MECHANISMS OF LIGAND EXCHANGE IN COMPLEXES OF COBALT, NICKEL AND ZINC

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SCOPE AND CONTENTS

One of the simplest types of reactions encountered in inorganic chemistry involves the exchange of a molecule coordinated to a metal ion (the ligand) with another molecule free in solution. This type of reaction is fundamental to much of synthetic inorganic chemistry and also constitutes the building blocks from which the complex multistep mechanisms typical of homogeneous catalysis are built. There has naturally been a great deal of research carried out on ligand exchange mechanisms. However, the majority of this research has been concerned with relatively slow reactions carried out in aqueous solution. Data on rapid ligand exchange reactions in non-aqueous solutions are relatively sparse. Such reactions are in many respects, the more interesting and certainly have greater relevance to the understanding of homogeneous catalysis. In particular, comparative studies of the effect of changes of metal ion, geometry of the complex and ligand substituent are lacking. The present thesis presents the results of such a study.

The group of compounds chosen for study are thiourea and substituted thiourea complexes of cobalt, nickel and zinc. Nuclear magnetic resonance has been used as the principal experimental technique. This technique provides information on both the solution structures of the complexes and the kinetics and mechanisms of the ligand exchange processes.

Two introductory chapters review previous work on ligand substitution and the use of nuclear magnetic resonance to study chemical rate processes. The thiourea ligands chosen can themselves undergo a rate process involving restricted rotation about the C-N bond and a third chapter describes some preliminary experiments designed to clarify the interpretation of the ligand spectra. The cobalt complexes are paramagnetic and tetrahedral in solution. Some replacement of thiourea by solvent occurs and equilibirium constants and thermodynamic data for this process have been obtained. A detailed study of the kinetics of ligand exchange has demonstrated two competing mechanisms. Rates and activation parameters for both processes for a series of complexes have been measured. Changes in both the enthalpies of activation and the entropies of activation are important in determining differences in reaction rate among the substitution reactions.

The nickel complexes exist in solution as equilibrium mixtures of paramagnetic tetrahedral, diamagnetic square-planar and paramagnetic octahedral compounds. These equilibria have been disentangled and the factors determining geometric structure in Ni(II) compounds are discussed. Rate and mechanism data for ligand exchange reactions are presented. An associative mechanism is demonstrated for the tetrahedral and square-planar compounds

and a dissociative mechanism for the octahedral complexes. NMR studies of a further series of nickel thiourea complexes containing Π-allyl ligands are described. These compounds are known to be catalytically active and the ligand exchange reactions prove to be too fast for measurement with the techniques used.

The zinc complexes are diamagnetic and tetrahedral in solution. The small chemical shifts preclude quantitative kinetic studies but qualitative comparisons with the analogous cobalt and nickel compounds are made. All of the complexes studied are very labile by the usual criteria and the overall study has allowed a more complete discussion of the factors determining ligand exchange rates in such compounds than has hitherto been possible.

An appendix describes some studies of complexes of diacetamide.

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ABBREVIATIONS OF FREE LIGANDS

Thiourea	Tu
N-methylthiourea	Mtu
N,N'-dimethylthiourea	Dmtu
N,N'-diethylthiourea	Detu
Tetrahydro-1,3-pyrazole-2-thione	Etu
1-(1-naphthyl)-2-thiourea	Nptu
1,1,3,3, tetramethylthiourea	Tmtu

CHAPTER I

INTRODUCTION

There have been many kinetic and mechanistic studies of ligand substitution reactions in recent years. The scope of such studies is shown by the large amount of data reviewed in the text-book of Basolo and Pearson[1], and in the monograph of Langford and Gray[2] on Ligand Substitution Processes. The large majority of the earlier studies dealt with relatively slow reactions which can be conveniently followed using the techniques of classical kinetics. More recently, relaxation spectroscopy techniques[3,4] have been developed for rapid reactions, but the Nuclear Magnetic Resonance (NMR) method[5,6] of observing line broadening during rapid ligand substitution reactions offers some powerful advantages. The spectral lines obtained in NMR experiments with liquid samples are usually extremely narrow, in contrast to those resulting from solid state studies. This is due to almost complete averaging of nuclear magnetic dipole-dipole interactions by random molecular motions. The lines often show multiplicity due to spin-spin coupling. They may also show broadening due to quadrupole coupling if nuclei with $I \geq 1$ are present, where I is the nuclear spin. The multiplicities of the lines, their widths and intensities (i.e. the line shapes) are also partly determined by dynamic processes such as hindered rotation or intermolecular rate processes leading to exchange of atoms or group of atoms between different chemical sites. The effect of such processes on the line shapes of some labile metal complex systems has been investigated in this thesis. The work has also involved some studies of hindered internal rotation.

Many transition metal complexes are labile. Labile complexes are defined as those for which ligand exchange occurs rapidly in solution. One criterion for ligand lability is provided by the condition for "fast exchange" in a NMR experiment. The average time a ligand remains complexed to a metal atom before exchange with free ligand is defined in this context as its life-time. The life-time range of 10^{-4} to 10^{2}s for ligand exchange rather nicely defines a class of complexes which can plausibly function as intermediates in homogeneously catalysed reactions. The mechanisms of such reactions catalyzed by transition metal complexes involve a sequence of ligand exchange steps. The occurrence of a more stable complex in such a sequence will slow down the reaction leading to ineffective catalysis. More labile complexes are likely to have such a transient existence that they are unimportant in determining the overall effectiveness of the catalysis. These considerations lead us to undertake some detailed studies of ligand exchange mechanisms involving systems at the shorter life time of the above scale. A number of additional considerations indicated the choice of systems for such studies. If the results are to have relevance to most homogeneous catalysis they should be restricted to exchange between neutral species in non-aqueous solvents. They also require a synthetically flexible system which will allow variation of the metal atom, the geometry of the complex, and both the exchanging and non-exchanging ligands in a fairly systematic manner. Paramagnetic metal complexes offer the advantage of large chemical shifts but this is often accompanied by the disadvantage of broader lines. The dominant relaxation mechanism in such compounds is likely to arise from the fluctuating magnetic fields produced at the nucleus by changes in the orientation of the electron spin. Thus the nuclear relaxation time is determined by the electron spin relaxation time. The necessary condition for observing sharpline NMR spectra is that the electron spin relaxation time should be very short.[7] Many of the complexes of Co(II) and Ni(II) satisfy this condition. NMR studies of exchange reactions involving ligands with many magnetic nuclei, e.g. phosphines, tend to lead to complex spectra which are not easily interpretable. Therefore, ligands with only one or two different magnetic nuclei are preferred. A combination of these factors lead to the choice of thiourea complexes of Co(II) and Ni(II) ions as a basis for the ligand exchange studies. A number of similar diamagnetic complexes with Zn(II) have been investigated for comparison purposes. Concurrent work in this laboratory has demonstrated that many of the complexes investigated are excellent catalysts for the reactions of ketones and amines to form anils. The present results are therefore directly relevant to the understanding of catalytic mechanisms.

Most of the early kinetic studies of substitution were concerned with the inert Cr(III), Co(III) and square-planar Pt(II) complexes[1] which undergo reaction at rates conveniently measured by classical techniques. This behaviour is attributed to the large crystal field stabilization of d^3, diamagnetic d^6 and d^8 systems. We first note that two basic types of ligand exchange mechanism have been postulated. The first type is described as "dissociative" and shows the basic feature that the rate-determining step involves loss of a ligand to give an intermediate of lower coordination number. For "associative" reactions, on the other hand, the rate-determining step involves the initial addition of a new ligand to give an intermediate of higher coordination number. Actual ligand exchange mechanisms do not necessarily correspond exactly to either of these limiting cases but the terms "dissociative" and "associative" provide a reasonable starting point for describing many processes. The generalization which has emerged from a large body of experimental data on ligand exchange processes is that octahedral complexes tend to exchange by dissociative mechanisms and square-planar and tetrahedral complexes by associative mechanisms.

Probably the most widely studied series of complexes are octahedral cobalt III compounds. The reasons for this are primarily the ready availability of many such complexes, their solubility in water, and the conveniently slow rate of their exchange reactions. The ligand exchange mechanisms depend on the pH of the solution. In acid solution, the primary process is always found to be the displacement of a ligand by solvent water. This is the rate-determining step. The subsequent displacement of water by the incoming ligand is always faster. As a result, rate data are only available for reactions in which one of the reacting ligands is water.[8,9,10] In no case is the rate for the replacement of one non-aqueous ligand by another known. However, a second type of reaction occurs at pH's greater than 5. This is known as the base hydrolysis reaction and shows the characteristic feature that the rates are dependent on the incoming ligand.

Studies on the rate of acid hydrolysis of a number of cobalt (III) chloro-ammines show that the kinetic data depend on various factors such as chelation, the size of the chelate ring, the charge on the metal complex, steric effects and the nature of the leaving group. It has been reported that cis-$Co(NH_3)_4Cl_2^+$ undergoes acid hydrolysis at a faster rate than cis-$Co(en)_4Cl_2^+$ and cis-$Co(trien)Cl_2^+$. This is attributed to the chelate effect.[11] A steric effect plays an important role in the hydrolysis of cobalt (III) complexes with ethylenediamine and its alkyl substituted derivatives [e.g. $Co(AA)_2X_2^+$]. It is found that the acid hydrolysis rate increases for every increase in the size of the substituents replacing the hydrogen atoms.[12] A similar trend is also noted if the size of the chelate ring is increased.[13] Such an increase in rate upon increased substitution or upon increase in the size of chelate ring is strongly suggestive of a dissociative mechanism. The influence of the charge [14,15] on the metal ion is readily noticeable in the acid hydrolysis of $Co(NH_3)_5Cl^{++}$ and cis- and trans- $Co(NH_3)_4Cl_2^+$. It is argued that a large amount of bond breaking in the transition state increases the over-all positive charge on the metal complex and is responsible for a reduction in the rate. The effect on the rate for these two complexes is of the order of magnitude of 10^2 to 10^3. Another effect which deserves mention in this area is the effect of solvation on the rate of hydrolysis. It has been reported that the rate of hydrolysis of $Co(NH_3)_5Cl^{++}$ in water is higher than that of the similar complex in D_2O.[16] This indicates that deuteration of the solvent interferes with effective solvation of the complex.[13] The last effect which influences the rate of ligand exchange is the nature of the leaving group. This is illustrated by the exchange reactions of $Co(NH_3)_5X^+$ in acid solutions.[17] The rate of this reaction is highly dependent on the nature of X, and decreases in the order[14] $X^- = NO_3^- > I^- > Br^- > H_2O > Cl^- > NH_3 > NCS^- > OH^-$. Although the majority of ligand exchange reactions in octahedral complexes appear to proceed by an essentially dissociative pathway, there may be exceptions. Studies of the effect of pressure on the kinetics of the exchange of ^{18}O between $Cr(H_2O)_6^{+++}$ and solvent water have been made by T.W. Swaddle et al.[18,19,20] For a dissociative mechanism the volume of activation ΔV^* should be a positive quantity. They found that $\Delta V^* = -9.3$ cm.^{3} mol^{-1} for the water exchange

$$Cr(H_2O)_6^{+++}(aq) + H_2^{18}O \longrightarrow [Cr(H_2O)_5(H_2^{18}O)]^{+++}(aq) + H_2O$$

This seems quite incompatible with a dissociative mode of reaction, but appears to be consistent with a rate-limiting step represented as

$$[Cr(H_2O)_6(H_2O)_x]^{+++}(aq) \longrightarrow [Cr(H_2O)_7(H_2O)_{x-1}]^{+++}(aq)$$

i.e., an associative process.

