with most of the typical Co(III) ligands such as H_2O, NH_3 and other amines, CN^- and SCN^-. Further this type of reaction seems to require an overall negative charge on the complex in the case of NO_2^- since only complexes containing more than four nitrites are exceptionally labile.

4.3.3 The variable ligand-field strength of nitrite

Having shed some new light on the decomposition of cobaltinitrite it is now time to reflect on the ligand-field strength of the nitrite ligand in cobaltinitrite. Unfortunately the usual process of extracting a Dq parameter from the UV-vis spectrum is now rendered impossible in view of the fact that we have shown quite convincingly that the 480 nm band probably belongs to an aquated species and not to cobaltinitrite. However, we can be quite sure now of the Co-59 chemical shift and using this we can get a reasonable estimate of the ligand-field strength. Before doing so we should consider the possibilty that the usual correlation (Laszlo, 1983b) between chemical shift and the lowest d-d excitation energy obtained for N-bonded ligands may not necessarily hold for species containing more than two or three nitrites. In other words the orbital reduction factor and/or $\langle r^{-3} \rangle$ for nitrite may differ significantly from values for ligands such as ammonia, alkyl amines and others. A simple solution to this is to base the correlation on the series

$Co(NH_3)_n(NO_2)_{6-n}$. As shown in Fig. 3 of the paper of Juranic et al (1979b), a good correlation exists for this series with the only obvious exception being $Co(NO_2)_6^{3-}$. If we use δ 7470 ppm as the chemical shift we obtain an excitation wavelength of 450 nm. This corresponds to a Dq value of about 2600 cm^{-1} which is significantly lower than the value of 3150 cm^{-1} obtained for NO_2^- in $Co(NH_3)_5(NO_2)^{2+}$.

One way to reduce the magnitude of this anomaly would be to invoke a modest contribution to the paramagnetic shift due to a charge-transfer excitation. This type of contribution has not been considered previously for Co(III) complexes since the d-d transition dominates but clearly the Ramsey formula (1950, 1951) applies to any type of transition as long as it involves the excitation of only one electron from the ground state to an excited state of the correct symmetry. The symmetry requirement is established by the symmetry properties of the angular momentum operator which in O_h transforms as T_{1g}. As Gray (1963) has shown for hexacyano complexes, if there exist in the ligand π^* orbitals at the correct energy then states of various T-type symmetries result including T_{1g} and intense charge-transfer transitions can be observed albeit only to T_{1u} states since that is how the dipole-dipole transition operator transforms. The symmetry of cobaltinitrite disregarding rotations of the nitrites is T_h. The energy level diagram for this symmetry is given in Fig. 6 of the paper of

Caulton and Fenske (1967). One-electron excitations from the $4t_g$ orbital which is a pure metal orbital to either $5t_g$ or $5t_g$ orbitals arising from symmetry-adapted linear combinations of nitrite π^* orbitals each give rise to a T_g state which is the symmetry of the angular momentum operator in T_h. Transitions to these states are Laporte-forbidden so they will unfortunately not be observed. Also the integrals in the Ramsey equation cannot be easily estimated without detailed calculations on the electronic structure of cobaltinitrite. Thus quantitative calculation of the chemical shift contribution from these excitations is beyond the scope of this thesis.

It remains to be seen in view of these complications whether a model can still be developed to accurately predict the Co-59 chemical shift of nitro-containing complexes. Since the model recently developed in this laboratory by Au-Yeung and Eaton (1983) was successful for such a large number of cases, we decided to investigate whether an empirical modification of the model could be made to solve the difficulties presented by the nitro compounds. An important clue to the source of the deviations could be deduced from the fact that quite consistently the usual ordering for cis-trans isomers was reversed in several cases. This suggested an empirical variation in the ligand chemical-shift parameter, S_L, for nitro such that its value is a function of the number of cis or trans nitro groups.

present in the complex. Since the $Co(NH_3)_x(CN)_{6-x}$ series produced some of the largest errors in the Au-Yeung/Eaton model we decided to attempt to improve the fit for this series as well. Before we examine this more fully, we should briefly review the Au-Yeung/Eaton model.

The basis of the model is the crystal-field hypothesis that the crystal-field along each axis in an pseudo-octahedral complex is a function of the sum of the charges produced by the ligands on that axis. Thus the expression for the paramagnetic chemical shift in the case of a completely asymmetric crystal-field can be written in terms of the excitation energies along each axis as:

$$\sigma(\text{para}) = \frac{A}{3}\left(\frac{1}{E_{xx}} + \frac{1}{E_{yy}} + \frac{1}{E_{zz}}\right) \qquad [4.1]$$

where A incorporates the usual set of constants including the orbital reduction factor which is assumed to be constant along each axis. Substituting $C_n + C_m$ for each E and defining S_n to be C_n/A, we obtain, after including the diamagnetic shift relative to cobalticyanide, the chemical shift relative to $Co(CN)_6^{3-}$ as follows:

$$\delta(\text{ppm}) = \frac{1}{3}\left(\frac{1}{(S_1+S_2)} + \frac{1}{(S_3+S_4)} + \frac{1}{(S_5+S_6)}\right) - 11{,}000 \qquad [4.2]$$

where S_L is the chemical shift parameter for a specific ligand some of which can be obtained from complexes with only that ligand and the others from mixed complexes in which the parameters of all but one ligand are known.

Although this model has been used to successfully calculate the chemical shifts of 39 complexes with a standard deviation of 108 ppm (Au-Yeung and Eaton, 1983), the quality of fit for the nitroammine and cyanoammine series is significantly poorer. To illustrate this we show in Table 4.5 the calculated $S(NO_2)$ parameters for the nitroammine series using a value of $S(NH_3) = 2.608E-5\ ppm^{-1}$ as calculated from the chemical shift of $Co(NH_3)_6^{3+}$. The chemical shifts of the last five members of the nitroammine series are taken from Fig. 4.7 which shows the spectrum of the mother liquor taken from the synthesis of trans-$Co(NH_3)_4(NO_2)_2^{+}$. These chemical shifts agree well with those reported in the literature by various authors. The other chemical shifts are taken from the literature. Similarly $S(CN)$ values for the cyanoammine series are shown in Table 4.6. The calculated values of $S(NO_2)$ and $S(CN)$ show a definite trend down the two series, with $S(CN)$ increasing and $S(NO_2)$ decreasing with increasing n. In both cases the effect of introducing a cis ligand is substantially different from the effect of introducing a trans ligand. Thus a new set of empirical formulae for the chemical shift parameters must be developed to obtain the best possible fit for the observed chemical shifts. These formulae are the following:

Table 4.5

Calculated Cobalt-59 NMR chemical shifts for the nitroammine series

$Co(NH_3)_n(NO_2)_{6-n}$

n	Observed δ (ppm)	Calculated S (10^{-8}ppm)	Calculated δ(ppm) Method 1	Calculated δ(ppm) Method 2
0	7470	2.711	5150	7511
1			5610	7182
cis 2	6880	2.893	6071	7061
tr 2	6815	2.918	6157	6935
mer 3	6980(850) (*)	2.969	6618	7024
fac 3	7221(<150)	2.880	6532	7122
cis 4	7275(415)	3.001	7078	7272
tr 4	7208(440)	3.072	7165	7204
5	7639(185)	3.082	7625	7625

Method 1: using Eq. 4.2 and $S(NO_2)$ - 3.096×10^{-8}
Method 2: using Eq. 4.2 and $S(NO_2)$ given by Eq. 4.3a

(*) δ's and linewidths for this and the next 4 isomers taken from Fig. 4.7.

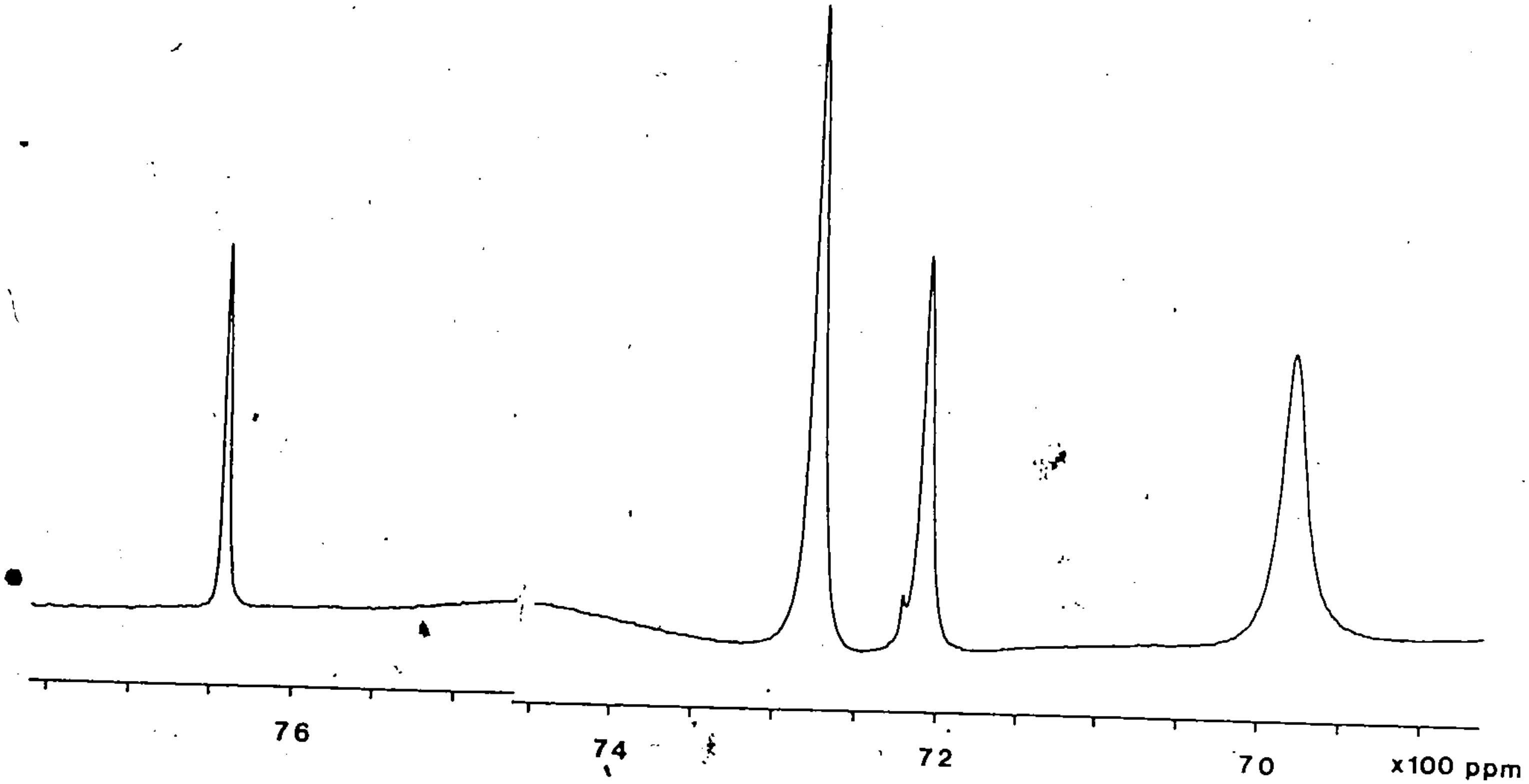

Figure 4.7 Co-59 NMR spectrum of nitroammine complexes.

Table 4.6

Calculated Cobalt-59 NMR chemical shifts for the cyanoammine series

$Co(NH_3)_n(CN)_{6-n}$

n	Observed δ (ppm)	Calculated S (10^{-3} ppm)	Calculated δ (ppm) Method 1	2	3
0	0	4.545	284	-92	-8
1	1168	4.469	1258	1141	1222
cis 2	2457	4.330	2232	2370	2452
tr 2	2744	4.533	2913	2726	2720
mer 3 (*)	3991	4.364	3887	3940	3950
fac 3	3314	4.378	3207	3596	3682
cis 4	5132	4.236	4862	5150	5180
tr 4	5498	4.484	5543	5481	5447
5	6675	4.203	6517	6675	6677

Method 1: Eq. 4.2, S(CN) = 4.431×10^{-3} for all
Method 2: Eq. 4.2, S(CN) given by Eq. 4.3b
Method 3: Eq. 4.4, S(NH3) = 1.382×10^{-3}; S(CN) = 1.683×10^{-4}

(*) Bramley et al (1985) assign this to the fac isomer but the large linewidth reported by Au-Yeung and Eaton (1983) (4540±500Hz) as compared to only 618 Hz for the other isomer makes this unlikely

$$S(NO2) = (3.096 - 0.093n_{cis} - 0.023n_{trans}) \times 10^{-6} \quad [4.3a]$$

$$S(CN) = (4.203 + 0.020n_{cis} + 0.301n_{trans}) \times 10^{-6} \quad [4.3b]$$

where n_{cis} is the number of NO_2 or CN ligands cis to the NO_2 or CN ligand for which the shift parameter is required and n_{trans} is the corresponding number of trans ligands. As shown in Table 4.5 and Table 4.6 in the columns for Method 2, the shifts calculated with the above formulae agree reasonably well with the experimental shifts and the observed anomalies of cis-trans and mer-fac pairs are reproduced. These formulae should be regarded as purely empirical and need not necessarily apply equally well to all nitro and cyano containing ligands since there may be similar inter-ligand interactions between unlike ligands (e.g. between nitro and cyano). However in lieu of anything better we have applied these formulae to the assignment of peaks observed in solutions produced by some reactions of cobaltinitrite.

These assignments will be discussed shortly but first we should consider the origin of the cis and trans effects. In the case of cyanide the apparent trans-effect can be very well simulated by the inclusion in the formula of a factor which takes into account the different orbital reduction factors for the two ligands. As Fujiwara et al (1969) have pointed out, the orbital reduction factor may be different along each axis so that a modified formula including a variable orbital reduction factor squared (k) would have the form:

$$\delta(\mathrm{ppm}) = \frac{1}{3}\left(\frac{k_x}{(S1+S2)} + \frac{k_y}{(S3+S4)} + \frac{k_z}{(S5+S6)}\right) - 11{,}000 \qquad [4.4]$$

where the k's would be some function of $k(NH_3)$ and $k(CN)$. A reasonable model for the calculation of the k's would be that the k on each axis is the average of the k's for the ligands on that axis, i.e. $k_x = 0.5(k_1+k_2)$, etc. Using Juranic's (1981) values for k, $k(NH_3) = .53$ and $k(CN) = .37$, we have recalculated the chemical shifts of the cyanoammine series as shown in the column labelled Method 3 of Table 4.6 using only one value for S(CN) showing that the apparent trans-effect can be simulated very well in this way. It should be noted that both models have similar difficulties in predicting the fac chemical shift. More to the point the chemical shift difference between mer and fac is poorly predicted although what is reproduced is the trend observed for the other two pairs of geometrical isomers that the shift difference between cis and trans is larger than predicted by e.g. a model in which the S(CN) parameter is constant as shown in the column labelled Method 1 in Table 4.6. The latter model actually predicts the shift difference between mer and fac very well.

In the case of the nitroammine series the case is quite different. As shown in the third column of Table 4.5, the calculated shift parameter $S(NO_2)$ decreases quite regularly with decreasing p (column 1) but in this case, for each pair of geometrical isomers, the isomer with the larger number of trans nitro's (trans and mer) has the largest $S(NO_2)$. This means that the normal chemical shift difference between the pairs of isomers will be smaller than usual. Actually examination of the observed chemical shifts shows clearly that the normal order within each pair is reversed. This can be simulated reasonably well by introducing Eq. 4.3b shown above. This formula does not represent a 'best-fit' model but is meant to illustrate that the cis-effect is larger than the trans-effect. The origin of the cis-effect is not clear but may in part result from steric interactions between cis nitro's although there is no strong evidence for this from the crystal structures published on members of this series. Perhaps the most important point to note is not how well or how poorly the data is reproduced by the model but rather that the anomalous behaviour of the nitrite results in bunching of peaks within a small chemical shift range making assignments based purely on chemical shifts speculative. The linewidth correlation as described by Au-Yeung and Eaton (1983) helps with the mer/fac assignment for the nitroammine series since the fac line is quite sharp indeed as predicted from it's pseudo-spherical symmetry. However the predicted linewidth ratio of 4:3:1:1 for trans:mer:cis:$(a)_5(NO_2)$ does not agree too well with the observed ratio of 2.3:4.6:2.4:1. The major factor causing this discrepancy is probably differences in rotational correlation time between the complexes. This would affect the quadrupolar relaxation which is directly proportional to the correlation time. Also the scalar relaxation contribution to the linewidth would vary due to the variation in the N-14 T_1 which governs the magnitude of this interaction.