The Cr(III)-ammine complexes are more labile than the corresponding Co(III) complexes. The rates of aquation of these complexes decrease along the sequence[21] $I^- > Cl^- > NCS^-$. The rates are about 10 times greater than those of the analogous cobalt compounds. Garner and his co-workers[22-24] suggested that the rate and stereo-chemistry in the acid hydrolysis reactions of cis- and trans-$Cr(en)_2Cl_2^+$ parallel those of Co(III) in structural effects and stereo-chemistry, and the activation energies are found to be almost identical. Jones et al.[25] observed that divalent anions such as maleate and o-phthalate catalyzed the loss of Br^-, and the catalytic effect of each anion was explained by an outer-sphere ion pair. The acid hydrolysis reactions of derivatives of $Cr(H_2O)^{+++}$ are found to show first-order kinetics. The rates increase in the sequence[26] $NCS^- < Cl^- < Br^-$. Good evidence for a dissociative mechanism is provided by the lack of entering group assistance in anation reactions. $Cr(H_2O)_6^{+++}$ undergoes anation reactions with a series of organic acids. It has been observed that the rates are independent of both the anion concentration and the nature of the anion.[26,27] Acetate, malonate, citrate and phthalate all enter at the same rate indicating a dissociative mechanism. The behaviour of Rh(III)-ammine complexes with a series of nucleophiles such as Br^-, OH^-, I^-, Cl^-, thiourea and NH_3

has been investigated. They all attack at the same rate[28]. The reactions of the Rh(III) ammines are slower than those of the analogous cobalt(III) complexes.

On the other hand, the reactions of the cobalt(III) amines with hydroxide are kinetically second order. They are generally very much faster than the acid hydrolysis reactions. They are pH-dependent and follow the rate law

$$\text{Rate} = k_1 \left[L_5CoX\right] + k_2 \left[L_5CoX\right]\left[OH^-\right]$$

k_2 for the base hydrolysis is some 10^4 times k_1 for the acid hydrolysis The most obvious interpretation of the second term in this equation would involve an associative process with an intermediate of coordination number greater than 6. There are however, other possibilities. Thus Garrick* has suggested a mechanism involving a so-called " conjugate base " and writes the reaction sequence -

$$Co(NH_3)_5Cl^{++} + OH^- \rightleftharpoons Co(NH_3)_4(NH_2)Cl^+ + H_2O$$

$$Co(NH_3)_4(NH_2)Cl^+ + H_2O \longrightarrow \left[Co(NH_3)_5OH\right]^{++} + Cl^-$$

* F.J. Garrick, Nature, 139, 507(1937).

The second step is rate-determing and the rate of exchange is given by

$$\text{Rate} = k.K \, . \, [Co(NH_3)_5Cl^+] \, [OH^-]$$

Thus the measured second-order rate constant is the product of the equilibrium constqnt (K) for the first step and the first-order rate constant (k) for the hydrolysis of the conjugate base of the complex. This mechanism requires at least one acidic proton on a non-leaving ligand of the complex. The rate of deprotonation is fast compared to the rate of displacement. According to this mechanism, in complexes having no acidic proton,acceleration by base should not be observed. This is in general true (as for 2,2'-bipyridine complexes*,for instance[2]) but there are a few cases in which reactions first-order in OH^- are observed.One of these is the base hydrolysis of $Co(EDTA)^-$ by OH^- for which the formation of a seven-coordination intermediate has been proposed. The conjugate base mechanism involves a second step.

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*The original studies assumed [2] that dinitro-bis(2,2'-bipyridine cobalt (III) ion has trans geometry but an X-ray structure determination of analogous chloride compound showed to have cis geometry. (H.Masayki,O.Shunichiro,K.Hisao,Bull Chem.,Jap., 44(2),586(1971); G.John Graham,E.D.Mc Kenzie,J.Chem. Soc. A,2478-80(15)(1970).

There is evidence[1,18] that the intermediate formed in this step has trigonal bipyramidal geometry and has a lifetime long enough to show discrimination with respect to the entering ligands.

All the data thus far discussed have been obtained in aqueous solution. The number of studies in non-aqueous solvents, is much smaller. Cobalt ammine complexes have been examined in several non-aqueous solvents including methanol, N,N'-dimethylformamide, dimethylsulfoxide, acetone, and N,N'-dimethylacetamide. All these solvents are polar having relatively high dielectric constants and the solutes behave as strong electrolytes. In general the kinetics are more complex than in aqueous solution and simple rate laws are not common. An example is provided by the reaction between cis-$Co(en)_2Cl_2^+$ and chloride ion in methanol. In this case, the suggested mechanism involves the initial formation of an outer sphere complex cis-$Co(en)_2Cl^{+}....Cl^-$ which reacts to give chloride exchange. This reaction is competitive with direct exchange leading to a two term rate law expression of the type

$$\text{Rate} = k_1 \left[Co(en)_2Cl_2^+\right] + k_2 \left[Co(en)_2Cl_2...Cl^-\right]$$

The reactions of this compound and also of the trans isomer have been studied in other solvents such as dimethyl formamide and dimethyl acetamide. Similar outer sphere mechanisms were demonstrated in these solvents. However, the outer sphere association constants are much smaller for the trans isomer than for the cis isomer.

By far the most stable square-planar complexes are those of Pt(II), and as a result, the synthesis and reactions of these compounds have long been the subject of extensive investigations[37]. During the past decade more quantitative studies have been made on these systems, and an appreciable effort has been devoted to investigations of the kinetics and mechanisms of their reactions[1,29]. Simple but pertinent theoretical arguments lead to the conclusion that from both steric and electronic considerations, an associative mechanism is expected to be the most useful model for discussions of square-planar (d^8) substitutions.

Substitution reactions of Pt(II) complexes proceed with retention of geometric configuration[1,2]. Most square - planar substitution reactions in solution generally follow a two-term rate law which may be shown to be

$$\text{rate} = \frac{-d\,[\text{complex}]}{dt} = (k_I + k_2[Y])\,[\text{complex}]$$

where k_I and k_2 are first-order and second-order rate constants, [Y] and [complex] represent the concentrations of entering ligand and the complex respectively. Kinetics of reactions in aqueous solution of $Pt(dien)Br^+$ with several entering groups, including OH^-, Cl^-, I^-, NO_2^-, and SCN^- have been studied[29] and the rate law, and pseudo first-order constants $k_{obs.}$ for these reactions determined for various concentrations of the entering ligand [Y]. The plots of $k_{obs.}$ versus [Y] are made in the concentration ranges studied. The plots are linear, with non-zero intercepts. The slopes of the lines give the various k_2's and the intercepts give the k_1's. Since the k_1 term arises from an associative mechanism involving specifically one molecule of solvent as reactant, the rate equation may be rewritten as

$$\text{rate} = (k_s[S] + k_2[Y])\,[\text{complex}]$$

$$k_I = k_s[S]$$

The experimental rate law is thus compatible with an associative mechanism for planar substitution, but the k_1 term could be due to a dissociative process.

The kinetic trans effect refers to the special effects of trans substitution on the lability of a leaving group. It is probably the most dramatic kinetic effect known, spanning several orders of magnitude in rate. Theories of the trans effect have been presented by many authors.[27,30-35]

It seems clear that both σ- and π- electronic effects are important.

Experimental evidence for an associative mechanism in Pt(II) complexes has been demonstrated. Large rate effects on blocking the entering group attack positions above and below the plane have been noted.[36] These can be nicely explained on the grounds that results of a study of the rates of reaction of various (cis- and trans-) $Pt(PEt_3)_2(R)Cl$ complexes with pyridine in ethanol solution have demonstrated that, if the ligand R is a mesityl group, the relative rates of exchange for chloride both in cis and trans positions are found to be 1:1. However, if R is replaced by a phenyl ring, the relative rates are found to be 80000:36. This is a direct evidence that cis blocking is more effective than trans blocking. The cis blocking causes the relative rate to drop by 1/80000 from R=phenyl to R=mesityl, whereas trans blocking only causes a drop of 1/36.

The role of the leaving group in Pt(II) complexes plays an important part in the substitution reactions. In the study of the reactions of $Pt(diene)X^+$ with pyridine in aqueous solution[37], it is found that the rates of exchange reactions decrease along the series:

$$X = NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$$

One of the most important requirements of an associative mechanism is that there be large differences in the reactivities of different entering groups. Numerous investigators[38-44] have established that this is indeed the case in square-planar Pt(II) substitutions. Values of the second-order rate constant in aqueous solution for the reactions[29] of $Pt(diene)Br^+$ with various entering ligands have been reported. The order of ligands in decreasing k_2 value is

Thiourea > SCN^- > I^- > N_3^- > NO_2^- > py > Cl^- > OH^-

A detailed study of reactions of different ligands with several substrates, especially trans-$Pt(py)_2Cl_2$ in methanol solution has been reported[40], and k_2 values are summarized. The results of these studies lead to the conclusion that the average ligand-reactivity order bears a remarkable resemblance to the trans- effect order. Thus a good trans labilizer is also a good entering group in square-planar substitutions.

The solvent dependence of the reaction rates of Pt(II) complexes provides another test of the suggestion of associative activation involving solvent for the k_I term in the rate law. The exchange reaction of trans-$Pt(py)_2Cl_2$ has been studied in several different solvents.[45] It was found that the k_I term is important in solvents that are capable of good co-ordination with Pt(II). The order of increasing k_I is ROH < H_2O, $MeNO_2$ < DMSO. In solvents that are expected to be poor entering groups, the k_2 term for the reaction is more important. These solvents include C_6H_6, CCl_4, t-C_4H_9OH, $(Me)_2C{=}O$, and EtOAc.

Martin and co-workers[46-48] have obtained conclusive evidence for an associative solvent path, by observing the lack of a larger rate effect in the k_I path for reactions of complexes carrying different net charges in aqueous solution. Preceding from $Pt(NH_3)_3Cl^+$ to $PtCl_4^=$, the first order rate constants stay roughly constant. This is not consistent with a bond-breaking mechanism but is reasonable assuming an associative mechanism. There are small but significant substrate-charge effects on the k_2 term with certain entering groups. In particular, $k_2(NO_2^-)$ is larger than $k_2(Cl^-)$ with $Pt(dien)Br^+$ as substrate, but $k_2(Cl^-)$ is larger than $k_2(NO_2^-)$ with $Pt(dien)OH_2^{++}$ as substrate.[39(a)]

Recently, R.G. Pearson et al.[39(b)] have reported the activation energy parameters for the reaction of $Pt(dien)X^+$ (diene=$NH_2C_2H_4NH_2$;X^-=Cl^-, Br^-, I^-, N_3^-, SCN^-, or NO_2^-) in water solution with several different nucleophiles such as H_2O, thiourea, $S_2O_3^=$, etc. They found that high rates of reaction parallel low enthalpies of activation. All reactions have an appreciable negative entropy of activation ranging from -18 cal. K^{-1} mole^{-1} to -30 cal. k^{-1} mole^{-1}. depending on the nature of each nucleophile. The most striking feature of these results is that the negative entropies of activation for the substitution processes with thiourea are the largest in magnitude and this is attributed to the formation of the transition state accompanied by a net increase in bonding.

A review published by Taube[49] in 1952 summarizes the situation at the beginning of the current period of active interest in ligand substitutions. At that point in time, most metal complexes could only be classified as labile since the experimental techniques were not available for obtaining quantitative data. This was still true when the theory of substitution processes was reviewed exhaustively by Basolo and Pearson in 1958.[27] In the years since, the situation has changed radically as a result of the introduction of methods for the study of reaction rates up to and including the diffusion-controlled limit. Some of the slower reactions of labile complexes have been measured by flow methods[51,52], but the break-through is a result of the application of the relaxation methods developed by Eigen and his collaborators[1,50], and the use of NMR relaxation-time studies, pioneered by Connick and his co-workers.[4] We will now briefly review some of the applications of these newer methods.

R.G. Wilkins et al.[51,52] applied stopped-flow photometry to the studies of the dissociation of Ni(II) complexes with ethylenediammine in aqueous acid solution. In this technique, free ligand and the complex ion are first rapidly mixed. The flow of the mixed solution is then suddenly arrested at a constant temperature, and changes in the optical density of the reacting solution are recorded on an oscilloscope. Reasonable optical density changes during reaction were obtained by using suitable concentrations of the reacting species. Half-lives of 10^{-3} to 10^{1} seconds can be estimated with reasonable accuracy using this method. The rates of dissociation, in an excess of acid, of Ni(II) complexes with a series of nitrogen-containing unidentate ligands have been investigated, by the stop-flow method. The ligands include NH_3, pyridine, aziridine, and hydrazine. The rate of dissociation appears to be independent of acid concentration. A comparison of the results for complexes of ammonia and pyridine with those of the corresponding bidentate ligands, viz., ethylenediamine and bipyridyl shows that the energies of activation for the former are some 6-7 K cals.mole^{-1} lower than those for the latter. In addition, the ammonia complex has a distinctly lower energy and entropy of activation due to the formation of H-bonds with the surrounding water molecules. The rates of dissociation, in acid, of Cu(II) complexes of ethylenediammine, racemic butane-2, 3-diamine and 2,3-dimethyl butane-2, 3-diamine and tetra-N-methyl isomer have also been investigated by the stop-flow method. In nitric acid solution, the first order dissociation of Cu(II) complexes is greater than those of Ni(II) complexes. Without exception, the Cu(II) complexes react more rapidly than the corresponding Ni(II) compounds and the reactivity sequence may be shown to be Zn $\geq$ Cu > Ni.

Much larger rates of reaction may be studied by the relaxation techniques developed by Eigen.[1,50] In such methods, a reaction system in equilibrium is disturbed by change of an external parameter(e.g. temperature, pressure or electric field). The perturbed system returns to equilibrium at a characteristic rate. The adjustment or "chemical relaxation" takes place with a characteristic spectrum of time constants which may be related to the rate constants of individual steps in the reaction. An analysis of the relaxation spectrum allows the determination of the absolute rate constants and gives information concerning the mechanism of the over-all reaction.

The most widely used relaxation technique in the study of rapid substitution reactions in solution is the temperature-jump method.[53,54] This method is, in fact, the most widely used and widely applicable of the relaxation methods reported in the literature. It can be employed for equilibrium reactions which are accompanied by a thermal change. The temperature variation of the equilibrium constant K is given by the equation

$$\frac{d \ln K}{dT} = \Delta H^{\circ}/RT^{2}$$

where T is the temperature and ΔH the heat of reaction. Relaxation curves are recorded oscillographically from the variation in the light absorption or the electrical conductivity of the solutions. For ionic solutions a jump in temperature is achieved by means of a pulse discharge from a capacitor charged to a high voltage. This feature limits the applications to conducting solutions. Equipment combining the flow method with the temperature-jump method is very promising for the study of complicated multistage reactions and also for fast irreversible processes.

The competing method for studying rapid substitution reactions is the pressure-shock method.[53,54] The effect of pressure on the equilibrium constant is represented by the equation

$$\beta = \exp\left(\int_{P_1}^{P_2} (d \ln K/\partial_p)dP\right) = \exp\left(\int_{P_1}^{P_2} (-\Delta V^\circ + \Delta H^\circ(\partial V/\partial T)_p C_p/RT)dP\right)$$

where ΔV° and ΔH° are the changes in volume and enthalpy, and $\beta = K_2/K_1$, in which K_2 and K_1 are respectively the equilibrium constant at $P + P_2$ and $P = P_1$: a change in pressure thus produces a change in the equilibrium constant, as a consequence of which relaxation processes occur at a rate determined by that of the chemical reactions involved. The magnitude of the β is 0.004 with $V^\circ = 1\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$ and a change in pressure from 1 to 100 atm. This shift can be easily recorded by various physicochemical methods. The great advantage of the pressure-shock method is the possibility of studying directly conversions of outer-sphere into inner-sphere complexes and conversely.

By means of ultrasonic vibrations it is possible to study chemical reactions whose duration approximates the period of the sound wave. The frequency dependence of the absorption of sound is influenced by the changes in free energy, entropy and volume occurring during the reaction, and also by the rates of the chemical reactions taking place in the system, so that both kinetic and thermodynamic data can be obtained by this method.

For single-stage reactions the ultrasonic absorption-frequency curve passes through a maximum, the position of which can be used to determine the relaxation time, and from which the reaction rate constant can be calculated. With multistage reactions, the mathematical processing of the experimental results is considerably more complicated. There exists a method of calculation which is applicable only to a two step process.

The equipment used in the study of fast chemical reactions by the acoustic method is that usually employed for measuring the velocity and absorption of ultrasound in liquids. The disadvantages of this method include the relative complexity of the apparatus used, the difficulties of processing the experimental results for complicated reactions, and also the large quantities of solutions necessary for an experiment.

NMR spectroscopy allows detection and study of rate processes which are not readily sensed by other conventional spectroscopic techniques. Rates and activation barriers for internal rotation were subjects of some of the earlier kinetic studies.[56] NMR studies of the rotational barrier about the central C-N bond in amides, thioamides and N-methylthiourea have been made.[57-62] The results of these studies have indicated that the energy barrier is greater than for a normal C-N bond because of electron delocalization.[59-64] Several authors have reported that the rotational barriers in thioamides are higher than for amides. The determination of kinetic parameters for the interconversion of geometrical isomers of amides and thioamides by NMR spectroscopy has been a controversial subject.[61,65,66] In addition to the errors involved in comparing results obtained by various NMR techniques, solvent and concentration effects seem important in these systems.

The presence of any paramagnetic centre will influence the NMR spectrum of a resonating nucleus.[67] In terms of chemical applications, the most significant effects is the interaction between the unpaired electrons and magnetic nuclei as revealed by the isotropic hyperfine shifts[68] and the changes in nuclear relaxation times.[67] These two effects can provide much information relating to the electronic and geometrical structures of paramagnetic species and the way in which they interact. Through their hyperfine interactions, unpaired electrons can cause shifts in nuclear frequencies and can provide effective relaxation mechanisms for nuclei. The only direct observations of NMR signals from paramagnetic species in solution have been for cases where the electron spin lattice relaxation times were so short that the hyperfine interactions almost averaged to zero.[69] However, signals have often been observed for nuclei which spend only a fraction of the time in the vicinity of unpaired electrons. When the line shapes or relaxation times for the nuclei can be related to the lifetimes of the exchanging species in solution, reaction rates can of course be determined. A discussion of the relevant theory will be deferred until Chapter II. Some of the more pertinent results obtained by this method are summerized below.

NMR studies of dilute aqueous solutions containing paramagnetic metal ions have been made by Swift and Connick.[4] Employing various limiting situations, these authors have evaluated the kinetic parameters for water exchange between bulk medium and solvated cation.

^{17}O NMR spectroscopy has been widely applied to ligand exchange studies.[71-75] A comparison of ^{17}O NMR data and proton NMR data for aquo metal ions in aqueous solution makes it possible to decide whether proton exchange occurs via proton ionization or the complete exchange of a water molecule. The similarity of the kinetic parameters from the ^{17}O and proton data suggest that the complete exchange of water molecules occurs in aqueous solutions of Mn(II), Co(II), Ni(II) and Cu(II) ions, whereas in solutions containing VO^{+2}, Cr(III) and Fe(III) ions, the acid dissociation of the hydrated metal ion appears to be the probable mechanism for the proton exchange.[76-78] The similarity of the kinetic data derived from the methyl and hydroxyl protons for methanol in the presence of Mn(II), Co(II) and Ni(II) ions indicates that the exchange between the bulk solvent and solvation shell involves whole methanol molecules and there is no significant contribution from hydroxyl proton exchange.[79-81] Comparable results have been obtained from ^{1}H and ^{14}N data on $Ni(NH_3)_6^{++}$ in an aqueous-ammonia medium, showing that exchange rate of the individual proton is no greater than that for the exchange of complete ammonia molecules.[82-84] The rates of elimination of water molecules from the first coordination sphere of vanadyl ions in aqueous solutions have also been determined from ^{17}O data.[73,74,85] The slow rate of water exchange, compared to other doubly charged metal ions, led to the conclusion that the high positive charge on V^{+4} is important in deciding the bonding of the four equatorial water molecules in the first coordination sphere, whilst the water molecule in the axial position undergoes rapid exchange. By comparing the NMR data on the vanadyl ion in a DMF solution at 25°C with that for aqueous solutions, it is found that the rate constants for water and DMF exchange are very similar, but that the activation energy for DMF exchange is much smaller indicating that it is a weaker ligand than water. The values for the entropy of activation suggest that the transition state is more disordered for water exchange possibly due to the effect of hydrogen bonding between water and the vanadyl ions.[86]

The kinetics of ligand exchange have been investigated recently in tetrahedral complexes as well as octahedral ones.[87,88,89,90,91] Proton NMR data are reported for complexes of type ML_2X_2 where M= Fe(II), Co(II) or Ni(II) and the exchanging ligand L can be triarylphosphine,[87,89,90] 2-picoline[88] or hexamethylphosphoramide[91] and X is a halogen. Co(II) hexamethylphosphoramide complexes exchange via a mixture of first and second order kinetics. All other complexes studied show only second order kinetics in their ligand exchange reactions. The necessity of a first order term for the hexamethylphosphoramide ligand has been rationalized in terms of the steric hindrance produced by its size which increases the tendency for the ligand to dissociate from the complex.[91] In the triarylphosphine series of ligands, it appears that the lability of the complex is not very dependent upon the nature of the phosphine, but that within a given series the lability increases slightly in the order I < Br < Cl. Moreover, the effect of metal upon the lability follows the order Co < Ni < Fe.