Keeping in mind the empirical nature of the formulae just developed, we now discuss the application of these formulae to the assignment of Co-59 spectra from three different sources. The first and most important is the spectrum from aged solutions introduced previously in Table 4.3 and Figure 4.3. The assignments for these peaks are also given in Table 4.3. We have assumed for the purpose of these calculations that only nitro, nitrito, aqua and hydroxo ligands are present in these compounds. The chemical shift parameters for the aqua, hydroxo (Au-Yeung and Eaton, 1983) and nitrito (Au-Yeung, 1983) ligands are taken from previous work. The assignments show that species with less than four nitrite ligands are not observed probably because they are readily reduced to Co^{2+}. The assignment of the line at δ 8052 ppm to the pentanitroaqua or -hydroxo species is as expected on the basis of the arguments presented previously. The other two lines most likely arise from conformational isomers of the aqua/hydroxo species since none of the remaining calculated shifts falls close except for the dinitrite isomers which are better assigned to the line at δ 7970 ppm. In this context, conformational isomers would be isomers which are identical in every way except for the relative angular orientation of the ligands. Although the idea of conformational isomerism has, as far as we are aware, not been suggested for complexes containing monodentate species we are almost forced to suggest it not only for this set of peaks but also for the set of peaks at δ 8700 ppm in this spectrum and for one set of peaks in two of the other spectra about to be discussed.

The source of conformational isomerism is most likely solvent interactions since one would expect an unperturbed molecule to have the conformation in which all cis nitro's are perpendicular as observed in the crystal structure of cobaltinitrite (Ohba et al, 1978). Deviations from this geometry are however observed in the crystal structures of mer- (Laing et al, 1971) and fac- (Nuber et al, 1979) $Co(NO_2)_3(NH_3)_3$ in which the NO_2 groups are twisted as much as 20-30 degrees from the planes defined by the axes of the octahedron. The differences in line-width among the three peaks arises presumably from differences in electric field gradient or in correlation time due to differences in solvation. Although one might expect a rather short lifetime for exchange between these species it should be noted that these spectra were obtained on the WM-400 leading to fairly large chemical shift diferences. At lower fields these lines are much less resolved suggesting that chemical exchange is taking place with a lifetime of about 2×10^{-4} s. Since this does seem rather long for solvent rearrangement processes, it seems likely that rotation of the nitrite ligand is required to interchange the isomers. The barrier to rotation for such a process is unknown but might be expected to be reasonably high since there is a definite steric interaction when two cis nitro's are coplanar.

To test the validity of these models we decided to try to synthesize some new nitro-containing compounds and to assign their structure in solution without first attempting the difficult task of isolating pure compounds from complex mixtures. Indeed this is one of the benefits of solution-state NMR. In our first example of the cobaltinitrite solution we have identified at least three previously unknown nitrito species and assigned Co-59 chemical shifts to the previously reported aqua and diaqua species. We have, in addition, reacted cobaltinitrite with ethylenediamine, cyanide and azide and obtained in each case a complex mixture of compounds as shown by Co-59 NMR. Some of these compounds have been observed previously while we have made plausible assignments for a number of new compounds.

Figure 4.8 shows the spectrum obtained from a seven day old solution originally containing 0.1M cobaltinitrite

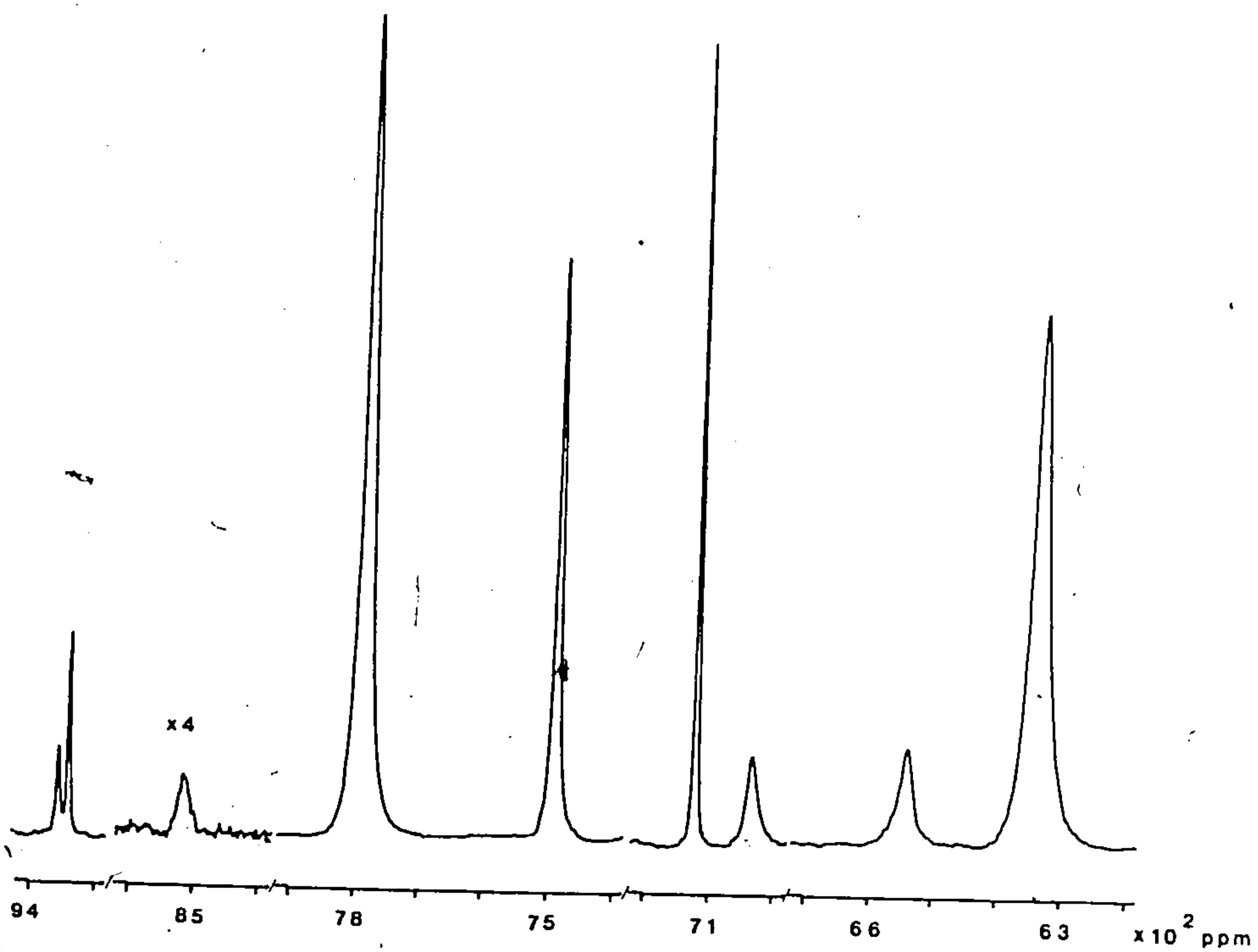

Figure 4.8 Co-59 NMR spectrum of reaction mixture of 0.1 M cobaltinitrite and 0.41 M ethylenediamine aged 7 days.

Table 4.7

Cobalt-59 NMR spectrum from the reaction of 0.1M sodium cobaltinitrite and 0.41M ethylenediamine

Obs. δ (ppm)	Linewidth (Hz)	Rel. Int.	Assignment	Lit. δ (ppm)(*)	Calc. δ (ppm)
9356	260	[illegible]	c-$Co(en)_2(H_2O)_2$	9150	9310
			c-$Co(en)_2(OH)_2$	9300	
9342	150	12	tr-$Co(en)_2(H_2O)_2$	9100	9780
			tr-$Co(en)_2(OH)_2$	9280	
8510	1350	2	c-$Co(en)_2(H_2O)(ONO)$		8781
7785	840	100	mer-$Co(NO_2)_3enH_2O$		7607
7530	150	(**)	fac-$Co(NO_2)_3enH_2O$		7669
7483	395	40	$Co(NO_2)_6$	7470	7510
7123	115	24	$Co(en)_3$	7145	7149
7035	1000	11	$Co(en)(NO_2)_4$	6795	6737
6539	1477	36	c-$Co(en)_2(NO_2)_2$	6551	6627
6337	1453	103	t-$Co(en)_2(NO_2)_2$	6323	6522

(*) Kidd and Goodfellow (1979), Au-Yeung (1983)

(**) observed only in fresh solutions

and 0.41M ethylenediamine (en). Table 4.7 shows the chemical shifts, linewidths, assignments and relative intensities of these peaks as well as one other peak observed in the fresh mixture. All members of the $Co(en)_x(NO_2)_{6-2x}$ series are observed with the chemical shifts agreeing reasonably well with those reported in the literature. The linewidth of the cobaltinitrite line is substantially higher than that observed at neutral pH (this solution is strongly basic) which is presumably due to extensive hydrogen-bonding between free en and the nitro groups. In fact the presence of en in the second-coordination sphere must stabilize the cobaltinitrite considerably since adding base normally results in the precipitation of cobaltic hydroxide. An alternative explanation is that a different species altogether has formed but its identity is not obvious.

The assignment of the two extreme low field lines is perhaps somewhat controversial since we are again suggesting that these two lines belong to conformational isomers of cis-$Co(en)_2(OH)_2$. It should be noted that the literature report (Yajima,et al, 1974) in which the assignment of these two lines to cis/trans isomers is made indicates that these lines were observed in decomposed samples and the assignment was made purely on the basis of the expectation of two isomers. However the calculated chemical shifts in column 6 of Table 4.7 show clearly that a much larger chemical shift difference is to be expected for the geometrical isomers and the calculated value for the cis isomer is the only one which is close to the observed shifts. The assignment of the line at δ 8510 is really dependent on the assignment of the line at δ 7785 which could either be due to cis-$Co(en)_2(H_2O)(NO_2)$ or to mer-$Co(NO_2)_3enH_2O$. The former assignment would justify the assignment of the δ 8510 line to the nitrito species since then the expected equilibrium constant for nitrito to nitro conversion, about 50, would be observed. In view of the previously observed rate constants for nitrito to nitro conversion (Miyoshi et al, 1983) it would be quite unlikely that any of the nitrito species would be observed if there was not a much larger amount of the nitro isomer present.

Some other comments can be made including the observation that, although a slight excess of en was used, trisethylenediaminecobalt(III) is not the major species formed presumably due to the extreme lack of reactivity of compounds with one or two nitro ligands. It should also be noted that trans-$Co(en)_2(NO_2)_2$ is formed in preference to the cis-isomer although this type of reaction is typically used to prepare the cis-isomer. A number of reports of the Co-59 shifts of these isomers have been published but the range of values reported for both isomers is rather large (Kidd and Goodfellow, 1978). Although we have followed our calculations in the assignment in the sense that the relative ordering is the same as the experimental, the agreement between the actual values is rather poor. However, the results of Au-Yeung (1983) in this lab indicate that this assignment is correct.

The reaction of cobaltinitrite with cyanide has been carried out with three different mole ratios, $CN^-/Co(NO_2)_6^{3-}$ = 5:1(A), 1:1(B) and 1:5(C), to try to obtain as many members of the cyanonitro(nitrito) series as possible. Table 4.8 lists the peaks observed in these reactions and two of the spectra, (A) and (C), are shown in Fig. 4.9. The third spectrum, (B), was taken at 2.1 T. The results show a predominance of nitrito-containing species which illustrates again the point that the nitro/nitrito equilibrium can be altered in complexes with a high degree of electron donation to the metal (vide supra). The pentacyanonitrito species is not necessarily more stable than the corresponding nitro isomer since the latter has been observed previously (Au-Yeung and Eaton, 1983) at δ 609 ppm (calculated δ 821 ppm) and interconversion between the two species may not be rapid. The previous report of a chemical shift of δ 1400 ppm for pentacyanonitro (Yamasaki et al, 1968) is close enough to our value (δ 1372 ppm) to lead us to believe that they had obtained the same compound as we did. Since there is no definitive structural assignment in their report, we can only assume that they have mistaken the nitrito species for the nitro species.

Table 4.8

Cobalt-59 NMR spectrum from the reaction of sodium cobaltinitrite and sodium cyanide

Observed δ (ppm)			Assignment	Calculated δ (ppm)
A	B	C		
0			$Co(CN)_6^{3-}$	-92
1340			$Co(CN)_5(ONO)^{3-}$	1372
2550			$c\text{-}Co(CN)_4(ONO)_2^{3-}$	2835
	3621		$tr\text{-}Co(CN)_4(ONO)_2^{3-}$	3601
		6477	$c\text{-}Co(NO_2)_4(CN)H_2O^{2-}$	6558
		6614	$m\text{-}Co(NO_2)_3(CN)ONO(H_2O)^{2-}$	6625
		7266	$Co(NO_2)_5(ONO)^{3-}$	7573
	7470	7470	$Co(NO_2)_6^{3-}$	7511
		7689		
	7711	7709		
		7715	???	
	7725	7725		
	7733	7733		
	8052	8052	$Co(NO_2)_5(H_2O)^{2-}$	8108

	[cobaltinitrite]/[cyanide]
A	0.2 M / 1.0 M
B	1.0 M / 1.0 M
C	0.5 M / 0.1 M

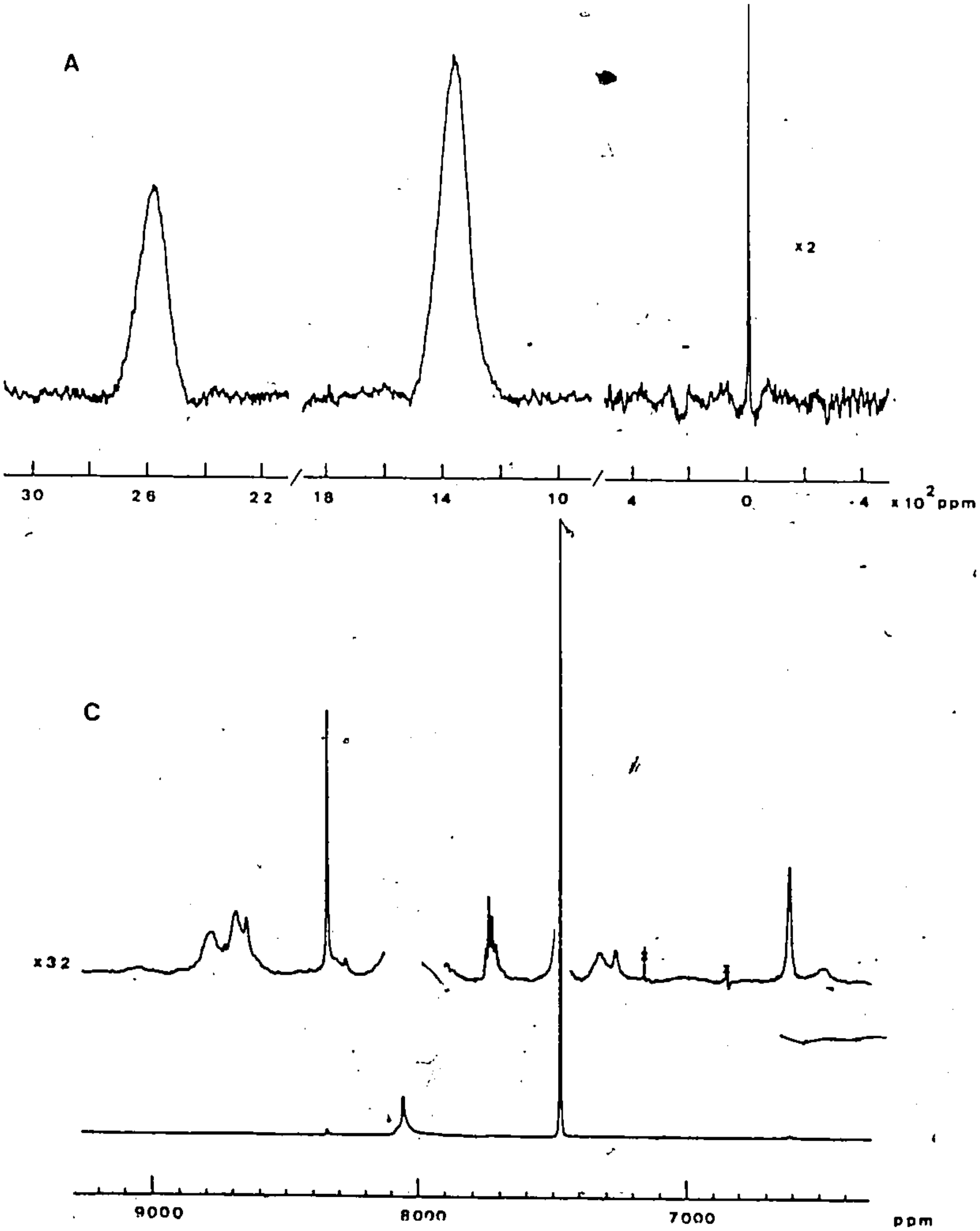

Figure 4.9. Co-59 NMR spectra of reaction mixtures of sodium cobaltinitrite and sodium cyanide. Spikes are marked with crosses. See Table 4.8 for more details.

The only dubious assignment would have to be that of the group of at least five narrow lines around δ 7700 ppm which are presumably conformational isomers of cyano containing species since these peaks are not observed in cobaltinitrite solutions. The small linewidth observed for all five peaks leads one to believe that the species involved is a fac isomer $Co(A_3B_3)$ but none of the possibilities fits anywhere close to the observed shift. The other high-field peaks observed in the spectrum of solution C are the same as observed in other cobaltinitrite solutions as expected since cobaltinitrite is in excess.

A final example to be considered is the spectrum obtained from a reaction mixture of 0.1M sodium cobaltinitrite and 1.0M sodium azide. The spectrum is shown in Figure 4.10 and the observed and calculated chemical shifts and the assignments based on these shifts are listed in Table 4.9. Only the six major peaks have been included in this Table and it is interesting to note that all six of the possible compounds containing three or more azides are formed. The small, sharp peak at the extreme high-field side of the spectrum (Obs.δ 8362, Calc.δ 8389) may very well be the trans-diazidotetranitro isomer. If so, then we have observed, all in one solution, six new members of the azidonitro series. As observed with the nitroammine series, the linewidth ratios are of little help with the assignments. Thus the expected ratio of 4:3:1:1 for

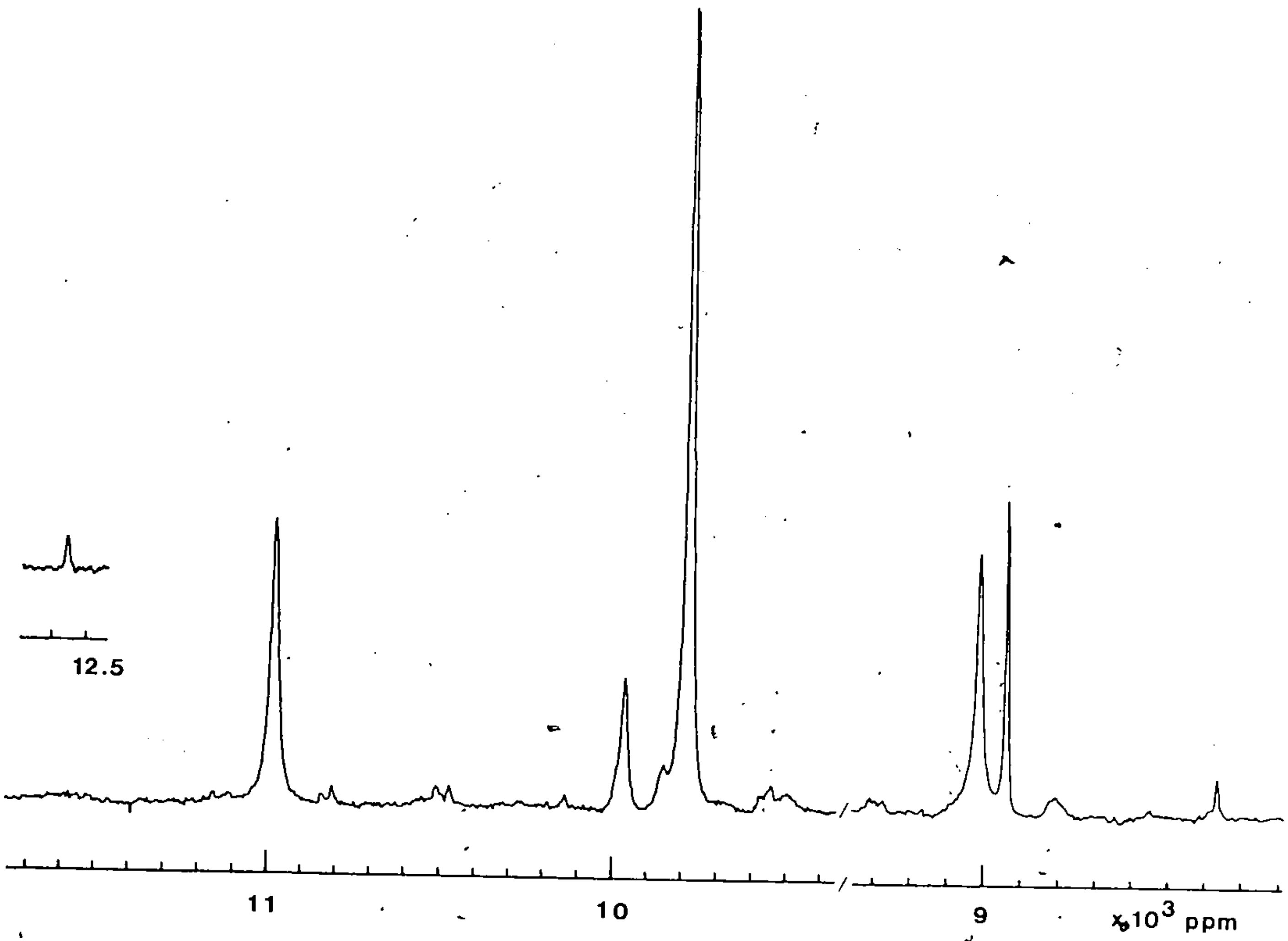

Figure 4.10 Co-59 NMR spectrum of reaction mixture of 0.1 M cobaltinitrite and 1.0 M sodium azide.

Table 4.9

Cobalt-59 NMR spectrum from the reaction of 0.1M sodium cobaltinitrite and 1.0M sodium azide

Observed δ (ppm)	Linewidth (Hz)	Rel. Int.	Assignment	Calc. δ (ppm)
8937	290	19	f-$Co(NO_2)_3(N_3)_3$	8861
9009	877	49	m-$Co(NO_2)_3(N_3)_3$	8966
9780	730	127	c-$Co(NO_2)_2(N_3)_4$	9844
9960	974	22	t-$Co(NO_2)_2(N_3)_4$	10110
10978	1072	39	$Co(NO_2)(N_3)_5$	11071
12558	310	5	$Co(N_3)_6$	12530

trans:mer:cis:mononitro is far from the observed ratios of 4:3.6:3.0:4.4. However, the linewidth for the facial isomer (290Hz) is considerably less than that of the others keeping in mind that scalar relaxation may contribute as much as 200 Hz to the linewidth. This observation is important as it confirms once again the reversal of the order of chemical shifts for the mer/fac and cis/trans pairs as predicted by our formulae.

It should be noted here that only a small number of all the possible isomers of complexes containing any number of azido, cyano, nitro, nitrito and aqua have been observed in these solutions but one should be careful about drawing conclusions about the relative stability of these isomers. A detailed study of the concentration and time dependence of the peaks observed here would have to be undertaken to yield this information and to gain an understanding of the mechanisms or, more properly, mechanistic network of these reactions. It seems clear, however, that solution work will be essential since such complex mixtures are obtained. From a synthetic point of view these reactions are not very useful or efficient but this should not stop the physical inorganic chemist from attempting to probe the equilibria involved and especially to elucidate the inter-ligand interactions observed here.

4.3.4 Addendum

Just before the writing of this thesis, we became aware of a recent publication by Tarasov et al (1984) in which some important experiments similar to ours on cobaltinitrite are reported. Without commenting on all the data in their paper, we would like to draw the attention of the reader to several serious errors in interpretation which are made. At the same time we wish to acknowledge that they have concurrently made some of the new discoveries which we report. First of all, they report Co-59 NMR chemical shifts and linewidths on aqueous cobaltinitrite. As observed by ourselves and many previous authors, they obtain peaks at δ 7465 ppm and δ 8067 ppm. They also report a 'new' peak at δ 8632 ppm analogously to one of our 'new' peaks but do not observe any of the other four 'new' peaks we have observed. The linewidth of the δ 7465 ppm is reported as 143 Hz which is considerably larger than the more accurate value of 55 Hz we obtain on high resolution instruments. As we also report, they have observed intensity ratio changes with dilution and addition of sodium nitrite consistent with aquation processes. However, they assign the δ 7465 ppm peak to the dinitritotetranitrocobaltate(III) species without giving a clear explanation. Apparently they base this assignment on the observation of a Co-59 NMR chemical shift of about δ 6000 ppm for polycrystalline sodium cobaltinitrite and, as they state at the beginning of their article, the expectation of a chemical shift between nitro and nitrito isomers of about 1200 ppm. This rationalization is weak for several reasons. The worst error they have clearly made in their calculation of the chemical shift of the solid compound. It seems quite likely that the chemical shift they quote is that of the high-field maximum rather than the required point 9/25 of the splitting to low-field of that point which is about δ 7500 ppm. The authors also quote some N-14 spectra which are of considerably lower quality than ours. However their interpretation of these spectra is basically sound and they confirm the large upfield coordination shift for nitrite.

Chapter 5

Field dependence of the Co-59 NMR of polycrystalline sodium cobaltinitrite

5.1 Introduction and Theory

The three principal interactions in the solid state are the dipolar, the quadrupolar and chemical shielding. The first arises from the fact that each nucleus acts as a magnetic dipole and thus exerts a magnetic force on all nuclei close to it. This interaction, as are the others, is angle dependent and thus in a single crystal causes the resonant line to shift as the sample is reoriented with respect to the magnetic field. The quadrupolar effect only arises with nuclei having nuclear spin of I>1/2 and requires a non-zero electric field gradient arising from an asymmetrical electron density distribution. The net result of this interaction is to split the resonance line of the quadrupolar nucleus into 2I+1 lines in first order. When the quadrupolar interaction becomes comparable to the Zeeman interaction then for half-integral spins the central line also shifts. In a powdered sample with random orientation of all the nuclei the spectrum consists in first order of 2I+1 lines with an intensity distribution as calculated by Cohen and Reif (1957). To second-order the satellites disappear and the central line appears as shown in Figure 5.1A. The splitting in this line is given by Eq. 5.1:

$$\delta\nu = \frac{25\,[I(I+1)-(3/4)]}{16\,[2I(2I-1)]\,\nu_0}\,A^2$$

where A is the quadrupolar coupling constant and axial symmetry is assumed. The third interaction, the shielding effect, arises from the presence of electron density around the nucleus. In a spherical atom, the net result is to shift the resonance line from that of the bare atom. In less than spherical symmetry the line position is again angle dependent and the familiar powder pattern as observed already by Bloembergen and Rowland (1953) results. This type of spectrum consists of a strong peak at the position of the second-largest principal (diagonal) value of the shielding tensor, σ_{22}, and shoulders or steps at the other two values, σ_{11} and σ_{33}.

The analysis of single-crystal data even if all three interactions are present is tedious but possible if accurate data can be obtained. However, the effort to obtain suitable single crystals and to set up and do the actual experiments is difficult enough to limit this technique to specialists only. Therefore the possibility of doing NMR on polycrystalline materials clearly has its attractions. The analysis of polycrystalline NMR spectra is in itself not always simple unless one is satisfied to just recover the isotropic chemical shift and eliminate all broadening interactions by 'magic angle' sample spinning (MASS) or multi-pulse techniques. If one is determined to recover information about dipolar interactions, quadrupole coupling constant and asymmetry parameter and values for the principal values of the shielding tensor, a lot of work must be done. Fortunately the theory for the most complicated case likely to be encountered has been worked out by Baugher et al (1969). They give formulae for the positions of the shoulders and singularities in the powder pattern for the central transition in the case of completely assymetric quadrupolar and shielding effects. For instance, the location of the low-field peak (ν_o) typically observed at low fields when quadrupolar dominates but shielding anisotropy (SA) is not negligible (which is the same peak which remains at very high fields when SA dominates) is given by the following equation:

$$\nu_L = \nu_o + R(3-\eta)^2/144\nu_o - \sigma_{22}\nu_o$$

where $R = \nu_Q^2[I(I+1)-3/4]$, $\nu_Q = 3A/2I(2I-1)$ and η is the asymmetry parameter for the quadrupolar effect and expresses the deviation from axial symmetry. Also more extensive treatments of simpler cases have been worked out by Jones et al (1963) who treat the case of axially symmetric quadrupolar and shielding anisotropy and by Narita et al (1966) who treats completely asymmetric quadrupolar. Apart from the difficulty of the analysis itself other complicating factors include crystallographic isomorphism (e.g. $K_3Co(CN)_6$) (Lourens and Reynhardt, 1972), crystallographic inequivalence ($Co(NH_3)_6Cl_3$) and the presence of molecular rotation (Reynhardt, 1977). In this thesis, the field dependence of the polycrystalline solid-state NMR of trisodium cobaltinitrite is discussed.

At present the scope of Co-59 NMR on polycrystalline solids appears to be quite limited. The reason for this is that both the quadrupolar interaction ($A > 10$ MHz) and the shielding anisotropy ($\sigma_{11} - \sigma_{33} > 500$ ppm) are very large in all but octahedral complexes. This typically results in a spectrum in which even the central line has been broadened beyond recognition. Although the dipolar linewidth is usually quite small (a few kHz) and can be reduced by MASS, the relatively small spinning rate of 4 kHz currently attainable on MASS probes does little to narrow peaks 50 kHz wide. It should be pointed out also that while shielding anisotropy effects, if small, theoretically average to zero under MASS, quadrupolar second-order splitting can at best be reduced by a factor of about 3.5. Slightly better results can be obtained by spinning at angles different from the 'magic angle', 54.7°. The optimum angle depends on the asymmetry parameter but if that is zero then rapid spinning at 36° or 75° can reduce the central line splitting by an order of magnitude (Ganapathy et al, 1982; Samoson et al, 1982). Oldfield has coined the name VASS (variable angle sample spinning) for this new technique which has been recently applied to O-17 solid-state NMR (Schramm et al, 1983). As far as we know, the Co-59 MASS experiment reported on in this thesis is the first to be attempted. Before we leave the subject of Co-59 solid-state NMR, we should note that when polycrystalline NMR is not feasible for the mentioned reasons both single-crystal work as elegantly performed by Spiess et al (1969) and nuclear quadrupole resonance (NQR) (Das and Hahn, 1958) remain as alternatives (Watanabe and Yamagata, 1967).