Kinetic data from NMR studies on solutions of acetonitrile in solutions containing Co(II) and Ni(II) ions have been reported. The rate of the solvent substitution reaction in a Co(II) complex is greater than that of the corresponding Ni(II) system. This arises from a difference in activation enthalpy for the two reactions. The relative decrease in stability of Co(II) octahedral complexes compared to those of Ni(II) in many donor solvents has been discussed in terms of crystal field stabilization effects.[92,93]

The rate of exchange, or limits to the rates, of several unidentate and bidentate ligands (ammonia, ethylenediamine, glycine, N-methylglycine and N, N-dimethylglycine) coordinated to Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been measured by proton NMR line broadening studies.[94] The usual order of reactivity has been found as Mn > Fe > Co > Ni ≪ Cu. Copper complexes exchange via a second order process in agreement with the S_{N2} mechanism common for planar complexes. All octahedral complexes undergo exchange reactions via first order kinetics. A solvent assisted dissociation mechanism is common for all octahedral complexes.

In the present section, a review of concepts, methods and a selection of experimental results have been presented. A detailed theory concerning the effects of chemical exchange on line shapes will be discussed in Chapter II. A selection of data on ligand exchange kinetics obtained by NMR experiments is shown in Table (1-1).

Table(1-1):Kinetic and Activation Parameters in Ligand Exchange Processes of First-row Transition Metals

Reaction	M	L	k_I sec^{-1}	K_{II} $mole^{-1}$ sec^{-1}	Conditions		ΔH‡ Kcal $mole^{-1}$	ΔS‡ eu	References
$M(H_2O^*)^{n+}+H_2O=M(H_2O)^{n+}H_2O^*$	Fe^{+3}	water	1.10^6		^{17}O NMR				(4)
	Mn^{+2}		1.10^7						
	Cu^{+2}	" water	6.10^5		Natural				–
	Co^{+2}		2.10^5						
	Ni^{+2}		4.10^4		Abund-ance				-
$M(NH_3^*)+NH_3=M(NH_3)+NH_3^*$	Cu^{+2}	Ammonia	$\sim7.10^6$		^{14}N NMR				
	Ni^{+2}		$\sim8.10^4$						(95)
									–
		Ethylene-diamine							-
$Cu(en^*)_2(H_2O)^+ +en=Cu(en)_2(H_2O)_2^{+2}+en^*$	Cu^{+2}			$2.4x.10^7$	^1H NMR				(96)
$Co(en^*)_3^{+2}+en=Co(en)_3^{+2}+en^*$	Co^{+2}		$4.8x10^3$		^1H NMR				(97)
$M(NH_3)_x^{n+}+OH^-=M(NH_3)_{x-1}(NH_2)^{(n-1)+}+H_2O$	Zn								-
	Cd			^1H NMR					(98)
	Hg								
$ML_x^*+L=ML_x+L^*$	Mn(II)	Ethylene-glycol	$\sim1.5x10^6$						(94)
	Fe(II)		$>2.5x10^3$						
	Co(II)		$>3.4x10^3$						
	Ni(II)		$4.4x10^3$				EA>6 Kcal		-
	Cu(II)		$>1.1x10^5$			27C			
	Cr(III)		$9.7x10^4$				EA=6 Kcal		
$Cu(NH_3^*)_4^{+2}+NH_3=Cu^*(NH_3)_4^{+2}+N^*H_3$	Cu(II)			$>1.9x10^7$			EA>4 Kcal		-
$Cu(NH_3^*)_5^{+2}+NH_3=Cu(NH_3)_5^{+2}+N^*H_3$	Cu(II)		$>5.7x10^6$						
$Ni(NH_3^*)_5^{+2}+NH_3=Ni(NH_3)_5^{+2}+N^*H_3$	Ni(II)	Ammonia	$>6.3x10^4$		^1H NMR	27 C			(94)
$Ni(N^*H_3)_6^{+2}+NH_3=Ni(NH_3)_6^{+2}+N^*H_3$	Ni(II)		$>4.5x10^4$						-
$Co(N^*H_3)_5^{+2}+NH_3=Co(N^*H_3)_5^{+2}+N^*H_3$	Co(II)		$>4.7x10^4$						-

Table(1-1)

$ML_n^{*+2}+L=ML_n^{+2}+L_n^*$	Ni(II)	Acetonitrile	1.24×10^4				11.8±0.8	-0.2±2.5	
					^{1}H NMR	25			(100)
	Ni(II)		0.39×10^4		^{14}N NMR		10.9	-8.8	—
	Ni(II)		0.24×10^4				11.7±0.1	-3.6±0.1	—
	Co(II)		15×10^4				8.4±0.6	-7±2	—
	Co(II)		14×10^4				8.1±0.3	-7.5±2	—
									—
$ML_2^*X_2+L=ML_2X_2+L^*$ X=Cl,Br	Co(II)Cl_2	Hexamethyl-	25.1	87.2		-26C	EA(k_1)=20±3	EA(k_2)=7±2	(91)
	Co(II)$_2$ Br_2	phosphoramide	57.4	260.0			EA(k_1)=15±2	EA(k_2)=5±1	—
	Co(II)$_2$	2-picoline			^{1}H NMR	-39C	EA (k_2)=5.3		
	Cl_2						$\Delta H^\ddagger$= 4.8	$\Delta S^\ddagger$=-14.5	(88)
									—

$M^{+2}+X^-=MX^+$			Values for both						(99)
$MX^++X^-=MX_2$		Halide ions	forward and back-	^{81}Br,					
			ward rates are	^{79}Br,					(99)
$MX_2+X^-=MX_3^-$ M=Zn,Cd,Hg			given for Zn,Cd,Hg	^{127}I					
$MX_3^-+X^-=MX_4^=$				NMR					
$MX_2L_2^*+L=MX_2L+L^*$	NiCl			3.2×10^5			8.1±0.8	-07±4	(87)
	Niby			6.9×10^3			4.7±0.4	-25±2	—
	NiI	Triphenyl-phosphine		6.4×10^2			6.9±0.6	-23±3	—
	CoCl			1.2×10^4	^{1}H NMR	25 C	8.8±0.8	-10±4	(87)
	CoBr			8.7×10^2			7.7±0.5	-19±3	
	CoI			2.6×10^2			9.1±0.7	-17±4	-
$MX_2L_2^*=MX_2L_2+L^*$	NiCl			1.9×10^4			5.2±0.8	-21±4	-
	NiBr			6.1×10^3			5.2±0.8	-24±4	
		Tri-p-tolyl			^{1}H NMR	25 C	5.2±0.8	-24±4	-
	NiI	phosphine		5.9×10^3					
	CoCl			2.2×10^3			4.4±0.9	-29±5	-
	CoBr			1.8×10^3			5.5±0.9	-25±5	(87)
	CoI			8.3×10^2			5.9±0.9	-25±5	-
	CoBy	N-butyldiphenylphosphine		8.3×10^3			7.1±0.5	-17±3	
					^{1}H NMR	25 C	7.7±0.6	-23±4	(87)

k_1 = first-order rate constant, k_{11}=second-order rate constant

CHAPTER II

THE USE OF NUCLEAR MAGNETIC RESONANCE IN KINETICS OF LIGAND SUBSTITUTION PROCESSES

The technique of Nuclear Magnetic Resonance has proved to be a very powerful tool for the investigation of many problems in a variety of fields. One of its most useful applications has been concerned with the kinetics of rapid ligand substitution reactions of labile complexes in solution. The NMR theory pertinent to this type of study is well-developed and several review articles are avaliable.[3,4] Paramagnetic compounds present some additional complexities and the relevant theory is also discussed in the present chapter.

(2-1) CHEMICAL SHIFTS AND SPIN-SPIN COUPLING

The relaxation properties of nuclear spins are affected by fast chemical reactions. This effect provides a potentially useful method for the measurement of reaction rates. The position of the resonance of a particular nucleus (i.e. the chemical shift) is determined by magnetic shielding within the molecule. This shielding (i.e. screening effect) arises from the circulation of molecular electrons and as a result, the magnetic field experienced by the nucleus is not the same as the magnetic field externally applied. If the field induced at the nucleus is opposed to the applied field, a diamagnetic shift arises. In the magnetic resonance experiment, therefore, it will be necessary to apply a higher field to bring about the resonance condition. Resonance may be attained at a lower radio frequency if the applied field is held constant. Conversely, a paramagnetic shift is one to lower field or higher frequency.

The chemical shift may be broken down into a number of factors. These include inductive effects, ring current effects and influences of magnetically anisotropic groups, hydrogen bonding and interactions with unpaired electrons. The theory for the magnetic shielding was developed by Lamb[101] and by Saika and Slichter.[102] Griffith and Orgel[103] developed a theory to account for the paramagnetic contribution to the chemical shift of ^{59}Co in octahedral Co(III) complexes. Several review articles are contained in various texts. In principle, important information can be extracted from chemical shift data concerning a detailed knowledge on the different types of magnetic environment. In practice, its greatest value still lies in empirical correlations with molecular structure. There is one class of compounds for which chemical shifts sometimes give unambiguous structural information. This class comprises certain paramagnetic transition metal complexes and will be discussed in detail in a subsequent paragraph. In addition to chemical shifts, the analysis of high resolution NMR spectra also yields spin-spin coupling constants.

Structural information of several types may be obtained from such data. The mere counting of the number of lines in the different multiplets suffices to determine the numbers of nuclei of the various chemically distinct types. The rough magnitudes of the coupling constants can often indicate whether two nuclei are directly bonded or are separated by other atoms, and the actual numerical values of the coupling constants may provide the information about the nature of the bonding. Several review articles are also available in various texts.

The other types of parameters obtained from the NMR spectra of solids are the dipole-dipole coupling and quadrupole coupling constants. These may provide additional information on the molecular geometry and on the electro-static environment of the nuclei.

(2-2) NMR OF PARAMAGNETIC COMPOUNDS

Paramagnetic species may be studied by either ESR or NMR. It is well known that the appearance of ESR or NMR spectra depends on the electron spin relaxation time T_{1e}. The necessary condition for observing well-resolved ESR hyperfine structure is that T_{1e} be long such that $A >> T_{1e}^{-1}$, where A is a hyperfine coupling constant. For NMR, the spectral properties are determined by the nuclear spin relaxation time which in turn depends on T_{1e}, since for a paramagnetic molecule, the nuclear relaxation mechanism is likely to arise predominantly from the fluctuating magnetic fields produced at the nucleus by changes in the orientation of the electron spin. The requisite condition for observing well resolved NMR spectra for a paramagnetic compound is either or both $T_{1e} << A^{-1}$ and $T_c << A^{-1}$ are fulfilled, where T_c is the exchange time for paramagnetic species. Electron spin lattice relaxation times are found to decrease with increasing temperature. Thus NMR experiments in solution are usually performed at relatively high temperature and ESR experiments tend to be most informative in solids at low temperature.

(2-3) CONTACT AND DIPOLAR SHIFTS

The magnetic interactions between electron and nuclear spins have been extensively reviewed by Abragam,[104] Winter,[105] and by Freeman and Watson.[106] The Hamiltonian for the electron-nuclear spin system in paramagnetic species is given by

$$H = - g_N \beta_N I . H + H_{LS} + H_{SS} + H_N + g\beta(L + 2S) . H + H_{II} \qquad (2\text{-}1)$$

The first and fifth terms represent the interactions of the nuclear and electron magnetic moments with external magnetic field. H_{LS} is the spin-orbit interaction for the electronic system. H_{SS} is the interaction between electron spins and H_{II} that between nuclear spins. H_N is the hyperfine interaction term and represents the interaction between the electron spin and orbital moments and the nuclear magnetic moment. This is the most important and interesting term for NMR in paramagnetic systems. The hyperfine interaction term which was derived by Fermi[107] from Dirac relativistic theory for the electron, can be written as

$$H_N = - g\, g_N\, \beta\, \beta_N \left(\frac{8\pi}{3}\right) \delta(r)(S.I) + \left(\frac{(L-S).I}{r^3} + \frac{3(S.r)(I.r)}{r^5}\right). \qquad (2\text{-}2)$$

The distance r is measured from the centre of the nucleus. The interaction involving the delta function is the Fermi contact term. This term has a non-zero value only for the s-electrons and then the last two terms are zero. The last two terms are dipolar interaction terms and have a form analogus to that of the classical expression for the interaction of point dipoles $g_n\beta_nI$ and $g\beta S$ plus the interaction of a point dipole $g_n\beta_nI$ with a moving charge of L angular momentum. The expression for the hyperfine interaction term has also been derived on the basis of Quantum Field Theory.[108]

As the result of this hyperfine interaction, the resonance of the nucleus is shifted to higher or lower field than that of a corresponding nucleus in an analogous diamagnetic compound. In solution, rapid tumbling of the molecules averages some terms in this expression to zero. The remaining terms give rise to an isotropic shift. The isotropic shift is usually composed of two factors: the first of which is the so-called "Fermi Contact Shift" which arises from the presence of unpaired electron spin density at the resonating nucleus. The second results from through space interaction between the magnetic dipoles produced by the unpaired electron(s) and the resonating nucleus. The general expression for the proton contact shift is given by Bloemgergen equation[109,110]

$$\frac{\Delta\nu_c}{\nu_o} = - A \frac{\gamma_e}{\gamma_N} \frac{g\ \beta\ S(S+1)}{3kT} \qquad (2\text{-}3)$$

The quantity $\Delta\nu_c$ is the NMR contact shift, ν_o the resonance frequency, S the electron spin, γ_e and γ_N the magnetogyric ratio for the electron and the nucleus, and A the electron spin-nuclear spin hyperfine coupling constant. The other symbols have the usual significance. The electron spin-nuclear spin coupling constant A may be related to the unpaired electron spin density $(\psi(0))^2$ at the nucleus in question by

$$A = \frac{8\pi}{3h} g\, g_N \beta\, \beta_N [\psi(0)]^2 \qquad (2\text{-}4)$$

The Curie law contact shift equation can be expressed in terms of the susceptibility as follows:

$$\frac{\Delta\nu_c}{\nu_0} = \frac{A}{N g_N \beta_N} \cdot \frac{N \mu^2}{3kT} = \frac{A}{N g_n \beta_n} \chi_M = c\, \chi_M \qquad (2\text{-}5)$$

where $\mu^2 = g^2 \beta^2 S(S+1)$ for spin contribution only and χ_M is the molar magnetic susceptibility.

Most of the contribution arising from the dipolar part of the Hamiltonian is anisotropic and average to zero for a rapidly tumbling molecule in solution but an isotropic part remains. The dipolar shift is given in general

$$\frac{\Delta\nu}{\nu} = \frac{\beta^2 S(S+1)}{27\, kT} (g_{II} + 2g_I)(g_{II} - g_I) \frac{(3\cos^2\theta - 1)}{r^3} \qquad (2\text{-}6)$$

where θ is the angle between the principle magnetic axis and a line joining the metal atom and the magnetic nucleus under consideration, r is the distance of this nucleus from the metal atom, and g_{II} and $g_{\perp}$ are the components of the g-tensor parallel and perpendicular to the magnetic field. Other symbols have the usual significance. Contribution of this term will be zero if g_{II} is equal to $g_{\perp}$.

A more general but complicated expression for the isotropic contact shift of a paramagnetic compound in solution has been derived by

Kurland and McGarvey.[111] It can be given as

$$\left(\frac{\Delta v}{v_o}\right)^{iso} = (1/3kTq) \sum_{x,y,z}^{i} \sum^{\Gamma_n,\Gamma_m} e^{-E_\Gamma/kT} <\Gamma_n|\mu_i|\Gamma_m> <\Gamma_m|A_{Ni}|\Gamma_n>$$

$$- KT \sum_{\Gamma \dagger \Gamma'}^{\Gamma_n,\Gamma_{m'}} \theta_{\Gamma\,\Gamma'} <\Gamma_n|\mu_i|\Gamma_m'> <\Gamma_m|A_{Ni}|\Gamma_n> \qquad (2\text{-}7)$$

where A_{Ni} and μ_i are the components of A_N and μ respectively along a set of axes i = x,y, and z which are fixed with respect to the complex. A similar complicated expression for the metal ion contribution to the dipolar shift has also been derived by Kurland and McGarvey.[111] For a complex with only one thermally populated multiplet of spin quantum number S,X_{ii} is given by

$$X_{ii} = \frac{\beta^2 S(S+1)}{3kT} g_{ii}^2 \qquad (2\text{-}8)$$

then the dipolar shift of the metal ion can be expressed as

$$\left(\frac{\Delta v}{v_o}\right)^D = \frac{\beta^2 S(S+1)}{9kT\, r^3} [\{g_{zz}^2 - \frac{1}{2}(g_{xx}^2 + g_{yy}^2)\} (1-3\cos^2\phi)$$

$$+ \frac{3}{2}(g_{yy}^2 - g_{xx}^2) \sin^2\theta \cos\ 2\psi] \qquad (2\text{-}9)$$

For the cases of axial symmetry, $g_{zz} = g_{II}$, and $g_{xx} = g_{yy} = g_{\perp}$, equation reduces to the corresponding equation (2-6), given by McConnell and Robertson.[110] A more detailed discussion is referred to the original paper.

The dipolar shifts arise from dipole-dipole interaction. Such interactions are in general anisotropic, i.e. their magnitude depends upon the orientation of the molecule with respect to the applied magnetic field. It is apparent that the dipolar shifts will be equal to zero if $g_{II} = g_{\perp}$. An odd electron may occupy the orbital which has directional properties, e.g. an atomic p or d orbital. In such a case, the dipole-dipole coupling is proportional to the average value $<(3\cos^2\theta - 1)/r^3>$. Numerical values of this average can be readily calculated for various d orbitals. In a covalent metal complex the odd electrons will be partly delocalized to the ligands. The values of $<1/r^3>$ for electrons located on the ligand will be much smaller than for an electron located in a metal d orbital and dipolar contributions from such a source are often neglected. Thus in a covalent complex, the anisotropic contribution to the hyperfine splitting will be reduced.

Finite values of A exist only for species with electrons whose wave-functions are nodeless at the nucleus so that a direct "contact" between electron and nucleus may occur. Consequently, Fermi interactions are frequently referred to as contact interactions. Since "s" atomic orbitals are nodeless at the nucleus, it is necessary for the unpaired electron to have "s" character if a contact shift mechanism is to operate. Contact shifts for isotropic complexes arise from covalency in the metal ion-ligand bond, for, an ionic interaction cannot give rise to electron delocalization. Thus measurements of contact shifts can offer a direct means of assessing covalency in transition metal ion comlexes. In some cases, they may provide the spin density at the nucleus, and the amount of electron delocalization can be assessed.

(2-4) TIME DEPENDENT FACTORS INFLUENCING SIGNAL SHAPE

The shape and width of NMR resonances are sensitive to time-dependent processes. Many of the processes which are of most interest to chemists involve chemical exchange of the nuclei or electrons. The nuclear spin finds itself jumping at random from one environment to another one with a different spin Hamiltonian, and this alters the NMR spectra in a selective way. Some lines broaden, but others stay sharp. Other group of lines coalesce into a single line. These effects are almost always due to motions which have much lower frequencies than the Larmor frequency.

The simplest example of chemical exchange is a nuclear spin which can jump at random between two sites A and B where it has different resonance frequencies w_A and w_M (radians sec^{-1}). There are two important limiting cases called fast and slow exchange. In the first case, the jumping frequency w_e is much greater than the separation Δw between two spectral lines of equal intensity which are affected by the motion. The result is a single line at the average frequency. The nuclear spin is jumping so rapidly compared with the difference in resonance frequencies that it hardly loses phase from one time it is on a particular site to the next, and so it sees an average of the two environments. At the other extreme, the motion is very slow with $w_e << \Delta w$ and both lines are resolved but each is broadened. This is a life time broadening; and once a spin leaves one site for another, it loses all phase coherency by the time it returns. General qualitative line shapes for such processes are shown in Fig.(2-1).

There are two main approaches to the study of line shape. The first

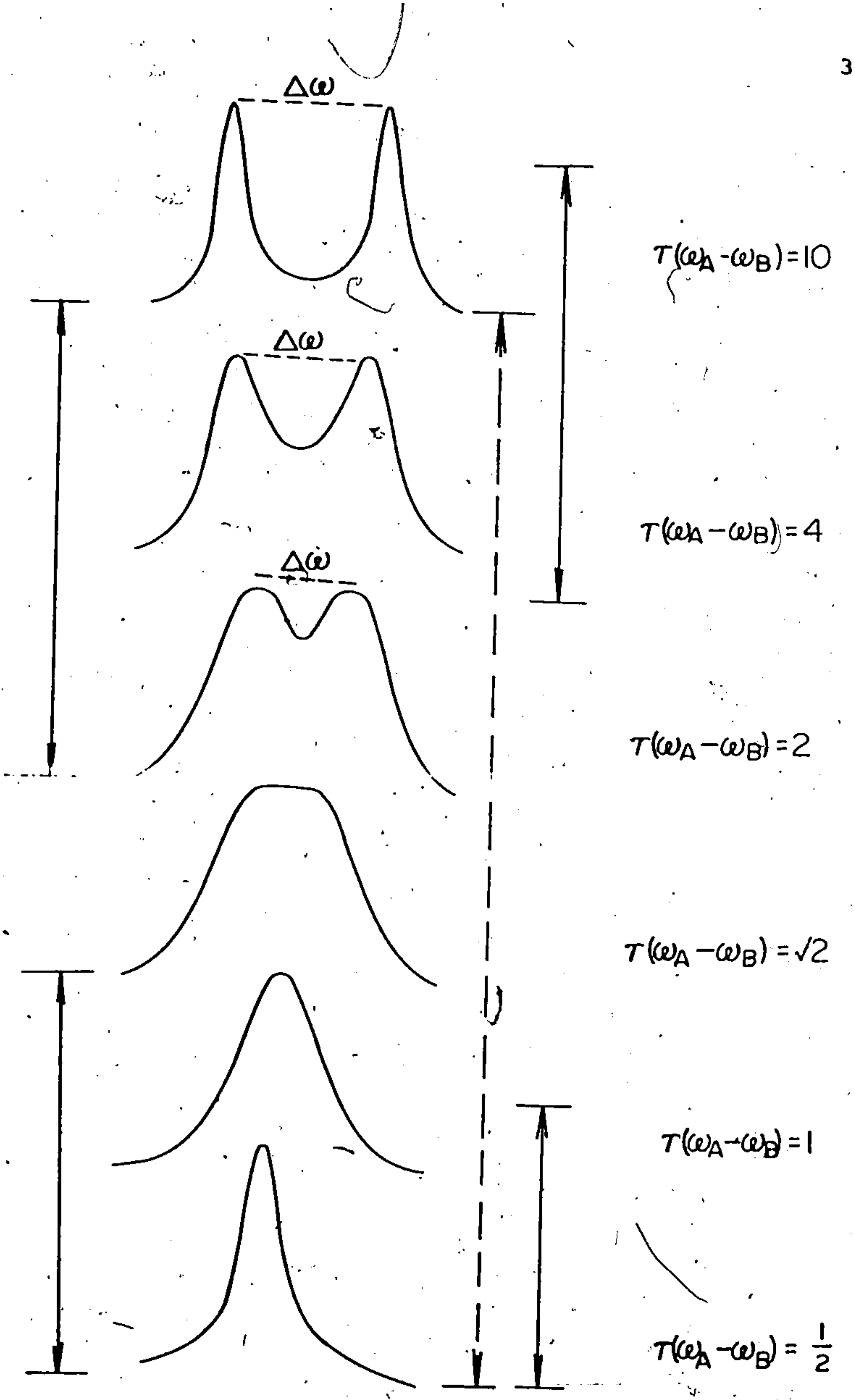


Fig.(2-1) : Line Shape for Two Simple Sites considers the steady state line shapes produced when the spectrum is swept through slowly (slow passage conditions). The second is concerned with line shapes produced under non-equilibrium conditions caused by sweeping quickly through the spectrum (fast passage conditions). Since most of the results in the present study have been obtained by the slow passage technique the theory associated with this case will be discussed.