5.2 Results and Discussion

We decided to investigate the field dependence of the quadrupolar splitting in sodium cobaltinitrite after our first measurement at 5.9 T yielded a value for the quadrupole coupling constant which was considerably lower than that reported earlier by Saraswati et al (1967). Spectra were taken at six different fields and the results are summarized in Table 5.1. Five of the spectra are shown in Figure 5.1 along with a MASS spectrum obtained at 4.7 T. Qualitatively the expected trend of decreasing second-order quadrupole splitting is observed but the calculated quadrupole coupling constants shown in column 3 of Table 5.1 vary with field which shows that something is amiss. In fact, at the two highest fields the quadrupole effect is barely noticeable as a slight asymmetry in the lines and the

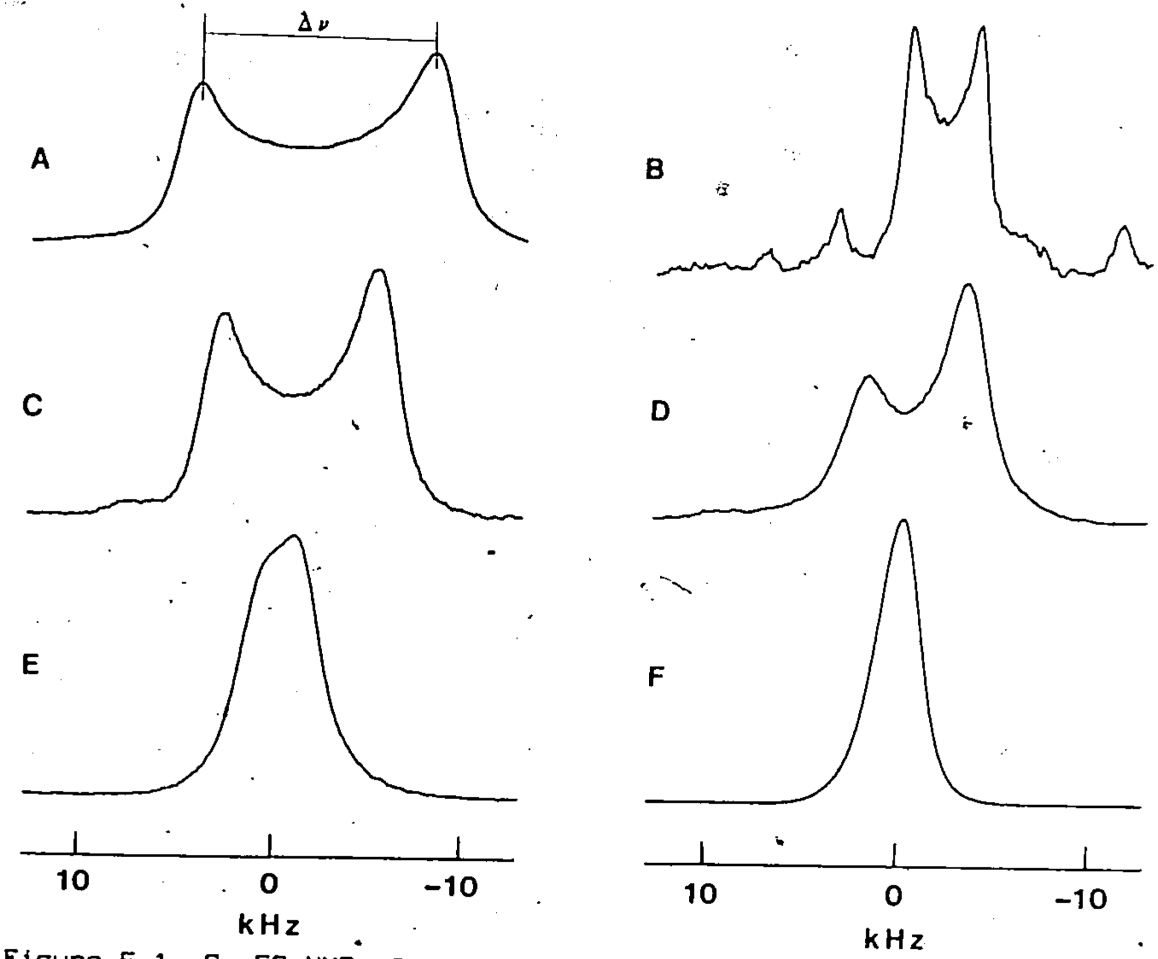

Figure 5.1 Co-59 NMR of polycrystalline sodium cobaltinitrite. A) 4.7 T.. B) 4.7 T, MASS at 3.85 kHz. C) 5.9 T. D) 7.1 T. E) 9.5 T. F) 11.8 T. All spectra except B run on static samples.

Table 5.1

Field dependence of the Cobalt-59 NMR of polycrystalline sodium cobaltinitrite

ν_o, MHz (a)	Splitting kHz	A MHz	Chemical Shift δ, ppm (b)
21.52	35	7.5	7601
47.85	12.3	6.6	7604
59.80	8.0	6.0	7603
71.75	5.2	5.3	7598
95.66	1.9 (c)	<3.7	7592
119.57	0.5 (c)	<3.7	7594

(a) For cobaltinitrite

(b) estimated error ±5 ppm

(c) estimated upper limit (only one maximum observed)

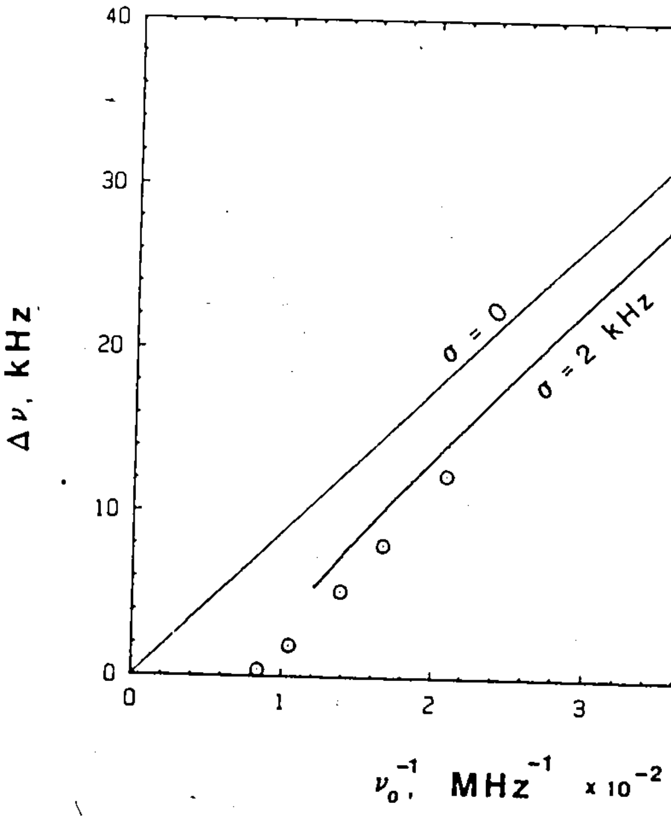

Figure 5.2 Plot of $\delta\nu$ vs ν_0^{-1}. Upper solid line calculated with A = 8.1 MHz. Lower line obtained from total lineshape calculation with σ = 2 kHz.

$\delta\nu$'s are probably overestimated. In Figure 5.2 $\delta\nu$ is plotted against ν_o^{-1} showing that the greatest deviation occurs at the highest field since a line passing through the experimental points does not pass through the origin. The upper solid line in the diagram is calculated with A = 8.1 MHz which we estimate on the basis of the considerations below.

There are two plausible contributions to this observed deviation. One is the effect of shielding anisotropy (SA) which, for Co-59, has been shown by Spiess et al (1969) to be present whenever an appreciable quadrupolar effect is observed. The absence of shoulders on the low-field spectra show that the electric field gradient possesses close to axial symmetry and it is reasonable to assume that any SA would also be axially symmetric. In this case the theory of Jones et al (1963) can be applied to determine the magnitude of the SA. The effect of SA depends on the sign. If the anisotropy is negative the plot of $\delta\nu$ vs. ν_o^{-1} actually curves upward at high fields whereas for positive anisotropy it curves downwards as we have observed. However, in both cases, one also expects an appreciable shift of the spectrum away from the isotropic shift. In the absence of SA this is found at a point 9/25 of $\delta\nu$ to high field of the smaller maximum. Chemical shifts calculated in this way are shown in Table 5.1 and while there is a progressive decrease in chemical shift with increasing field the magnitude is far too small to add appreciably to the downward curvature of the plot in Figure 5.2. Also if the SA was quite large, say -60 ppm, one might expect the development of a prominent shoulder to low field of the high-field spectra which is not observed in the case of the 9.5 T and 11.8 T spectra. However, a small shoulder is observed on the low-field edge of both the 5.9 T and 7.1 T spectra. This may be an artifact. Thus we conclude the shielding anisotropy is less than -10 ppm as estimated from the field dependence of the chemical shift and in view of that we may estimate the isotropic chemical shift to be δ 7601 ± 5 ppm. For a comparison of this value to that obtained in solution, see the previous chapter. It should be noted here that the lack of axial symmetry for the shielding anisotropy would have no effect on the conclusions just reached. For instance the lack of field dependence of the chemical shift could be the result of a totally asymmetric (eta = 1) anisotropy but again the lack of shoulders in the high-field spectra shows that the magnitude of the anisotropy must be small.

The only other obvious source of deviation from the normal field dependence of the second-order quadrupolar splitting is the dipolar linewidth which as Casabella (1964) and others have noted causes the quadrupolar splitting to be smaller than expected. Only in the limit of zero linewidth is the true quadrupolar splitting observed since the convolution of the powder pattern with a dipolar linewidth causes the intensity distribution on the high field side of the low field singularity to increase more rapidly than that on the other side since the powder pattern intensity is zero on the low field side and vice versa for the high field singularity. While the effect of a dipolar linewidth, σ, is easily calculated for spectra in the dispersion mode where the peak separation increases by 2σ, the effect on the absorption spectrum is not as simple to calculate. In this case, a complete simulation of the lineshape is necessary using the method outlined by Casabella (1964), which we have implemented using a FORTRAN program which uses a sophisticated IMSL integration routine, DCADRE. The results of these calculations using a linewidth of 2 kHz are shown in Figure 5.2 as the lower solid line. It ends at the high field limit at the point where only one maximum can be distinguished. This explains why only one maximum is observed in the two high field spectra. Although the fit to the experimental line is significantly improved by the inclusion of the dipolar effect, the fit is not perfect. An increase of the dipolar linewidth is not possible since then the calculated half-widths would be far too large for the two single line spectra. As it is, the calculated linewidth is already twice too large for these peaks using the above-mentioned parameters. Also the value of 2 kHz agrees well with that estimated from the two-peak spectra from the distance from e.g. the low field peak to the point to low field where the height is one-half that of the maximum. An exact theoretical calculation of the dipolar linewidth is not possible since the detailed crystallographic structure of our molecule is not known. A calculation including the six neighbour nitrogens, six sodiums at a distance of 5.5 A and twelve sodiums at a distance of 7.0 A, as found in the crystal structure of the dipotassiumsodium salt, yields a minimum dipolar linewidth of 1.5 kHz. This calculation was carried out using the formula of Kambe and Ollom (1956) for the dipolar second moment for unlike particles and Van Vleck's (1948) formula relating the half-width to the second moment.

There is then clearly a small but reasonably well established discrepancy between the experimental results regarding the field dependence of the Co-59 solid-state NMR of sodium cobaltinitrite and the theoretical calculations. Considering that the theory itself is not likely to be incorrect although some new phenomena may not have been taken into account, the only reasonable explanation for this behaviour is that some degree of motional narrowing is taking place. This would qualitatively be expected to have more effect the higher the field where the splittings are smaller which explains why the largest relative reductions are observed at the highest fields. The nature of the motion required to do the averaging depends of course on the origin of the electric field gradient. As suggested in the discussion in the previous chapter, this is probably related to the same effect which causes the splitting in the IR spectrum. Whatever this effect is, it must surely have a second sphere origin since the symmetry of an isolated cobaltinitrite ion can reasonably be expected to be T_h if the nitro groups are not rotating and effectively O_h if they are. The deviations from this symmetry could be averaged either by rapid rotation of the nitro groups or by motion of the cations with respect to the anion. Motional narrowing has been detected in solid $Co(NH_3)_6Cl_3$ (Reynhardt, 1977) and $K_3Co(CN)_6$ (Lourens and Reynhardt, 1972) by observing the temperature dependence of the Co-59, proton and deuteron (in the perdeuterated compound) NMR parameters of these molecules. We have not attempted such studies because of the instability of our molecule at elevated temperatures.

The origin of the electric field gradient in the second coordination sphere rather than in the first sphere is not too surprising considering the results and discussion of the previous chapter. As mentioned before, Spiess et al have shown with several examples that the quadrupole coupling constant is roughly proportional to the size of the shielding anisotropy when the origin of both effects arises primarily from an asymmetric ligand field. Although only one other simultaneous determination of quadrupole coupling constant and shielding anisotropy on a spherically symmetrical molecule has been made, it is interesting to note that the same deviation from this correlation we obtain for cobaltinitrite is not observed in this other case. In $K_3Co(CN)_6$, where the effects must also arise from the second sphere, the observed quadrupolar coupling constant of 5.88 MHz (eta = 0.9) is accompanied by a reasonably large SA ($\sigma_{11} - \sigma_{33}$) of 180 ppm (Lourens and Reynhardt, 1972) whereas the molecule trans-$Co(en)_2(NO_2)_2$ with a relatively small coupling constant, 13.2 MHz (eta = 0.7272), has a ($\sigma_{11} - \sigma_{33}$) of 400 ppm (Spiess et al, 1969).

Finally, the effect of MASS on the Co-59 NMR of polycrystalline sodium cobaltinitrite is illustrated in Figure 5.1B which shows the result of an experiment carried out at a field of 4.7 T and a sample spinning rate of 3.85 kHz. This represents the first attempt at Co-59 MASS that we know of and one of few experiments carried out to date on quadrupolar nuclei. The observed decrease in the apparent linewidth is due, of course, to the reduction of the dipolar linewidth. The reduction in the second-order quadrupolar splitting by about a factor of 3.5 is roughly as expected from the theoretical work of Samoson et al (1983) and Ganapathy et al (1982). As noted earlier, better results could be obtained by VASS at 75°.

Chapter 6

Rotating-Frame Relaxation Time Experiments

6.1 Introduction

In this chapter we describe the application of the $T_{1\rho}$ method to some problems involving scalar relaxation of the second kind (SR2). A fairly extensive literature review of the applications of $T_{1\rho}$ in the liquid state, including the study of chemical exchange, has been given in Ch. 1. Some details of the experimental aspects of these experiments have been given in Ch. 2. Before analyzing our own results, we will briefly review some relevant literature work.

The first set of experiments involves determining the contribution of SR2 to the Co-59 NMR linewidth of symmetrical Co(III) complexes. Several studies of this problem have been made using various techniques but, to our knowledge, we have carried out the first study using Co-59 $T_{1\rho}$. Typically what previous authors had done was to measure the Co-59 T_1 and T_2 and the X-nucleus T_1 (or T_2) and then to calculate the Co-X coupling constant using Eq. 7.1:

$$\frac{1}{T_1^{X}} - \frac{1}{T_2^{X}} = \frac{(2\pi J)^2\, T_1^{S}\, n_S\, S(S+1)}{3} \qquad [7.1]$$

where T_n^X refers to Co and n_s is the number of X-nuclei. This formula is only valid when $(\omega_X^2 - \omega_s^2)(T_1^s)^2 >> 1$ which is usually the case. Also other contributions to T_2^X must be negligible. The latter criterion may fail when the instrumental inhomogeneity is large or when chemical exchange broadening is relatively large. In the case of less symmetrical molecules which nevertheless have a fairly long T_1 (e.g. trans-$Co(en)_2(NO_2)_2$ in CH_3CN; $T_1^{Co} = 2.1$ ms (Au-Yeung, Buist and Eaton, 1983)) but inequivalent X-nuclei this formula cannot be used directly unless all but one of the coupling constants have been determined separately. Applications of this formula have been made by Rose and Bryant (1979a, 1979b) to several complexes. Since they obtained the Nitrogen-14 T_1's by measuring the N-14 linewidths and assuming that $T_1 = T_2$, their calculated J values have to be considered somewhat inaccurate since, as Au-Yeung et al (1983) have recently shown, T_2^N is usually less than T_1^N due to SR2 by Co. Furthermore, as we have already mentioned, their results for cobaltinitrite are incorrect since they mistook a free nitrite signal for coordinated nitrite.