(2-5) THE LINE SHAPE FOR A JUMPING SPIN

A nuclear spin can jump at random between two sites A and B where it has different resonance frequencies w_A and w_B respectively. These sites may be in different molecules, as in a proton exchange reaction; or they may represent two distinct states of the same molecule, as internal rotation; or different conformations. When the jumping rate is slow, the NMR spectrum shows distinct A and B spectra, but if the rate is fast, just one spectrum characteristic of the average environment which the nucleus sees.

The quantitative description of this system is best developed by suitable modifications of the Bloch phenomenological equations which may be found in various texts.[111,112] This approach was first used by Gutowsky, McCall, and Slichter.[113] Later, a simplified method was presented by McConnell,[70] to include the chemical exchange. These modified equations can be represented as follows:

$$\frac{dG_A}{dt} + a_A G_A = - i r H_1 M_{0A} + \tau_B^{-1} G_B - \tau_A^{-1} G_A$$

$$\frac{dG_B}{dt} + a_B G_B = - i r H_1 M_{0B} + \tau_A^{-1} G_A - \tau_B^{-1} G_B \qquad (2\text{-}10)$$

where G is a complex moment defined by G = u + iv and u and v are the tranverse components of bulk magnetic moment M along and perpendicular to the rotating field H_1. G_A and G_B are two corresponding complex G components for exchange of nuclei between A and B positions respectively. Thus, $\tau_B^{-1} G_B$ in equation (2-10) represents the rate of increase of G_A due to transfer of magnetization from B to A sites. Similarly, $\tau_A^{-1} G_A$ is the corresponding rate of loss. While a nucleus is in an A position, there is a constant probability τ_A^{-1} per unit time of its making a jump to a B position. τ_A is then the mean lifetime for a stay on A sites. Another corresponding time τ_B can be defined for the lifetime of B positions. The fractional populations of A and B sites p_A and p_B are related to τ_A and τ_B by

$$p_A = \tau_A/(\tau_A + \tau_B), \qquad (2\text{-}11)$$
$$p_B = \tau_B/(\tau_A + \tau_B),$$

where

$$p_A + p_B = 1$$

The solution of equations (2-10) appropriate for slow passage is obtained by putting

$$\frac{dG_A}{dt} = \frac{dG_B}{dt} = 0 \qquad (2\text{-}12)$$

The equations can be solved for G_A and G_B. Noting that the total complex moment is given by

$$G = G_A + G_B$$

$$G = -i\ \gamma_1 M_0 \frac{\tau_A + \tau_B + \tau_A\tau_B(a_A p_A + a_B p_B)}{(1 + a_A\tau_A)(1 + a_B\tau_B) - 1} \tag{2-13}$$

This was first obtained by Gutowsky, McCall, and Slichter using a more complicated argument.[113] The intensity of absorption at a frequency w is then proportional to the imaginary part (v) of G. Its behaviour in the two limiting cases when the lifetimes are short and long can be examined as follows.

(2-5a) LIMIT OF RAPID EXCHANGE

In the limit of rapid exchange, τ_A and τ_B are small. This will represent a resonance line centered on a mean frequency as

$$w_{mean} = p_A w_A + p_B w_B \tag{2-14}$$

with a line width given by

$$\frac{1}{T_2'} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} \tag{2-15}$$

If the rate process is slow enough to contribute to its width but is still well beyond the rate corresponding to separated signals, a corrected form of equation (2-15) can be obtained by putting $w = w_{mean}$ in equation (2-13) and expanding in powers of τ. This gives the effective tranverse relaxation time, T_2' as

$$\frac{1}{T_2'} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} + p_A^2\, p_B^2 (w_A - w_B)^2 (\tau_A + \tau_B). \qquad (2\text{-}16)$$

the second term on the right corresponds to the excess broadening due to slow exchange. This equation has been used by Meiboom, Luz, and Gill[114] to interpret the difference between T_1 and T_2 for water in terms of the breaking and reforming of hydrogen bonds.

(2-5b) LIMIT OF SLOW EXCHANGE

If the lifetimes τ_A and τ_B are sufficiently large compared with the inverse of the separation $(w_A - w_B)^{-1}$, the spectrum will consist of distinct signals in the vicinity of the frequencies w_A and w_B. The broadened signal centered at w_A will have a width given by

$$T_{2A}'^{-1} = T_{2A}^{-1} + \tau_A^{-1} \qquad (2\text{-}17)$$

There will be a corresponding signal centered on w_B. This shows that the exchange leads to an additional broadening of the individual signals. If T_{2A}^{-1} is known, measurements of the width of these broadened signals provide a means of estimating of τ_A. This method is valid, provided the broadening is not large enough to cause appreciable overlap of the signals and has been successfully applied in the studies of kinetics and ligand exchange processes of paramagnetic complexes in solutions.[87]

(2-5c) REGION OF INTERMEDIATE EXCHANGE

The transition from a spectrum of two lines to one line occurs when the lifetimes τ_A and τ_B are of the order of $(\omega_A - \omega_B)^{-1}$. The full expression for the intensity of absorption in this range is obtained from the imaginary part of the general expression for the complex-moment G (Eq. 2-13). The following simplifying conditions are assumed for the intermediate behaviour.

(a) Equal populations and lifetimes so that

$$p_A = p_B = 1/2 \qquad \text{and} \qquad \tau_A = \tau_B = 2\tau \tag{2-18}$$

(b) Large tranverse relaxation times so that we may take

$$T_{2A}^{-1} = T_{2B}^{-1} = 0 \tag{2-19}$$

This means that we are dealing with signals whose width in the absence of exchange is small compared with their separation. The line shape function in terms of frequencies in Hz is given by the equation[111]

$$g(\nu) = K \frac{\tau(\nu_A - \nu_B)^2}{(1/2(\nu_A + \nu_B)-\nu)^2 + 4\pi^2 \tau^2(\nu_A - \nu)^2(\nu_B - \nu)^2} \tag{2-20}$$

where K is a normalizing constant and $\nu = \frac{\omega}{2\pi}$ respectively. It turns out that the actual shape of this function depends only on the product $\tau|\nu_A - \nu_B|$. For large τ it will give two lines at ν_A and ν_B, while for small τ it will give one line halfway between. The form of the function for some intermediate values of $\tau(\nu_A - \nu_B)$ is shown in (Fig.2-1). These diagrams show that, as τ decreases from infinity, the two individual signals broaden and their maxima draw closer together. This continues until τ reaches the intermediate value of $2^{1/2}/2\pi(v_A - v_B)$, i.e.

$$\tau = 1/\{[\sqrt{2}\pi(v_A - v_B)]\} \qquad (2\text{-}21)$$

and the peaks coalesence into one broad band signal with a maximum at the mean position. As τ decreases below this value, the central peak sharpens until eventually there is a single sharp line.

(2-6) ESTIMATION OF RATE CONSTANTS FROM τ_A AND τ_B

In the present work, the rate constants for the hindered internal rotation of C-N bond in thiourea and some of its related compounds have been measured by using the equation in the limit of fast exchange and the rotational energy parameters are calculated. A similar method has been used to study ligand exchange in some neutral labile complexes of Co(II), Ni(II) and Zn(II) with thiourea and diacetamide ligands in a non-aqueous solvent like acetone. The effective transverse relaxation time T_2' is related to the line width $\Delta v'$ of the complexed resonance under fast exchange such that

$$1/T_2' = \pi\,\Delta v' \text{ (radians sec.}^{-1}) \qquad (2\text{-}22)$$

and p_A and p_B, the fractions complexed and un-complexed are calculated from the frequencies of fully complexed resonance (i.e. the limiting shift) and the observed resonance at a particular concentration of added ligand. T_{2A} is obtained by direct measurement of the limiting line width of the complexed resonance, and T_{2B} from the observed line width of free ligand resonance over the temperature range of the experiment. A detailed discussion of measurements of T_{2A} and T_{2B} is made in the last section of Chapter IV. Therefore,

$$\begin{aligned} 1/T_{2A} &= \pi\,\Delta\nu_A \text{ (radians sec}^{-1}\text{)} \\ 1/T_{2B} &= \pi\,\Delta\nu_B \text{ (radians sec}^{-1}\text{)} \end{aligned} \qquad (2\text{-}23)$$

where

$$\begin{aligned} w_A &= 2\pi\,\nu_A \text{ (radians sec}^{-1}\text{)} \\ w_B &= 2\pi\,\nu_B \text{ (radians sec}^{-1}\text{)} \end{aligned} \qquad (2\text{-}24)$$

ν_A and ν_B are the frequencies of both resonances in Hz. All shifts are measured from the corresponding diamagnetic free ligand position.