Another method of determining the contribution from scalar relaxation of the second kind if other mechanisms are thought to be present is to decouple the X-nucleus. This has been carried out by Doddrell et al (1979b) who showed that decoupling both N-14 and H-1 reduced the linewidth of hexaamminecobalt. These authors also made use of isotopic substitution of the X-nucleus and subsequent X-nucleus detection. They determined J to be 47 ± 3 Hz which compares favourably with the results of similar work by Yamasaki et al (1979) who obtained J = 45.5 Hz. The latter authors also determined J for trisethylenediaminecobalt(III) by the same method. Other determinations of coupling to Co have been from the X-nucleus spectrum where X is spin 1/2 or much more rarely from the Co-59 spectrum in cases when the Co T_1 is long as it is in cobalticyanide which allows J(Co-59 - C-13) (126Hz) to be determined readily (Chacko and Bryant, 1984). The coupling constant can also be very large which means that the Co-59 T_1 would have to be quite short to prevent observation of the coupling. A good example is that of $Co(PF_3)_4$ for which a J(Co-59 - P-31) of 1222 Hz has been measured in the Co-59 spectrum (Lucken et al, 1967). Another method which may have some potential is the spin-echo method which has been applied in several cases of SR2, the first example being reported in 1952 (Hahn and Maxwell).

The second set of $T_{1\rho}$ experiments involved the study of SR2 in thiourea protons in the free molecule and in two zinc complexes. Study of the free thiourea was carried out primarily as a check to ensure the method gave correct results. Although no previous study of SR2 in thiourea has been made, the chemical exchange process which exchanges 'inner' and 'outer' protons has been studied by several workers beginning with the work of Eaton and Zaw in 1976. None of these studies mention the possibility of SR2 since at the low temperatures required to freeze out the exchange the contribution from SR2 is quite small. Nevertheless, since the activation energy is small, it is clear that an accurate determination of the contribution of SR2 is necessary if an accurate analysis of chemical exchange is to be carried out. In the case of thiourea, the SR2 contribution can be easily calculated given the known coupling constant determined from the N-15 enriched compound. However the N-14 T_1 must also be measured at each temperature required for the chemical exchange measurements. So far, the temperature dependence of the N-14 spin-lattice relaxation time has not been determined.

A similar difficulty exists in the case of the zinc thiourea complexes studied in this thesis. Previous work on chemical exchange processes in these complexes has been carried out by Eaton and Zaw (1976). In acetone solutions of $Zn(tu)_2Cl_2$ containing excess tu, a single peak is obtained at room temperature indicating that both exchange between free and complexed tu and rotation about the C-N bond are fast. Both exchange processes can however be frozen out leading to the observation that four peaks are obtained at very low temperatures. Curiously enough only a single peak could be observed for $Zn(tu)_4(ClO_4)_2$ even down to -80 °C. Since this work was done at a modest field strength we decided to repeat the variable temperature studies and to determine a suitable temperature for studying SR2 in these complexes. Although the studies in the thesis were carried out primarily out of interest for the spectroscopic properties, it should be noted that these and other tu complexes of Zn, Co and Ni are important catalysts for various reactions such as that between carbonyl compounds and anilines (Eaton, Majid and Tong, 1982) and isomerization of anils (Eaton and Tong, 1980). Other important references in this area include the work of Boate and Eaton (1976, 1977). Since the catalytic activity may depend on the rates of ligand exchange, it is important to be able to obtain estimates of these rate constants.

6.2 Results and Discussion

6.2.1 Co-59 $T_{1\rho}$ experiments

As mentioned in the Experimental Section, the high-power CXP-200 instrument is particularly well suited for $T_{1\rho}$ experiments allowing multinuclear $T_{1\rho}$ experiments, in particular, to be carried out with ease. This led us to the idea of performing a Co-59 $T_{1\rho}$ experiment to confirm in some way the N-14 results we obtained for cobaltinitrite. By measuring the N-14 T_1 using the $T_{1\rho}$ method and comparing it to the directly measured value of 150 μs we could confirm, in admittedly a rather indirect fashion, that the

N-14 signal we observed was in fact due to cobaltinitrite. More importantly an accurate value for the coupling constant could be determined.

The test case for the Co-59 $T_{1\rho}$ method was chosen to be trisethylenediaminecobalt(III). The results obtained for this compound were quite satisfactory with reasonably exponential decays being observed at the spin-locking powers used. Using the measured T_1 of 9.5 ms, which agrees reasonably well with previous reports, the following analysis was possible. Since the measured value of $T_{1\rho}$ at any spin-locking power contains a contribution from T_1 processes as well as T_2 processes, the contribution from T_1 processes must first be subtracted. In the extreme narrowing limit, it is sufficient to subtract the spin-lattice relaxation rate from the rotating frame relaxation rate to obtain the combined contributions of SR2 and CE. In the case of trisethylenediaminecobalt(III), we can assume that contributions from SR1 and CE are negligible if present and thus we obtain Equation 7.2:

$$\frac{1}{T_{1\rho}} - \frac{1}{T_1} = \frac{8(\pi J)^2 . T_1^N}{3\,(1 + \omega_1^2 . {T_1^N}^2)} \qquad [7.2]$$

If we invert both sides of Eq. 7.2, as suggested by Morgan and Strange (1969), we can then plot the L.H.S of the resulting equation versus ω_1^2 and obtain a straight line with slope $3T_1^N/8(\pi J)^2$ and intercept $3/8(\pi J)^2 T_1^N$. With two independent expressions containing T_1^N and J, it is easy to see that both these quantities can be obtained. The data for the trisethylenediamine complex has been analyzed in the above manner and the plot is shown in Figure 6.1. The original data is listed in Table 6.1. The values for the slope, intercept, T_1^N and J are shown in Table 6.2.

The agreement with the literature values, which are also shown in Table 6.2, is quite good allowing for an error of 5-10%. This error is considerably larger than the statistical error obtained from the least-squares analysis. However, one can never be cautious enough about the absolute errors involved in relaxation time measurements. A good way to test the results of an experiment such as this is to repeat several times preferably on different days, on different solutions and, best of all, on a different instrument, if possible. With this set of data in particular one has to be somewhat cautious since we are pushing the limits of the given equation for SR2 at both limits of spin-locking power strength. As has been pointed out previously, this equation is strictly valid only for certain values of the spin-locking field strength. At the low power limit, the spin locking field strength must be substantially larger than the observed linewidth. However the exact point at which the error due to encroaching on this limit becomes larger than say 10% is not known.

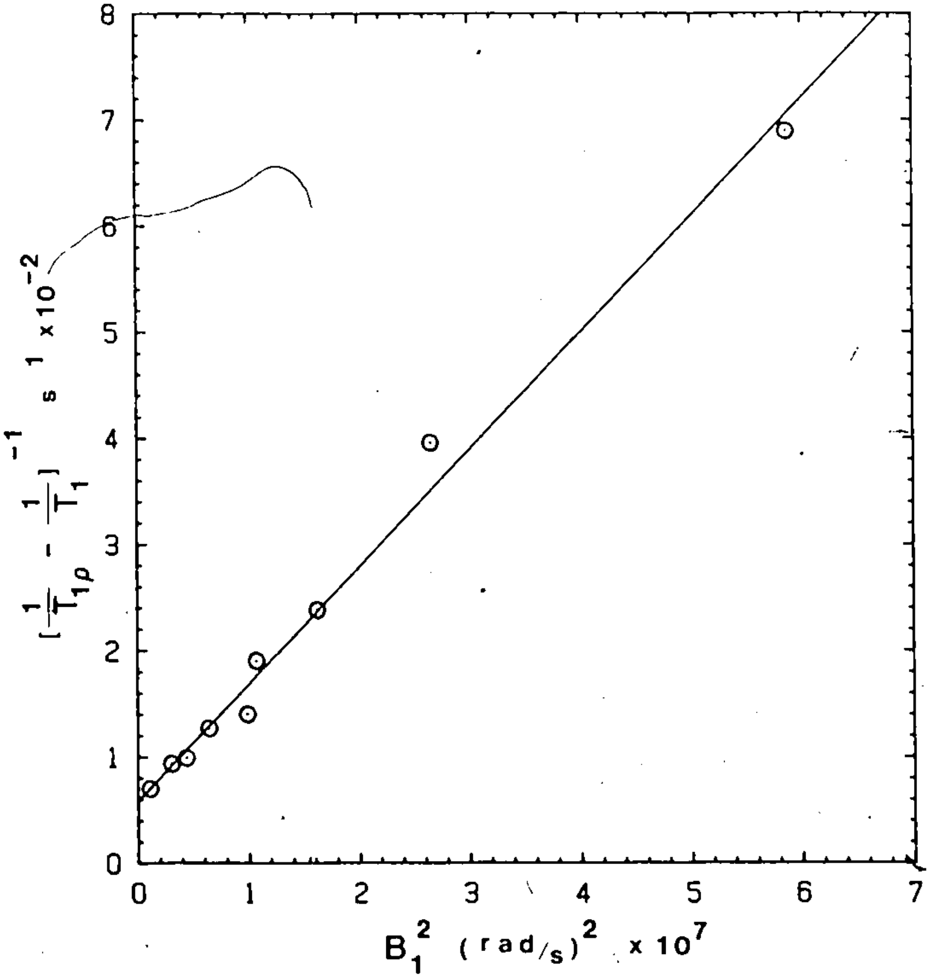

Figure 6.1 Plot of Co-59 $T_{1\rho}$ data on trisethylenediaminecobalt(III)

Table 6.1

Co-59 $T_{1\rho}$ data on trisethylenediaminecobalt(III) and cobaltinitrite

T - 294 K

$Co(en)_3$		$Co(NO_2)_6$	
B_1 (rad/s)	$T_{1\rho}$ (s)	B_1 (rad/s)	$T_{1\rho}$ (s)
7660	.00796	12300	.0209
5150	.00733	10600	.0188
4030	.00653	9130	.0171
3270	.00611	7480	.0156
3140	.00580	6283	.0139
2530	.00557	5067	.0121
2090	.00495	4080	.0111
1750	.00481		
1050	.00410		

Table 6.2

Analysis of Co-59 $T_{1\rho}$ data

	$Co(en)_3$	$Co(NO_2)_6$
T_1(Co-59): (ms)	9.5 (a)	34.1 (a)
T_2(Co-59): (ms)	2.8 (b) (3.65)	5.3 (b) (9.41)
slope: (s^3/rad^2)	1.10×10^{-7}	2.56×10^{-10}
intercept: (s/rad^2)	5.94×10^{-3}	1.30×10^{-2}
J(Co-59 - N-14): (Hz)	49.8 (Lit. 45.5) (c)	58.9
T_1(N-14): (ms)	0.431 (Lit. 0.445) (d)	0.140 (0.150) (a)

(a) measured directly in this work by inversion-recovery

(b) obtained from the measured linewidth; B_0 inhomogeneity unknown (value in parenthesis calculated from the intercept and T_1)

(c) from analysis of N-15 spectrum (Yamasaki et al, 1979)

(d) direct measurement by Au-Yeung et al (1983)

The results for cobaltinitrite are shown in Fig. 6.2 and Tables 6.1 and 6.2. The quality of data is somewhat better here perhaps because of the higher S/N. However, there is a marked difference between the T_2 back-calculated from the observed intercept and the measured linewidth. In retrospect, a similar effect, though much smaller and explainable in terms of the above error discussion, is also observed for the trisethylenediamine complex. The possibility arises that another mechanism is contributing to T_2 although part of the discrepancy can be assigned, of course to B_0 inhomogeneity. It is encouraging to note that the T_1^N obtained in this way agrees very well with that measured directly. The coupling constant is somewhat smaller than one would calculate using the observed linewidth but this discrepancy is significantly less than the difference between our results and that calculated by Rose and Bryant (1979b).

The fact that the cobaltinitrite value is substantially larger than that measured for both the trisethylenediamine and the hexaamminecobalt complexes can be qualitatively explained on the basis of changes in hybridization (Frei and Bernstein, 1963). If the Co-N bond was 100% covalent, then the coupling constant would be approximately proportional to the amount of s-character in the N orbital (sp^2 hybrid for NO_2; sp^3 for NR_3) forming the bond. This leads to the qualitative prediction of a larger

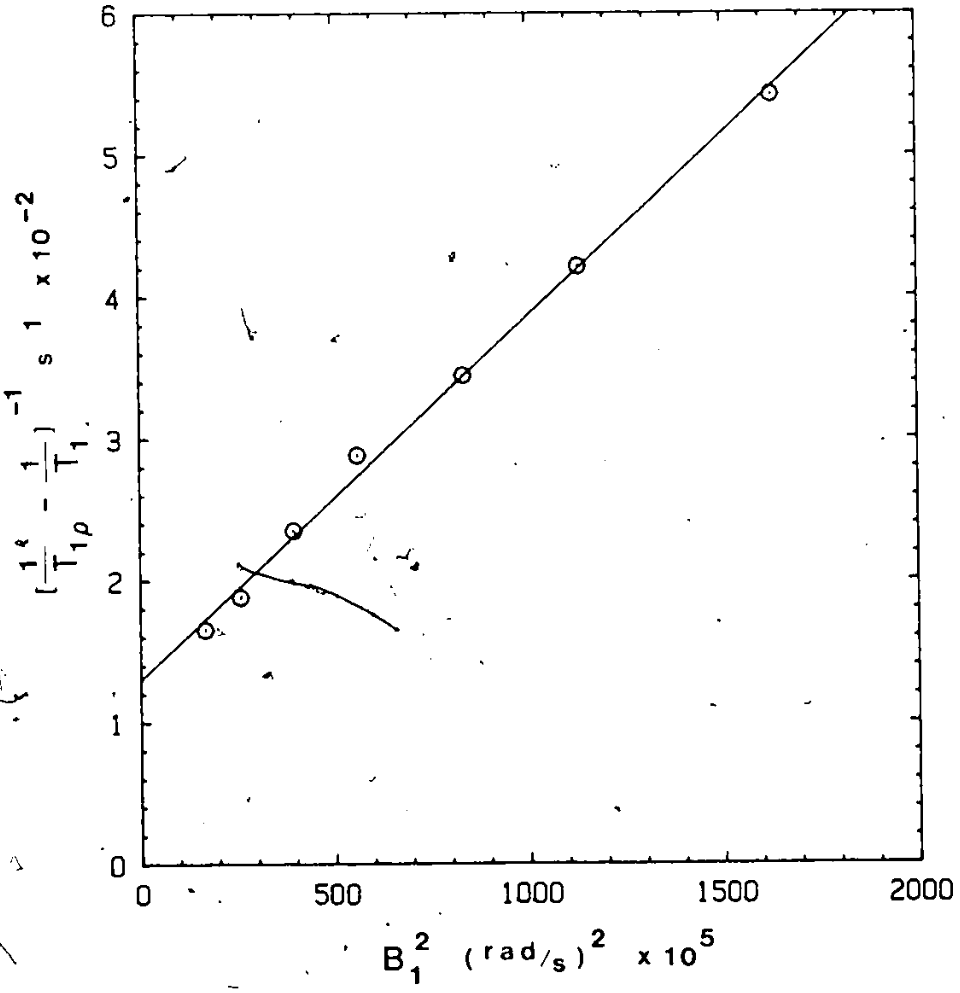

Figure 6.2 Plot of Co-59 $T_{1\rho}$ data on cobaltinitrite

J for cobaltinitrite. Other effects such as changes in the spin-dipolar and orbital terms may also play a role (Wasylishen, 1977). Unfortunately a detailed discussion of the magnitude of spin-spin coupling constants is difficult enough even with a detailed knowledge of the electronic structure of a molecule and since the latter is hardly well known for Co complexes such a discussion will clearly have to await additional theoretical insight.