By substituting these experimental parameters into the equation (2-16), a sum of lifetimes, i.e. $(\tau_A + \tau_B)$ can be obtained as follows:

$$1/T_2' = p_A/T_{2A} + p_B/T_{2B} + (p_A p_B)^2(w_A - w_B)^2(\tau_A + \tau_B)$$

$$\pi\,\Delta\nu' = \pi\,p_A.\Delta\nu_A + \pi.p_B.\Delta\nu_B + 4.\pi^2.(p_A p_B)^2(\nu_A - \nu_B)^2(\tau_A + \tau_B)$$

$$\tau_A + \tau_B = \frac{\Delta\nu' - p_A.\Delta\nu_A - p_B.\Delta\nu_B}{4\pi.(p_A p_B)^2(\nu_A - \nu_B)^2} \qquad (2\text{-}25)$$

where $(\nu_A - \nu_B)$ is the frequency in Hz (60 MHz) for the limiting contact shift. The lifetimes τ_A and τ_B can be calculated by introducing the equation (2-11). The mean lifetime of a species A between exchange, τ_A can be related to the conventional chemical rate constant k by the following expression[3]

$$1/\tau_A = (1/[A]).\ \frac{d[A]}{dt} = k\,[A]^{m-1}[B]^n\ldots \qquad (2\text{-}26)$$

where m,n,... are the orders of the reaction with respect to the concentrations of A,B, etc. In order to evaluate m,n..., τ_A is measured as a function of concentrations of A,B, etc. For two simple sites A and B, the rate constant can be written as

$$k_1^* = 1/\tau_A = k_s + k_{II}[L] \qquad (2\text{-}27)$$

where [L] is the concentration of the added ligand, k_{II} is the second order rate constant and k_s is the first-order rate constant associated with solvent. k_s can be defined as follows:

$$k_s = k_1[S] \qquad (2\text{-}28)$$

where k_1 and [s] are the second-order rate constant and solvent concentration. A plot of τ_A^{-1} versus the concentration of added ligand at a particular temperature can provide k_s, k_I or k_{II} respectively. In the study of hindered internal rotation of C-N bond in thioureas, p_A and p_B are measured from the integrated areas of two resonances of "inside" and "outside" protons, and $(\nu_A - \nu_B)$, T_{2A} and T_{2B} are obtained from the frequencies and line widths of similar resonances under a completely slow exchange situation (i.e. from the limiting spectrum). Application of equations (2-16) and (2-11) allows the estimation of lifetimes τ_A and τ_B from which the rate constants for internal rotation can be calculated.

(2-7) ACTIVATION PARAMETERS

Determination of life times at various temperatures directly provides the enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation for exchange of a ligand between coordination sphere and the bulk of the solution. In a unimolecular rate process, the first order rate constant can be related to free energy of activation as

$$k_1 = 1/\tau_A = (kT/h).\ e^{-\Delta G_1^{\ddagger}/RT} \qquad (2\text{-}29)$$

and

$$\Delta G_1^{\ddagger} = \Delta H_1^{\ddagger} - T.\Delta S_1^{\ddagger} \qquad (2\text{-}30)$$

Therefore,

$$k_1 = 1/\tau_A = (kT/h).\ e^{-(\Delta H_1^{\ddagger}/RT) + \Delta S_1^{\ddagger}/R}$$

$$\frac{k_1}{T} = (k/h).\ e^{-(\Delta H_1^{\ddagger}/RT) + \Delta S_1^{\ddagger}/R}$$

$$\ln(k_1/T) - \ln(k/h) = -(\Delta H_1^{\ddagger}/RT) + \Delta S_1^{\ddagger}/R \qquad (2\text{-}31)$$

or,

$$\ln k_1 - \ln(kT/h) = -\Delta H_1^{\ddagger}/RT + \Delta S_1^{\ddagger}/R \qquad (2\text{-}32)$$

where k is the Boltzmann's constant, h the Planck's constant and T the absolute temperature respectively, i.e. ($k = 1.3805\times10^{-16}$ erg.deg.$^{-1}$, $h = 6.6256\times10^{-27}$ erg.sec. and $R = 1.987$ cal. deg.$^{-1}$mol^{-1}.)

A similar equation can be written for a bimolecular exchange process, i.e.

$$\ln k_{II} - \ln(kT/h) = -\Delta H_{11}^{\ddagger}/RT + \Delta S_{11}^{\ddagger}/R \qquad (2\text{-}33)$$

A plot of ($\ln k^* - \ln(kT/h)$) against the reciprocal of the absolute temperature allows the slope ($-\Delta H^{\ddagger}/R$) and the intercept ($\Delta S^{\ddagger}/R$) from which the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be calculated. Alternatively, these parameters can be obtained from a direct estimation of the free energy of activation $\Delta G^{\ddagger}$. Thus,

$$\ln k^{*} = \ln(kT/h) - \Delta G^{\ddagger}/RT$$

$$\ln k^{*} - \ln(kT/h) = -\Delta G^{\ddagger}/RT$$

$$-\Delta G^{\ddagger} = R.T.(\ln k^{*} - \ln(kT/h)). \qquad (2\text{-}34)$$

where

$$k^{*} = k_1 \text{ or } k_{11}$$

A plot of $\Delta G^{\ddagger}$s against the absolute temperatures yields the required activation parameters. The procedure adopted in the present work has been to first investigate the mechanism of the ligand exchange[115] reaction by examining line broadening in the slow exchange region and to then calculate activation parameters from data obtained in the fast exchange region. In the slow exchange region, the line widths for an associative process of the type:

$$ML_n + L^{*} \rightleftharpoons ML_nL^{*} \rightleftharpoons ML_n^{*} + L$$

are given by

$$\tau_c^{-1} = k[L]$$

and

$$\tau_L^{1} = k[ML_n].$$

For a dissociative mechanism on the other hand

$$\tau_c^{-1} = k$$

and

$$\tau_L^{-1} = k[ML_n][L]^{-1}$$

Qualitative observation of the variation of the free and complexed ligand line widths with ligand concentration therefore determines the predominant mechanism.

Double resonance and pulse NMR methods are also available for studying the processes but have not been used in the present work.

(2-8) SOURCES OF ERRORS

Errors may arise from either mathematical sources or experimental sources. Mathematical problems occur when the theoretical model is an oversimplification of the actual system studied. They also arise when the theoretical model is adequate, but a simplified, approximate equation is used beyond its region of accuracy. The further one goes from the region of validity for the approximate expressions, generally the larger will be the error, which thus will usually be systematic in character. Some equations which relate to the exchange rate require approximations, and the accuracy of such approximations depend upon the relative value for the exchange rates, as compared to the chemical shifts, the coupling constants, the natural line widths in the absence of exchange, all assumed in units of sec.$^{-1}$ or Hz. Neglect of this dependence, as frequently has been the case, leads to appreciable, systematic errors. A detailed discussion is referred to the paper by Gutowsky et al.[116]

Another problem associated with the use of equation (2-17) for exchange rates below the coalescence temperature is that for commonly encountered chemical shifts the range of accessible rates is rather limited. So, if one is seeking activation parameters, the temperature range is correspondingly short, and systematic errors in the rates or temperatures can produce quite large errors in the apparent enthalpy and entropy of activation. Because of this, it is desirable to obtain exchange rates above the coalescence temperature, when only a single line is observed.

The experimental problems can be classified as arising from instrumental instabilities, calibration errors, or other inaccuracies in the measurements, and spectral distortions. Examples of instabilities in steady-state work are temperature drifts, frequency changes, magnetic field drifts, and variation in sample spinning rate.

Temperature fluctuations and changes are important in the measurements. The magnitude of errors which result from temperature fluctuations depend upon both the heat capacity and amount of sample present. It may also depend upon the spinning rate. There may be a loss in resolution produced by changing the temperature of the sample. Several factors contribute including the changes in sample position produced by thermal expansion, and perturbations in field distribution produced by changes in bulk magnetic susceptibility. Such loss in resolution has generally less effect upon peak separation than upon line shapes. Thus the resolution must be "peaked up" at each temperature; moreover, if errors are to be avoided, the resolution should be the same at each temperature.

Most of these effects were considered in the present work. Isotropic shifts were large and they were measured within the experimental error of ±50 Hz and the corresponding line widths within ±10 Hz. These measurements were made at various concentrations of added ligand above the coalescence temperatures. The temperature of the samples varied within ±3° for each experiment.

Taking into consideration the various sources of errors noted above, we consider that rate constants may be obtained with an absolute accuracy of approximately 50%. Since many of these errors are of a systematic nature, comparisons of relative rates are considerably more reliable but we would not place significance on differences of less than 10 or 20%. Errors in the activation parameters have been estimated graphically. The quoted errors are generally in the range ±2 to ±3 cal.K^{-1}mole^{-1} for the entropies of activation and ±0.6 to ±0.9 k cal. mole^{-1} for the enthalpies of activation. These quoted errors make no allowance for the systematic errors discussed above. The absolute accuracy of the data is therefore less than indicated by these errors. We are however mainly concerned with comparisons between different exchange processes and the data suffices for this purpose.

CHAPTER III

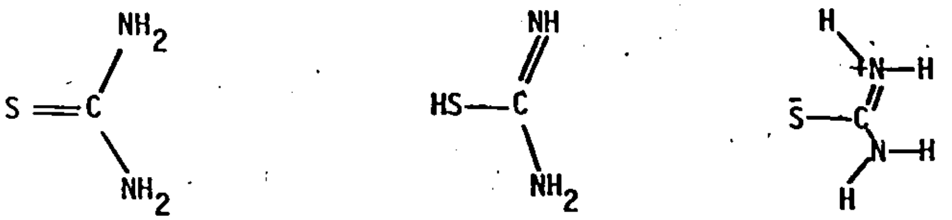
SOLUTION STRUCTURE AND HINDERED ROTATION IN THIOUREA AND SUBSTITUTED THIOUREAS

This thesis discusses NMR studies of metal complexes of thiourea (tu) and substituted thioureas (Rtu) in some detail. Before describing these results it will be necessary to present some preliminary NMR work on the thiourea ligands themselves and this is the intent of the present chapter. There are two aspects which require consideration. Firstly we need to know the assignments and chemical shifts of the various ligand protons before proceeding to an analysis of the spectra of the complexes. Secondly a rate process occur in thioureas which is associated with restricted rotation about the C-N bond. It will be necessary to disentangle the effects of this rate process from those of the rate processes concerned with ligand exchange. It is also of interest to compare the barriers to rotation of free and complexed thioureas. For over a decade, NMR has been successfully applied with varying levels of sophistication to such similar problems associated with hindered internal rotation in amides and thioamides[57-62], but thioureas have not been extensively examined.

(3-1) STRUCTURE

Thiourea is fairly soluble in acetone. The proton spectrum of it does not appear to have been previously examined in solution although there are reports of solid state NMR studies.[117,118] ^{14}N NMR study has also been reported.[119] A recent study discusses restricted rotation in

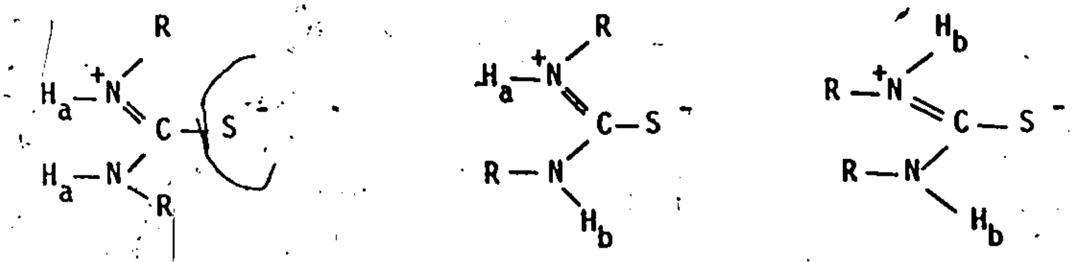
N-methylthiourea (Mtu) using NMR as the experimental technique and the results of this study will be discussed below. The structures of urea and thiourea constitutes a classic problem involving tautomerism but there is now a consensus of [illegible] that structure I rather than II is correct (Fig. 3-1).