6.2.2 H-1 $T_{1\rho}$ experiments

The H-1 $T_{1\rho}$'s on thioureas were carried out on both the CXP-200 and WM-250. Fairly extensive measurements were made on free thiourea (tu) on both instruments to compare the results obtained. The two instruments gave comparable numbers at low to intermediate fields but at the highest fields the CXP-200 gave the more accurate results. The results plotted in Fig. 6.3 and listed in Table 6.3 were all obtained on the CXP-200. Before discussing the calculated results tabulated in Table 6.4, we should mention that all the information obtainable by the $T_{1\rho}$ method is actually obtainable in the spectrum itself given the possibilty of some simple spectral manipulation.

The interesting question to be asked here is 'What are the relative contributions of scalar relaxation of the second kind and chemical exchange?' The simple solution to this problem is to observe the N-15 satellites if

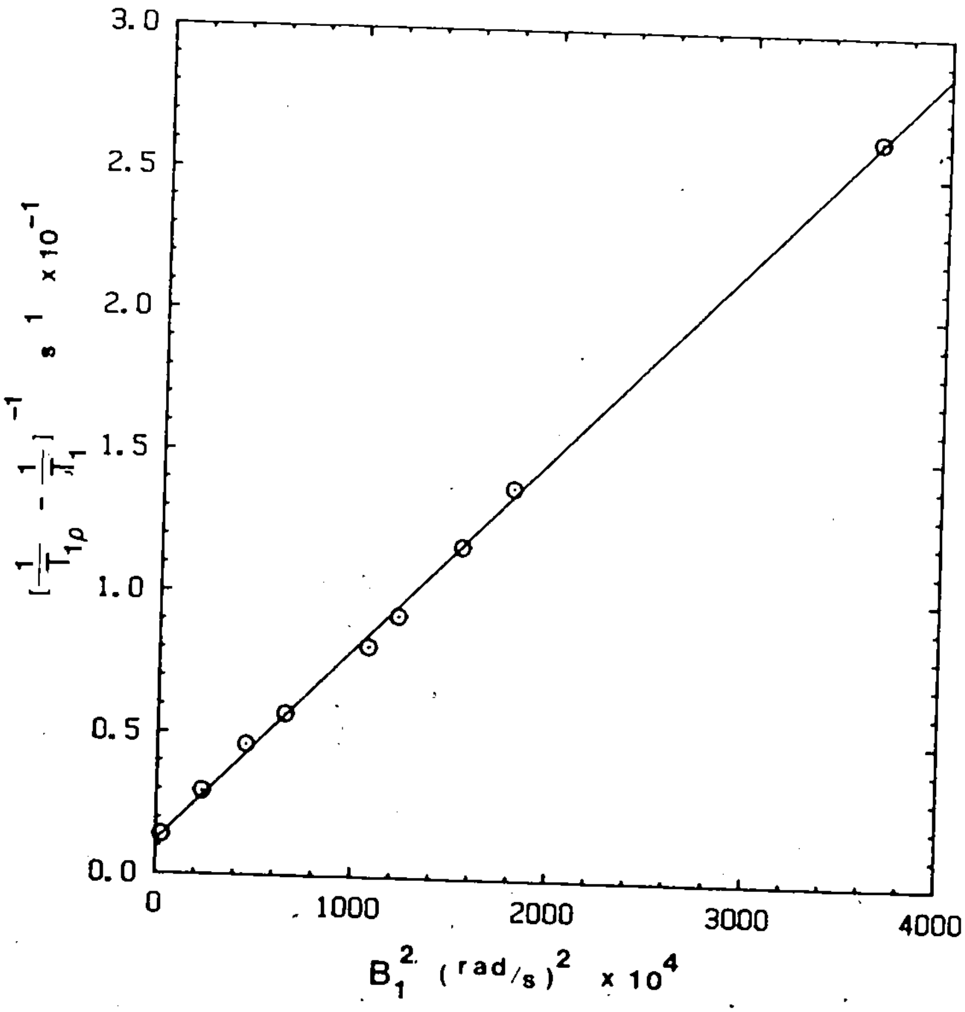

Figure 6.3 Plot of H-1 $T_{1\rho}$ data on thiourea

Table 6.3

Proton $T_{1\rho}$ data on thiourea and $Zn(tu)_4ClO_4$

T = 294 K

thiourea		$Zn(tu)_4ClO_4$	
B_1 (rad/s)	$T_{1\rho}$ (s)	B_1 (rad/s)	$T_{1\rho}$ (s)
6040	0.235		
4250	0.130	3490	0.058
3930	0.111	3080	0.048
3490	0.0886	2830	0.044
3270	0.078	2690	0.041
2560	0.056	2310	0.037
2140	0.045	1800	0.032
1530	0.029	1500	0.0273
532	0.0138		

Table 6.4

Analysis of proton $T_{1\rho}$ data

	thiourea	$Zn(tu)_4ClO_4$
T_1(H-1): (s)	2.2	0.815
T_2(H-1): (s)	0.011	0.023
slope: (s^3/rad^2)	6.860×10^{-7}	3.249×10^{-7}
intercept: (s/rad^2)	0.0118	0.0212
J(H-1 - N-14): (Hz)	64.9	67.7
T_1(N-14): (ms)	0.761	0.396

possible. The usual difficulty here is that the N-15 satellites are so weak (nat. abund. 0.365%) that they are typically lost in the noise especially if they are broadened by chemical exchange. Although this is the case at lower temperatures, the N-14 line is much broader at high temperatures since, as the width of the N-15 satellites shows, the chemical exchange broadening is less than 2 Hz whereas the scalar relaxation broadening is about 30 Hz. Thus in a spectrum of tu with high S/N (requiring 64 scans at R.T. on a 0.5M solution at 250 MHz) one can just barely make out the satellites as little shoulders on the main peak.

To confirm this assignment by accurately measuring the relative areas and to obtain a more accurate measure of the linewidth, we decided to carry out a SEFT experiment (Rabenstein and Nakashima, 1979) which magnifies small, sharp peaks with long T_2 at the expense of large, broad peaks with short T_2. The spectrum obtained in this way with a τ value of 0.05 s (total delay time, $2\tau = 0.1$ s) allowed an accurate measure of the linewidth (1.9 Hz) and the intensity, after correcting for a decay due to T_2 of about 45%, corresponded very well to that expected for natural abundance N-15.

Having obtained this linewidth which contains contributions from both chemical exchange and instrumental inhomogeneity (estimated from the solvent resonance as 0.3

Hz) we can clearly establish the contribution due to SR2 as 28.0 Hz. Also the coupling constant to N-15 of 90.8 Hz can be used to calculate that for N-14 (assuming isotopic effects are small) by multiplying by the appropriate ratio of gyromagnetic ratios for the two nuclei. A value of J = 64.7 Hz is obtained. As shown in Table 6.4 which summarizes the analysis of the data in Figure 6.3, this is in very good agreement with the $T_{1\rho}$ result and since in this case the T_2 (w=0) intercept agrees well with the observed linewidth, the T_1^N obtained from both methods also agrees quite well.

Encouraged by these results we decided to evaluate the contribution of SR2 to H-1 resonances from coordinated tu's. At the same time we wished to reinvestigate the exchange processes important for these molecules at least qualitatively since the previous results were obtained at low field (54 MHz). The spectra obtained for $Zn(tu)_2Cl_2$ were as expected taking into account the higher field of these experiments. Thus the coalescence temperature was found to be 300 K which is substantially higher than that found in free tu. However rather than pursue the $T_{1\rho}$ method on this system, we decided to attempt measurements on the $Zn(tu)_4(ClO_4)_2$ compound which Eaton and Zaw (1976) had found to exhibit rather unusual behaviour.

The anomaly with this compound was that even when taken down to a temperature of -90 °C, a solution of this compound in acetone revealed no splitting due either to hindered rotation or stopping exchange between free and complexed tu if the complex actually dissociated. We have confirmed the conclusion of Eaton and Zaw that the reason for this anomaly is that the chemical shift difference between inner and outer protons is much smaller than that observed for any of the other similar systems studied. Taking advantage of the 5x larger field available at our disposal (on the WM-250), we were able to freeze out the exchange and found a chemical shift difference of only 9.5 Hz, at least a factor of 10 smaller than earlier observed for Zn(tu)$_2$Cl$_2$. The coalescence temperature was found to be -60°C. We thought it would be interesting to investigate SR2 at room temperature and determine if chemical exchange of some sort was still taking place. This might have been expected if one were to suppose that the chemical shift difference in this molecule was strongly temperature dependent and increased with increasing temperature to a value more comparable to that of other tu molecules.

The results for the $T_{1\rho}$ experiment are shown in Fig. 6.4 and Tables 6.3 and 6.4. A good set of data was obtained and the values show no obvious anomalies indicating that chemical exchange contributions to the linewidth are negligible. As might be expected, the N-H coupling constant for coordinated tu is within experimental error equal to

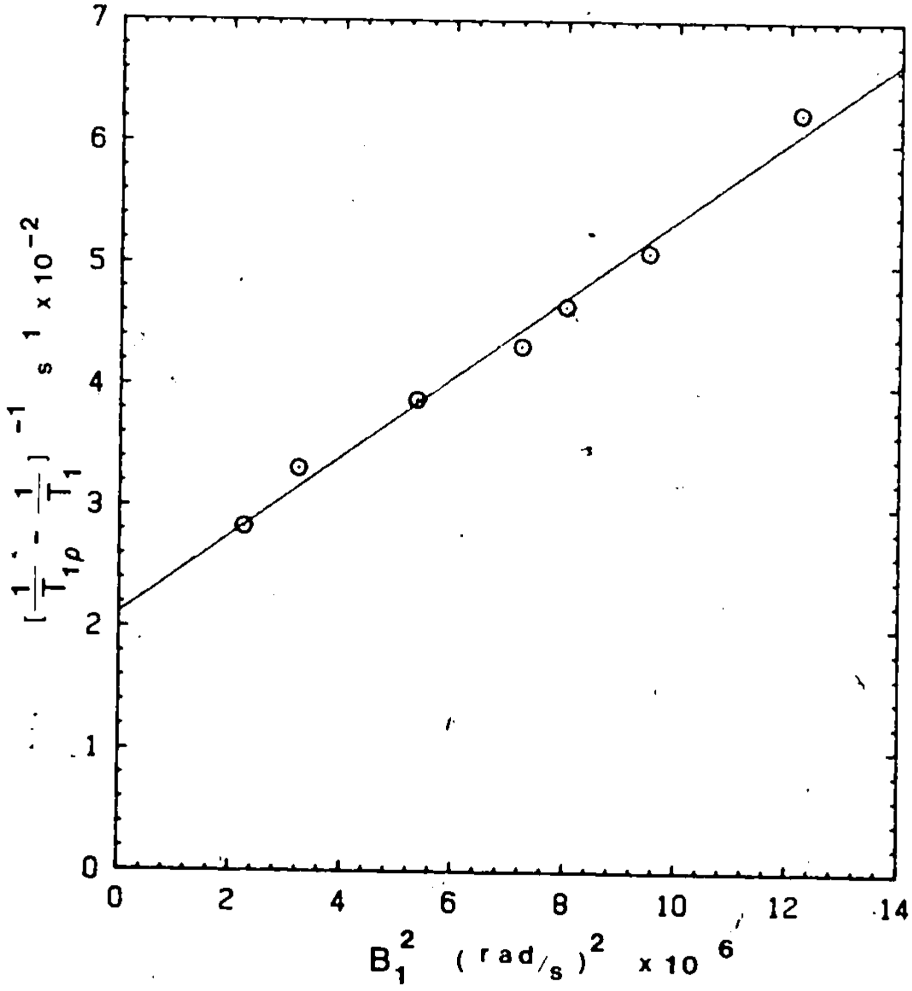

Figure 6.4 Plot of H-1 $T_{1\rho}$ data on tetrakis(tu)zinc(II)

that observed in free tu. Since the nitrogen atom is two bonds removed from the coordinating sulphur, this is quite reasonable. Our data is not accurate enough to pick up small changes of the order of 2-5% which might nevertheless be of some theoretical interest. The measured T_1^N is substantially lower than that for free tu as expected since the τ_c for the larger molecule would be expected to be somewhat longer. The change in the H-1 T_1 is of the same magnitude and reflects the same effect.

6.2.3 Evaluation of the method

We have demonstrated that the $T_{1\rho}$ method can be profitably applied to study scalar relaxation of the second kind. Let us now consider some of the advantages and disadvantages. The major advantages of the $T_{1\rho}$ method are that T_2^*, the contribution to the linewidth from B_0 inhomogeneity, does not have to be determined and both of the remaining significant variables are determined in one set of experiments on the same sample at the same temperature. It is not necessary to obtain data in the region of slow exchange nor to measure the X-nucleus T_1. In the former case, physical constraints on the system such as the freezing point of the solution or solubility of the compound may prevent the attainment of a low enough temperature. Furthermore, if the chemical shift difference is known to be temperature dependent (Drakenburg et al, 1970), then the temperature must be lowered still further adding to the possibility that problems will arise. In this case the errors due to extrapolation of the chemical shift difference can be easily avoided by using the $T_{1\rho}$ method. When used to study SR2, the $T_{1\rho}$ technique can prove exceptionally powerful when the X-nucleus T_1 is simply too short to be measured by direct methods. Another advantage of this method is the ability to separate the contributions to T_2 from two different processes occurring simultaneously at the same temperature. An example would be the well-known case of restricted rotation about an amide C-N bond if H-1 NMR on the amide protons is used. Since these protons are experiencing SR2 due to the adjacent nitrogen, the linewidth of the peaks will be somewhat temperature dependent and this must be taken into account. If the exchange lifetime is at least an order of magnitude different from the nitrogen T_1, then the $T_{1\rho}$ method should, in principle, be able to separate out the two contributions. This would be particularly useful in the region of fast exchange when the exchange broadening becomes a relatively small fraction of the total linewidth.

Some disadvantages of the technique should also be mentioned here. One obvious difficulty is that such a large number of experiments need to carried out to obtain only two pieces of information. Thus any study of concentration or temperature dependence would require a good deal of instrument time. In our experience the results obtained by the $T_{1\rho}$ method are usually accurate to 5-10%. This could be improved but again a considerable investment of instrument time would be required. In particular, a highly accurate determination of the spin-locking field strength would be time-consuming. Unfortunately this needs to be redetermined for every new sample and preferably at each different temperature to be safe.

In spite of the afore-mentioned difficulties, the potential for the $T_{1\rho}$ technique still remains largely untapped. As NMR spectrometers become more and more sophisticated it is hoped that the NMR spectroscopist will make use of the instrumentation available to perform experiments a couple steps beyond the routine acquisition of spectra.

Chapter 7

Summary and Suggestions for Future Work

7.1 Summary and Conclusions

Dynamic, multinuclear NMR spectroscopy has been carried out on first and second coordination sphere complexes of Cobalt(III) and Zinc(II). The formation of second coordination sphere complexes between the hexacyanocobaltate(III) anion and a number of phenols, anilines and benzoic acids has been studied using Co-59 chemical shifts and linewidths. The largest and most readily interpretable effects were observed with the phenols. For these molecules, the Co-59 shifts were used to calculate effective equilibrium constants and chemical shifts for the hydrogen-bonded complexes. Supplementary experiments have been carried out on the para-nitrophenol complex to establish limits on the lifetime of this complex. This involved measuring H-1 and C-13 spin-lattice relaxation times (T_1) and showed that the lifetime is long compared to the rotational correlation time. Use of the C-13 T_1's allowed an estimation of the correlation time for the complex and the calculation of a Co-59 quadrupole coupling constant of 8.3 MHz. The data for the anilines and benzoic acids could not be analyzed as thoroughly as the phenol data and only the product of the equilibrium constant and the limiting Co-59 chemical shift could be obtained.

The second object of study in this thesis was the hexanitrocobaltate(III) anion. In contrast to the hexacyano complex which is kinetically inert under mild conditions, hexanitrocobaltate(III) seems to be inherently unstable in aqueous solution. In view of this anomalous behaviour and the reports by several groups of apparently anomalous spectroscopic behaviour, a thorough study has been carried out with the intention of explaining some of these anomalies. First of all, a detailed comparison of the solid-state and solution spectroscopies showed that the hexanitro species is fully N-bonded in its most stable form. Secondly, we have shown using Co-59, O-17 and N-14 NMR and UV-vis spectroscopy that the first step in the decomposition of this compound is the aquation of at least one nitro group with a reaction lifetime of approximately three minutes. Thirdly, the Co-59 chemical shift predictor model of Au-Yeung and Eaton has been modified somewhat to improve the calculation of shifts for nitro-containing molecules by effectively allowing for a nitro-nitro cis-effect. Also the calculation of shifts for molecules with ligands exhibiting different orbital reduction factors has been improved. As an example, the shifts for the cyanoammine series have been recalculated. Using these two changes, assignments have been made for the Co-59 spectra of mixtures obtained by reacting cobaltinitrite with cyanide, cobaltinitrite with cyanide, ethylenediamine and azide as well as the species observed in cobaltinitrite itself.

A study of the field dependence of the Co-59 NMR polycrystalline sodium cobaltinitrite has been carried out at six different fields. A quadrupole coupling constant of 8.1 MHz is estimated (assuming eta=0) and the shielding anisotropy is shown from the field dependence of the chemical shift to be less than -10 ppm. Using these parameters and a dipolar linewidth of 2 kHz, the field dependence of the second-order quadrupolar splitting of the central transition has been calculated and shown to deviate slightly but consistently from the observed splitting at low fields and from the observed linewidth at high fields. The reason for this discrepancy is postulated to be some type of motional narrowing. We have also reported the first Co-59 MASS spectrum and the results are shown to agree well with theory.

Another 'first' to be reported here is the first set of Co-59 $T_{1\rho}$ experiments which we have carried out on trisethylenediaminecobalt(III) and cobaltinitrite. Dispersion of the contribution of scalar relaxation of the second kind from the coordinating nitrogen's allowed the measurement of the Co-59 - N-14 scalar coupling constant and the N-14 T_1. The results for the trisethylenediamine complex agreed well with those obtained by other methods. The N-14 T_1 for cobaltinitrite was in good agreement with that directly measured while the calculated coupling constant was obtained as 59 Hz. Studies by $T_{1\rho}$ of scalar relaxation in free and coordinated thioureas were also carried out along with the measurement of variable temperature spectra for several Zinc thiourea complexes.

7.2 Suggestions for Future Work

Some additional work could be proposed for each of the three areas studied in this thesis. The problem of dimerization of benzoic acids which affected the analysis of the cobalticyanide Co-59 NMR chemical shifts could perhaps be overcome by an independent measurement of the dimerization constant for the series of benzoic acids used here. This could be carried out by an analysis of the concentration dependence of the proton chemical shifts.

Further work is required to establish a definitive assignment for the peak observed at δ 168 ppm in the natural abundance O-17 NMR spectrum of cobaltinitrite. Some clue to its identity may be found by preparing cobaltinitrite from Co^{2+} and nitrite enriched in O-17 and following the relative time dependence of the intensities of the δ 168 ppm peak and the coordinated nitro peak. Such an experiment could be an interesting complement to research which needs to be done on the cobalt(II)-nitro system for which no solution work has been published although solid salts of the hexanitrocobaltate(II) anion have been prepared. N-14 NMR could prove useful here as well as E.S.R. The intermediates involved in the oxidation of these species to the Co(III) species would also be an area of interest. Preliminary Co-59 NMR results in this lab indicate that peroxide oxidations may involve a peroxy intermediate. The validity of the new empirical models for Co-59 NMR chemical shift calculation for nitro- and cyano-containing complexes needs to be more thoroughly tested by application to a larger number of molecules.

As $T_{1\rho}$ experiments become more readily accessible to the non-specialist, some theoretical work will have to be carried out on systems where both T_1^I and T_1^S are less than the inverse of the coupling constant. In cases such as these the scalar relaxation contribution has been shown to be incorrectly calculated using the usual formula (Au-Yeung, Buist and Eaton, 1983). This is especially important as heteronuclear $T_{1\rho}$'s become more popular since more cases of scalar relaxation involving two quadrupolar nuclei will naturally arise. Also the theory of $T_{1\rho}$ needs to be further developed for more complicated dynamic rearrangements such as those involving more than one exchange process.

Appendix 1

Listing of BASIC I_1-calculation programs

(i) 'GRAPTECH'

```
10 PRINT "NONLINEAR REGRESSION BY GRAPHICAL TECHNIQUES"
20 PRINT
30 DIM X(35),Y(35),LY(35)
40 K=0
50 REM -
60 REM - INPUT DATA
70 INPUT "ENTER DATA FROM TERMINAL 'T' OR DISK 'D'";ZZ$
80 IF ZZ$="T" GOTO 180
90 IF ZZ$="D" GOTO 110
100 GOTO 70
110 INPUT "DISKDRIVE:FILENAME";Z$
120 OPEN "I",#1,Z$
130 INPUT "NO. OF POINTS";N
140 FOR I=1 TO N
150 INPUT #1,X(I),Y(I)
160 NEXT I
170 GOTO 360
180 INPUT "WOULD YOU LIKE TO STORE DATA (Y/N)";ZZ$
190 IF ZZ$="N" GOTO 290
200 INPUT "DISKDRIVE:FILENAME";Z$
210 OPEN "O",#1,Z$
220 INPUT "NO.OF POINTS";N
230 FOR I=1 TO N
240 PRINT "X,Y OF POINT ",I
250 INPUT X(I),Y(I)
260 PRINT #1,X(I),Y(I)
270 NEXT I
280 GOTO 370
290 PRINT "NUMBER OF KNOWN POINTS";
300 INPUT N
310 FOR I=1 TO N
320 PRINT "X,Y OF POINT ";I
330 INPUT X(I),Y(I)
340 NEXT I
350 REM -
360 REM - EXAMINE DATA AND MAKE ANY CHANGES AS NECESSARY
370 FOR I=1 TO N
380 PRINT "X,Y OF POINT ";I,"ARE";X(I),Y(I)
390 NEXT I
400 PRINT "IF SATISFIED TYPE '1'";
410 INPUT M
420 IF M=1 THEN 830
430 PRINT "IF YOU WISH TO CHANGE A POINT,TYPE 1"
440 PRINT "OTHERWISE TYPE 2";
450 INPUT KIL
460 IF KIL=1 THEN GOTO 470 ELSE GOTO 560
470 PRINT "NO. OF POINT TO BE CHANGED IS";
480 INPUT LIK
490 IF LIK>N THEN 470
500 PRINT "X,Y OF POINT";LIK;"IS";
510 INPUT X(LIK),Y(LIK)
```

```
520 PRINT "MORE POINTS TO BE CHANGED? TYPE 1";
530 INPUT AA
540 IF AA=1 THEN 470
550 PRINT
560 PRINT "IF YOU WISH TO DELETE A POINT "
570 PRINT "TYPE THE NUMBER OF THE POINT TO BE DEL-"
580 PRINT "ETED, OTHERWISE TYPE 0";
590 INPUT BB
600 IF BB<=0 OR BB>N THEN 710
610 IF B=N THEN N=N-1
620 FOR ILL=BB TO N
630 X(ILL)=X(ILL+1)
640 Y(ILL)=Y(ILL+1)
650 NEXT ILL
660 N=N-1
670 PRINT
680 PRINT "YOU NOW HAVE ";N;"POINTS"
690 PRINT
700 GOTO 560
710 PRINT "IF YOU WISH TO ADD MORE POINTS, TYPE 1"
720 PRINT "OTHERWISE TYPE A 3";
730 INPUT CC
740 IF CC=1 THEN GOTO 750 ELSE GOTO 830
750 PRINT "X,Y OF POINT";N+1;"IS";
760 INPUT X(N+1),Y(N+1)
770 N=N+1
780 GOTO 710
790 REM -
800 REM - CALCULATE M(0) USING THE TWO DERIVED EQUATIONS
810 REM - AND A SELECTED RANGE OF T1 VALUES
820 REM -
830 PRINT "ESTIMATE T1 BY NULL POINT METHOD"
840 PRINT "CHOOSE T1MAX TO BE AT LEAST TWICE THAT"
850 PRINT "MAX. T1 VALUE IS ";
860 INPUT T1MAX
870 PRINT "MIN. T1 VALUE IS ";
880 INPUT T1MIN
890 T1S=(T1MAX-T1MIN)/10
900 PRINT " THE IDEA IS TO FIND T1 FOR WHICH MO(1)=MO(2)
910 PRINT "  T1              MO(1)          MO(2)          MO(1)-MO(2)
920 FOR T1=T1MIN TO T1MAX STEP T1S
930 RESTORE
940 READ A#,B#,C#,D#,E#,F#,G#,H#,O#
950 DATA 0,0,0,0,0,0,0,0#,0#
960 REM - CALCULATE SUMS
970 FOR I=1 TO N
980 A#=A#+Y(I)*EXP(-X(I)/T1)
990 B#=B#+EXP(-X(I)/T1)
1000 C#=C#+Y(I)
1010 D#=D#+EXP(-2*X(I)/T1)
1020 E#=E#+X(I)/T1^2*EXP(-X(I)/T1)
1030 F#=F#+X(I)/T1^2*EXP(-2*X(I)/T1)
1040 G#=G#+X(I)/T1^2*Y(I)*EXP(-X(I)/T1)
1050 H#=H#+X(I)^2*EXP(-2*X(I)/T1)
1060 O#=O#+(1-EXP(-X(I)/T1))^2
1070 NEXT I
1080 MO1=(A#*B#-N*A#-C#*D#+C#*B#)/(B#^2-N*D#)
1090 MO2=(C#*E#-C#*F#+B#*G#-N*G#)/(B#*E#-N*F#)
```

```
1100 IF L=1 THEN 1320
1110 PRINT T1,MO1,MO2,MO1-MO2
1120 NEXT T1
1130 PRINT "MO VALUES SHOULD BE CLOSE TO ESTIMATE"
1140 PRINT "IF NOT, TRY DIFFERENT RANGE OF VALUES"
1150 PRINT "IF THEY ARE, NARROW RANGE OF CALCULATION"
1160 PRINT "IF SATISFIED TYPE '1'";
1170 INPUT L
1180 IF L=1 THEN 1270
1190 PRINT "IF YOU WOULD LIKE TO RE-EXAMINE DATA"
1200 PRINT "TYPE A '1'";
1210 INPUT LL
1220 IF LL=1 THEN 370
1230 REM -
1240 REM - IF SATISFIED, CHOOSE BEST T1 AND CALCULATE
1250 REM - M(0) AND M(OO)
1260 GOTO 850
1270 PRINT "BEST VALUE OF T1 IS";
1280 INPUT T1B
1290 T1MIN=T1B
1300 T1MAX=T1B+1
1310 GOTO 920
1320 MO=(MO1+MO2)/2
1330 MOO1=(MO*B#-C#)/(B#-N)
1340 MOO2=(-MO*F#+G#)/(E#-F#)
1350 PRINT "ESTIMATES OF M(0) ARE ";MO1,MO2
1360 PRINT "ESTIMATES OF M(OO) ARE ";MOO1,MOO2
1370 PRINT "AVE. M(OO) IS ";(MOO1+MOO2)/2
1380 MOO=(MOO1+MOO2)/2
1390 PRINT "AVE, M(0) IS ";MO
1400 PRINT "ESTIMATE OF T1 IS ";T1B
1410 REM -
1420 PRINT "IF YOU WOULD LIKE CALCULATION OF Y* VALUES "
1430 PRINT "AND EST. OF STAND. ERRORS, TYPE A '1'";
1440 INPUT CAL
1450 IF CAL<>1 THEN 1730
1460 EE=E#*T1^2*(MOO-MO)
1470 FF=F#*T1^2*(MOO-MO)
1480 HH=H#*(MOO-MO)^2
1490 P#=B#-D#
1500 S#=FF#/T1^2
1510 Q#=EE#/T1^2-S#
1520 T#=HH/T1^4
1530 ZZ=O#*(D#*T#-S#^2)-P#*(P#*T#-S#*Q#)+Q#*(P#*S#-Q#*D#)
1540 Z=N*(D#*HH-FF^2)-B#*(B#*HH-EE*FF)+EE*(B#*FF-EE*D#)
1550 PPMOO=(D#*HH-FF^2)/Z
1560 PPMO=(O#*T#-Q#^2)/ZZ
1570 PPT1=(N*D#-B#^2)/Z
1580 RSS=0
1590 PRINT "  X(I)            Y(I)          CALCULATED Y    DIFF "
1600 FOR JI=1 TO N
1610 YT=MOO+(MO-MOO)*EXP(-X(JI)/T1)
1620 RSS=RSS+(YT-Y(JI))^2
1630 PRINT X(JI),Y(JI),YT,YT-Y(JI)
1640 NEXT JI
1650 PRINT "RESIDUAL SUM OF SQUARES IS ",RSS
1660 SMOO=SQR(RSS/(N-3)*PPMOO)
```

```
1670 SMO=SQR(RSS/(N-3)*FFMO)
1680 ST1=SQR(RSS/(N-3)*FFT1)
1690 PRINT "STANDARD ERROR IN M(OO) IS ";SMOO
1700 PRINT "STAND. ERROR IN M(0) IS ";SMO
1710 PRINT "STANO. ERROR IN T1 IS ";ST1*T1^2
1720 REM -
1730 PRINT "IF SATISFIED WITH NON-LIN. ESTIMATION TYPE '1'";
1740 INPUT NOL
1750 IF NOL=1 THEN 1790
1760 L=0
1770 GOTO 370
1780 REM -
1790 PRINT "IF YOU WISH TO CALCULATE T1 BY LINEAR REGRESSION "
1800 PRINT "OF LN(Y-M(OO)) VS TIME, TYPE '1'";
1810 INPUT D
1820 IF D<>1 THEN 2230
1830 REM -
1840 PRINT "IF YOU WISH TO USE M(INFINITY) FROM 3-PARAMETER"
1850 PRINT "FIT, TYPE A "1", OTHERWISE TYPE RETURN"
1860 INPUT MINF
1870 IF MINF=1 GOTO 1900
1880 PRINT"ENTER A REASONABLE M(INFIN) VALUE"
1890 INPUT MOO
1900 A=0
1910 B=0
1920 C=0
1930 D=0
1940 E=0
1950 PRINT "HERE IS LINEARIZED DATA"
1960 PRINT "  I            X(I)         Y(I)"
1970 FOR I=1 TO N
1980 IF Y(I)>=MOO THEN 2060
1990 LY(I)=LOG(MOO-Y(I))
2000 PRINT I,X(I),LY(I)
2010 A=A+LY(I)
2020 B=B+X(I)
2030 C=C+X(I)^2
2040 D=D+X(I)*LY(I)
2050 E=E+LY(I)^2
2060 NEXT I
2070 M=(A*B/N-D)/((B^2)/N-C)
2080 BB=A/N-M*B/N
2090 RSS=E-BB*A-M*D
2100 PRINT "RSS";RSS
2110 DM=SQR(N*RSS/(N-2)/(N*C-B^2))
2120 DB=SQR(DM^2*C/N)
2130 DT1=DM/M^2
2140 TI=-1/M
2150 PRINT "CALCULATED T1 IS ";TI
2160 PRINT "CALCULATED M(OO)-M(O) IS";EXP(BB)
2170 PRINT "STANDARD EST. OF ERROR IN T1 IS";DT1
2180 PRINT "STANDARD EST. OF ERROR IN LN(M(OO)-M(O)) IS";DB
2190 REM -
2200 PRINT "IF SATISFIED WITH LINEAR REGRESSION TYPE '1'";
2210 INPUT T
2220 IF T<>1 THEN 1730
2230 END
```

(ii) 'RLENKT1'

```
10 FOR I=1 TO 32:PRINT:NEXT I
20 PRINT "TO FIT THREE CONSTANTS TO A FUNCTION"
30 REM - THE METHOD IS GENERAL, THE PARTICULAR FUNCTION IS FOR
40 REM - T1 DETERMINATION IN NMR, AND LOCATED IN STATEMENT 580
50 REM -
60 DIM X(50),Y(50),R(50)
70 INPUT "ENTER DATA FROM TERMINAL 'T' OR FROM DISK 'D'";AS$
80 IF AS$="T" THEN 180
90 IF AS$="D" THEN 110
100 GOTO 70
110 INPUT "DISK DRIVE:FILENAME";ZZ$
120 OPEN "I",#1,ZZ$
130 INPUT "NO. OF POINTS";N
140 FOR I=1 TO N
141 IF X(I)=-1 GOTO 170
150 INPUT #1,X(I),Y(I)
160 NEXT I
170 CLOSE:GOTO 370
180 INPUT "DO YOU WISH TO STORE DATA ON DISK (Y/N)";ZZ$
190 IF ZZ$="N" GOTO 300
200 INPUT "DISKDRIVE:FILENAME";Z$
210 OPEN "O",#1,Z$
220 INPUT "NO. OF POINTS";N
230 FOR I=1 TO N
240 PRINT "X,Y OF POINT ",I
250 INPUT X(I),Y(I)
260 PRINT #1,X(I),Y(I)
270 NEXT I
275 PRINT #1,-1,-1
280 CLOSE
290 GOTO 370
300 PRINT"INPUT X (TIME), Y(INTENSITY), NEGATIVE X &Y TO END LIST"
310 FOR G=1 TO 50
320 INPUT X(G),Y(G)
330 IF X(G)<0 GOTO 370
340 N=G
350 NEXT G
360 CLOSE
370 PRINT"INPUT INITIAL ESTIMATES OF A,B,C"
380 INPUT A1,B1,C1
390 PRINT "INPUT T, 0=CALCULATE, 1=FINAL TABLE, 2=DELETE 1 POINT,"
400 PRINT"3=ADD 1 POINT, 4=ABSOLUTE END, 5=DIFFERENT A,B,C"
410 INPUT T
420 IF T=0 THEN 480
430 IF T=1 THEN 1070
440 IF T=2 THEN 1260
450 IF T=3 THEN 1500
460 IF T=4 THEN 1540
470 IF T=5 THEN 370
480 H=1
490 IF H=6 GOTO 990
500 M1=0:M2=0:M3=0:M4=0:M5=0:M6=0:M7=0
510 M8=0:M9=0:S1=0
520 FOR G=1 TO N
530 IF (H=1) AND (G=1) THEN 580
540 GOTO 590
```

```
550 REM -
560 REM - T1=F'A, T2=F'B, T3=F'C, T4=R=Y-(F(A,B,C))
570 REM - SECTION FOR SPECIFIC FUNCTION FOLLOWS, NOTE JUMP INTO IT
580 PRINT"PARTICULAR FUNCTION IS Y=A-A EXP(-X/B)-AC EXP(-X/B)"
590 T5=EXP(-X(G)/B1)
600 T1=1-T5-C1*T5
610 T6=A1*X(G)*T5/(B1*B1)
620 T2=-T6-C1*T6
630 T3=-A1*T5
640 T4=Y(G)-(A1-A1*T5-A1*C1*T5)
650 REM-
660 REM - COMPLETE SECTION SPECIFIC FOR FUNCTION
670 R(G)=T4
680 REM - CALCULATION OF SUMS
690 M1=M1+T1*T1
700 M2=M2+T1*T2
710 M3=M3+T1*T3
720 M4=M4+T2*T2
730 M5=M5+T2*T3
740 M6=M6+T3*T3
750 M7=M7+T1*T4
760 M8=M8+T2*T4
770 M9=M9+T3*T4
780 S1=S1+T4*T4
790 NEXT G
800 REM -
810 REM - CALCULATIONS USING SUMS -- CRAMER'S RULE
820 REM - ALSO CALCULATION OF APPROPRIATE VARIANCE-
830 REM - COVARIANCE MATRIX ELEMENTS AND DETERMINANT
840 S3=2*M2*M3*M5-M3*M3*M4-M1*M5*M5+M1*M4*M6-M2*M2*M6
850 S3=1/S3
860 S4=M4*M6-M5*M5
870 A2=S3*(M3*M5*M8-M3*M4*M9+M2*M5*M9-M2*M6*M8+M7*S4)
880 Q3=S3*S4
890 S5=M1*M6-M3*M3
900 B2=S3*(M2*M3*M9+M8*S5+M3*M5*M7-M1*M5*M9-M2*M6*M7)
910 Q4=S3*S5
920 S6=M1*M4-M2*M2
930 C2=S3*(M2*M5*M7-M3*M4*M7+M2*M3*M8-M1*M5*M8+M9*S6)
940 Q5=S3*S6
950 A1=A1+A2
960 B1=B1+B2
970 C1=C1+C2
980 H=H+1:GOTO 490
990 S2=SQR(S1/(N-3))
1000 PRINT"STD DEV OF Y = "S2;"FOR 5 REPEATS"
1010 PRINT"NEW A = ";A1;"NEW B = ";B1;"NEW C = ";C1
1020 PRINT
1030 GOTO 390
1040 REM -
1050 REM - FINAL TABLE OF CALCULATED Y VALUES AND
1060 REM - STANDARD ERRORS
1070 PRINT "  X                Y           YCALC          Y-YCALC  "
1080 FOR G=1 TO N
1090 PRINT X(G),Y(G),Y(G)-R(G),R(G)
1100 NEXT G
```

```
1110 PRINT "TO CONTINUE TYPE RETURN"
1120 INPUT K
1130 A$="":GOSUB 1570
1140 A$="A= "+STR$(A1)+"    STD ERROR= "+STR$(S2*SQR(Q3))
1150 GOSUB 1570
1160 A$="B= "+STR$(B1)+"    STD ERROR= "+STR$(S2*SQR(Q4))
1170 GOSUB 1570
1180 A$="C= "+STR$(C1)+"     STD ERROR= "+STR$(S2*SQR(Q5))
1190 GOSUB 1570
1200 A$="NUMBER OF POINTS= "+STR$(N)+"     STD ERROR OF Y= "+STR$(S2)
1210 GOSUB 1570
1220 A$="":GOSUB 1570:GOSUB 1570
1230 GOTO 390
1240 REM -
1250 REM - SORT DATA SET AND DELETE WRONG X AND Y
1260 PRINT"INPUT WRONG X AND Y"
1270 INPUT T4,T5
1280 FOR G=1 TO N
1290 IF X(G)<>T4 OR Y(G)<>T5 THEN 1310
1300 X(G)=9999
1310 NEXT G
1320 FOR H=1 TO N
1330 C=0
1340 FOR G=1 TO N-1
1350 IF X(G)<X(G+1) THEN 1430
1360 T4=X(G)
1370 T5=Y(G)
1380 X(G)=X(G+1)
1390 Y(G)=Y(G+1)
1400 X(G+1)=T4
1410 Y(G+1)=T5
1420 C=1
1430 NEXT G
1440 IF C=0 THEN 1470
1450 NEXT H
1460 IF X(N)<>9999 THEN 390
1470 N=N-1
1480 GOTO 390
1490 REM -
1500 PRINT"INPUT ADDITIONAL X & Y"
1510 INPUT X(N+1),Y(N+1)
1520 N=N+1
1530 GOTO 390
1540 END
1550 REM -
1560 REM - SUBROUTINE FOR OUTPUT
1570 A$=A$+CHR$(10)+CHR$(13)
1580 PRINT A$
1590 A$=""
1600 RETURN
```

Appendix 2

Co-59 NMR Chemical Shifts and Linewidths

Phenols

Substituent	Concentration (M)	Chemical Shift (ppm)	Linewidth (Hz)
H	0.000	0.0	52
	0.094	-15.3	152
	0.269	-31.0	256
	0.433	-53.3	360
	0.632	-74.9	520
	0.918	-83.3	560
	1.103	-92.1	600
p-C_4H_9	0.000	0.0	45
	0.107	-14.3	212
	0.183	-23.2	292
	0.290	-34.9	396
	0.474	-50.9	568
	0.659	-60.8	725
	0.819	-68.5	852
p-F	0.000	0.0	35
	0.062	-8.7	108
	0.172	-23.7	194
	0.323	-38.9	285
	0.530	-56.0	342
	0.776	-70.0	498
	1.010	-81.0	570
	1.336	-93.5	562
p-CN	0.000	0.0	30
	0.109	-29.7	246
	0.239	-52.6	451
	0.438	-75.8	700
	0.683	-97.7	912
	0.884	-105.1	910
m-NO_2	0.000	0.0	54
	0.149	-24.1	300
	0.355	-47.4	440
	0.734	-74.6	900
	0.994	-87.4	1050

Phenols (cont'd)

Substituent	Concentration (M)	Chemical Shift (ppm)	Linewidth (Hz)
p-NH_2	0.000	0.0	64
	0.066	-9.2	130
	0.333	-16.0	186
	0.562	-27.1	288
	0.792	-34.8	348
	1.018	-43.0	412
	1.249	-50.0	608
p-OCH_3	0.000	0.0	44
	0.148	-14.1	148
	0.270	-25.1	258
	0.397	-33.8	324
	0.561	-44.3	384
	0.775	-56.7	444
	1.020	-67.4	568
p-NO_2	0.000	0.0	48
	0.093	-66.9	558
	0.433	-85.7	710
	0.632	-103.2	970
	0.918	-108.1	1050
	1.103	-128.9	1233
p-COOH	0.000	0.0	48
	0.021	- 3.4	110
	0.065	-12.7	200
	0.147	-27.7	416
	0.204	-34.6	530
	0.257	-41.7	600
	0.304	-45.3	749
	0.360	-52.2	812
m-NH_2	0.000	0.0	34
	0.150	-18.5	120
	0.392	-39.2	285
	0.661	-54.7	392
	0.916	-66.0	470
	1.145	-71.7	610

Anilines

Substituent	Concentration (M)	Chemical Shift (ppm)	Linewidth (Hz)
H	0.0000	0.00	40
	0.0219	-0.96	45
	0.0438	-1.17	46
	0.0767	-1.38	43
	0.1095	-2.07	43
	0.1643	-2.69	46
	0.2190	-3.30	40
	0.2957	-3.79	44
	0.3724	-4.41	46
	0.4600	-5.23	49
	0.5476	-5.85	50
	0.6571	-6.95	47
	0.7667	-8.06	45
	0.8762	-8.81	47
	1.0952	-9.92	54
p-NO_2	0.0000	0.00	52
	0.0785	-3.44	49
	0.1419	-6.13	55
	0.2715	-12.05	68
	0.4347	-18.59	81
	0.6660	-26.98	98
	0.9379	-35.45	112
	1.2191	-43.09	136
p-Cl	0.0000	0.00	41
	0.0388	0.00	43
	0.1211	-1.03	49
	0.2151	-2.55	47
	0.3366	-4.61	47
	0.5263	-7.37	50
	0.6889	-9.36	66
	0.8656	-12.05	65
	1.0549	-14.80	63
p-OCH_3	0.000	0.0	44
	0.134	-0.1	49
	0.180	-0.4	53
	0.271	-1.3	52
	0.351	-1.9	53
	0.421	-2.7	54
	0.493	-2.9	53
	0.579	-3.9	54
	0.680	-4.8	53
	0.770	-4.9	56
	0.862	-5.7	55

Anilines (cont'd)

Substituent	Concentration (M)	Chemical Shift (ppm)	Linewidth (Hz)
m-OCH_3	0.000	0.0	45
	0.089	-0.4	43
	0.116	-1.0	41
	0.161	-1.4	41
	0.214	-2.1	43
	0.286	-3.2	44
	0.375	-3.6	47
	0.509	-4.4	50
	0.643	-5.9	49
	0.777	-7.2	51
	0.911	-8.1	55
	1.09	-9.5	57
p-Br	0.000	0.0	46
	0.055	-0.7	47
	0.079	-1.2	44
	0.105	-2.0	43
	0.150	-2.7	44
	0.186	-3.4	46
	0.226	-3.9	48
	0.271	-4.9	51
	0.329	-5.7	49
	0.384	-6.8	48
	0.447	-7.5	52
	0.508	-8.2	52
	0.560	-8.7	56
	0.634	-9.6	55
m-NO_2	0.000	0.0	42
	0.038	-0.5	42
	0.059	-0.7	47
	0.083	-1.2	49
	0.117	-1.6	49
	0.222	-4.1	52
	0.297	-5.3	54
	0.361	-7.4	57
	0.442	-9.2	60
	0.543	-11.0	66
	0.643	-12.7	72
N,N-dimethyl	0.000	0.0	38
	0.020	-0.1	38
	0.059	-0.1	38
	0.138	-0.1	37
	0.335	-0.5	41
	0.650	-0.5	38

Benzoic Acids

Substituent	Concentration (M)	Chemical Shift (ppm)	Linewidth (Hz)
H	0.000	0.0	41
	0.033	- 3.4	100
	0.107	-10.8	210
	0.180	-17.9	297
	0.285	-25.6	432
	0.380	-33.9	575
	0.461	-38.7	660
	0.553	-42.8	720
	0.659	-50.5	826
	0.752	-54.7	996
p-OH	0.000	0.0	48
	0.021	- 3.4	110
	0.065	-12.7	200
	0.147	-27.7	416
	0.204	-34.6	530
	0.257	-41.7	600
	0.304	-45.3	749
	0.360	-52.2	812
p-F	0.000	0.0	49
	0.042	- 3.2	113
	0.092	- 7.9	194
	0.153	-13.4	282
	0.246	-21.3	336
	0.354	-27.7	488
	0.530	-37.3	714
	0.712	-44.5	945
p-NO_2	0.000	0.0	41
	0.062	- 8.3	234
	0.134	-17.4	345
	0.223	-28.2	625
	0.332	-35.9	876
	0.456	-44.4	1050
	0.632	-54.3	1470
p-Cl	0.000	0.0	120
	0.104	- 8.6	290
	0.289	-21.3	492
	0.448	-30.7	640
	0.586	-38.5	1050
	0.744	-44.6	1250

Benzoic Acids (cont'd)

Substituent	Concentration (M)	Chemical Shift (ppm)	Linewidth (Hz)
m-NH_2	0.000	0.0	38
	0.0190	- 2.07	62
	0.0474	- 3.86	90
	0.0809	- 6.33	124
	0.1243	- 9.09	152
	0.1827	-12.81	228
	0.2461	-16.53	285
	0.3187	-22.17	372
	0.3733	-25.20	468
p-NH_2	0.000	0.0	46
	0.0459	- 1.24	72
	0.0901	- 3.51	100
	0.1429	- 6.33	130
	0.2363	-11.29	182
	0.2862	-14.12	220
	0.3752	-17.70	265
	0.4663	-21.87	322
	0.5680	-25.82	368
	0.6807	-30.50	448
	0.8014	-35.18	532
	0.9366	-39.32	580
	1.0573	-44.55	738

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