I II III

Fig. (3-1)

The ^{1}H NMR spectrum of thiourea in acetone-d_6 is consistent with structure I, having a single proton peak at 380 ± 10 Hz to low field of TMS. On cooling to -70°C, this peak splits into a doublet of equally intense lines. This is still inconsistent with involvement of the tautomer II and a more reasonable explanation invokes restricted rotation about the C-N bond arising from contribution of structure III. Such a structure would be planar with different environments for the "inside" and "outside" hydrogens. Restricted rotation is scarcely surprising since it occurs in many other amides. Given this explanation, the interpretation of the spectra of N-methyl-thiourea, N,N'-dimethylthiourea (Dmtu) and N,N'-diethylthiourea (Detu) follows naturally. There are three possible configurations for each of these derivatives with the exception of N-methylthiourea and N-naphtylthiourea (Nptu) which have only two possible configurations (Fig. (3-2) and Fig. (3-3)).



cis-cis cis-trans trans-trans

Fig.(3-2)

N-methylthiourea is less soluble in acetone-d_6. At room temperature, the ^1H NMR spectrum of it shows a broad signal due to NH protons and a sharp signal due to CH_3 protons. On cooling the solution to -29°C., both NH and CH_3 lines split into two separate doublets attributed to "inside" and "outside" NH or CH_3 protons arising from restricted rotation about the C-N bond. This is the compound studied by Tompa, Barefoot, and Pryce.[118] Their work was carried out in a variety of solvents which did not include acetone. We have chosen to work in acetone to maintain consistency with the metal complex studies. However, the spectra in acetone generally agree well with those reported in other solvents. Tompa et al[118]. based the CH_3 assignments on the following two factors. First, molecular models indicate that the trans isomer is expected to be less favoured than the cis form because of steric interaction between the trans-methyl and the trans-hydrogen. Therefore one would expect to find two unequal doublets in the NMR spectrum. Second, the CH_3 protons cis to the thiocarbonyl group are expected to appear more upfield than the CH_3 protons on the opposite

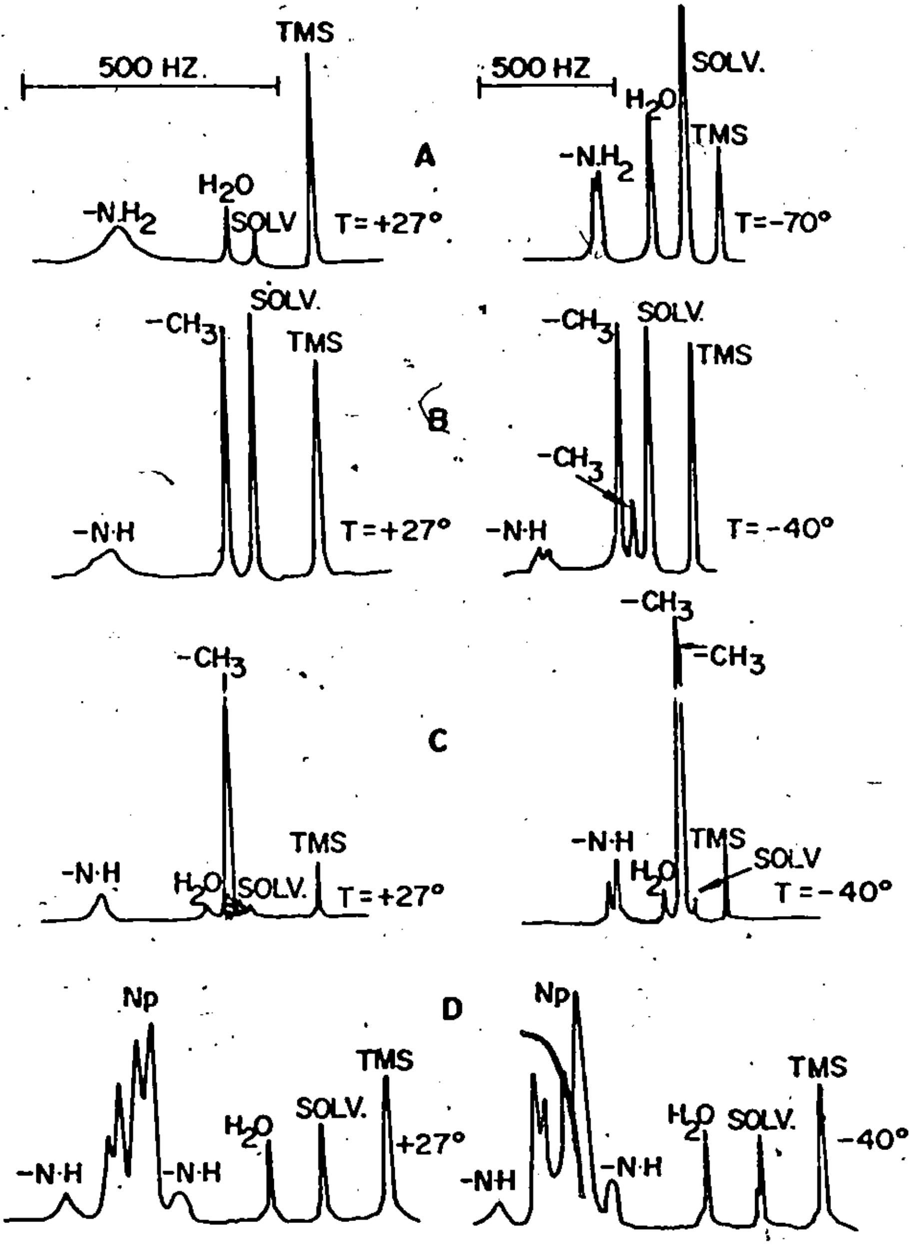


Fig.(3-3) ^1H NMR spectra of thiourea ligands; A, thiourea; B, N-methylthiourea; C, N,N'-dimethylthiourea; D,1-Naphtyl -2-thiourea.

side because of anisotropic diamagnetic shielding by thiocarbonyl group.[119] With this reasoning, they assigned the high field line of CH_3 doublet to "outside" CH_3 and the low field line to "inside" CH_3. They found that the high field line is more intense than the low field line. However, in the present study we found that the high field line of the methyl doublet is relatively less intense than the low field line. On steric grounds the isomer with "outside" CH_3 group (cis isomer) is more stable than the isomer with "inside" CH_3 group (trans isomer). Therefore, we assign the "outside" CH_3 group to low field line (more intense) and the "inside" CH_3 group to high field line (less intense). A reverse assignment is made of the NH lines and the difference in the assignment made in the present and previous study probably arises from a solvent effect.

Tompa et al. also assigned the two resonances in the NH region to the NH_2 group and the NH group respectively. This does not appear to be correct since the NH protons clearly participate in the same exchange process as the CH_3 protons. Rotation about the C-N bond does not exchange the NH_2 and the NH protons. It seems more reasonable to assign the peaks to "inside" and "outside" protons as was done for the unsubstituted thiourea. The fact that the barrier to rotation we obtain from studies of the NH protons agrees well with that obtained by Tompa et al from the CH_3 resonances substantiates this assignment.

C.N. Rao et al.[120] have reported normal coordinate analyses of N,N'-dimethylthiourea and tetramethylthiourea (Tmtu). Two distinct bands in the C$=$S stretching region are found due to strong vibrational mixing.

The C-N bond of the thiourea and its derivatives possess appreciable double bond character, and the molecules take the nearly planar form. The most striking feature which can be extracted from their study is that such rotamers in solution can be distinguished by their NH stretches. The higher N-H stretching frequency was assigned to the cis isomer and lower frequency to the trans isomer. N,N'-dimethylthiourea and N,N'-diethylthiourea show one sharp N-H stretching mode due to the cis isomer in solid. In various solvents, however, both two peaks due to cis and trans isomers are observed and the relative intensities of the two peaks vary with the nature of the solvent indicating the presence of an equilibrium between these two. The energy differences between these two forms are reported to be of the order 500 ± 200 cal. $mole^{-1}$.

Turning to N,N'-dimethylthiourea, the ^1H NMR spectrum shows a single NH line (398 ± 10Hz) and a single methyl peak (168 ± 5Hz) to low field of TMS. This is consistent with either a trans-trans structure or a cis-cis structure or a rapid exchange involving two or more structures. On cooling to -26°C, each resonance splits into a doublet of unequal intensity arising from the contribution of cis-cis or cis-trans isomer. The trans-trans isomer is most unlikely due to steric reasons. On further cooling to -50°C, a limiting spectrum consisting of two NH lines (intensity ratio 1:2) is obtained. It is noticeable that the high field line is relatively more intense than the low field line. The reverse is true for the methyl resonances. We believe that cis-cis structure is relatively more stable than the cis-trans structure. It is therefore more reasonable to assign the high field line to "inside" NH and low field line to "outside" NH. A similar assignment is made for methyl resonances although Tompa et al. would have made the reverse assignment on the basis of their arguments. The corresponding N,N'-diethylthiourea shows similar behaviour. At low temperatures, the ^{1}H NMR spectrum shows a doublet of NH resonances in the ratio of intensity (1:3). The less intense line (low field) is assigned to "outside" NH and the more intense line (high field) to "inside" NH. 1-(1 naphthyl)-2-thiourea is, however, exceptional. The ^{1}H NMR spectrum of this compound at room temperature exhibits two NH resonances and the naphthyl group attributed to restricted rotation of C-N bond. It is possible that a single isomer with "outside" naphthyl group is present in solution due to the higher barrier of rotation. All the chemical shift data for thiourea and alkylthioureas are summarized in Table (3-1).

(3-2) ^{1}H NMR LINE BROADENING STUDIES

The NMR technique has proved to be a powerful tool for the study of internal rotation. The relevant theory was considered in Chapter II. The expected behaviour of the spectrum is shown in Fig.(3-4). Thiourea gives a coalescence temperature of approximately -40°C. Above -42°C, it is found that the line width of the signal decreases as the solution is warmed. The temperature range of -18° to -38°C is the optimum range for kinetic measurements. Since this is the fast exchange region, equation (2-25) shown in Chapter II is applicable. T_{2A} and T_{2B} are obtained from the limiting spectrum at -50°C where the exchange process is completely

Table (3-1)

Chemical Shifts of Thiourea and its Related Ligands in Acetone at Various Temperatures (56.4 MHz)

Reference = TMS

Ligands	27°C N-H Hz	Low Temps N-H Hz	$-CH_3$ Hz	$-CH_2$ Hz	Naphthyl Hz
Tu	-380 ± 10	-421 ± 5 -410 ± 5 (-70°C)	- -	- -	- -
Mtu	-380 ± 10	-414 ± 5 -389 ± 5 (-30°C)	-168(27°C) -189(-30°C) 167(-30°C)	- - -	- - -
Dmtu	-398 ± 10	-450 ± 5 -417 ± 5 (-30°C)	-168(27°C) -167(-30°C) -161(-30°C)	- - -	- - -
Detu	-390 ± 10	-436 ± 5 -412 ± 5 (-60°C)	- 66(27°C) - 66(-60°C)	-196(27°C) -198(-60°C)	- -
Nptu	-521 ± 10 -386 ± 10	-554 ± 10 -409 ± 10 (-80°C)	- -	- -	-435(27°C) -435(-80°C)
Tmtu	-	-	-167(27°C) -171(-90°C)	- -	- -

Tu = thiourea, Mtu = N-methylthiourea, Dmtu = N,N'-dimethylthiourea, Detu = N,N'-diethylthiourea, Nptu = 1-(1-Naphthyl)-2-thiourea, Tmtu = tetramethylthiourea

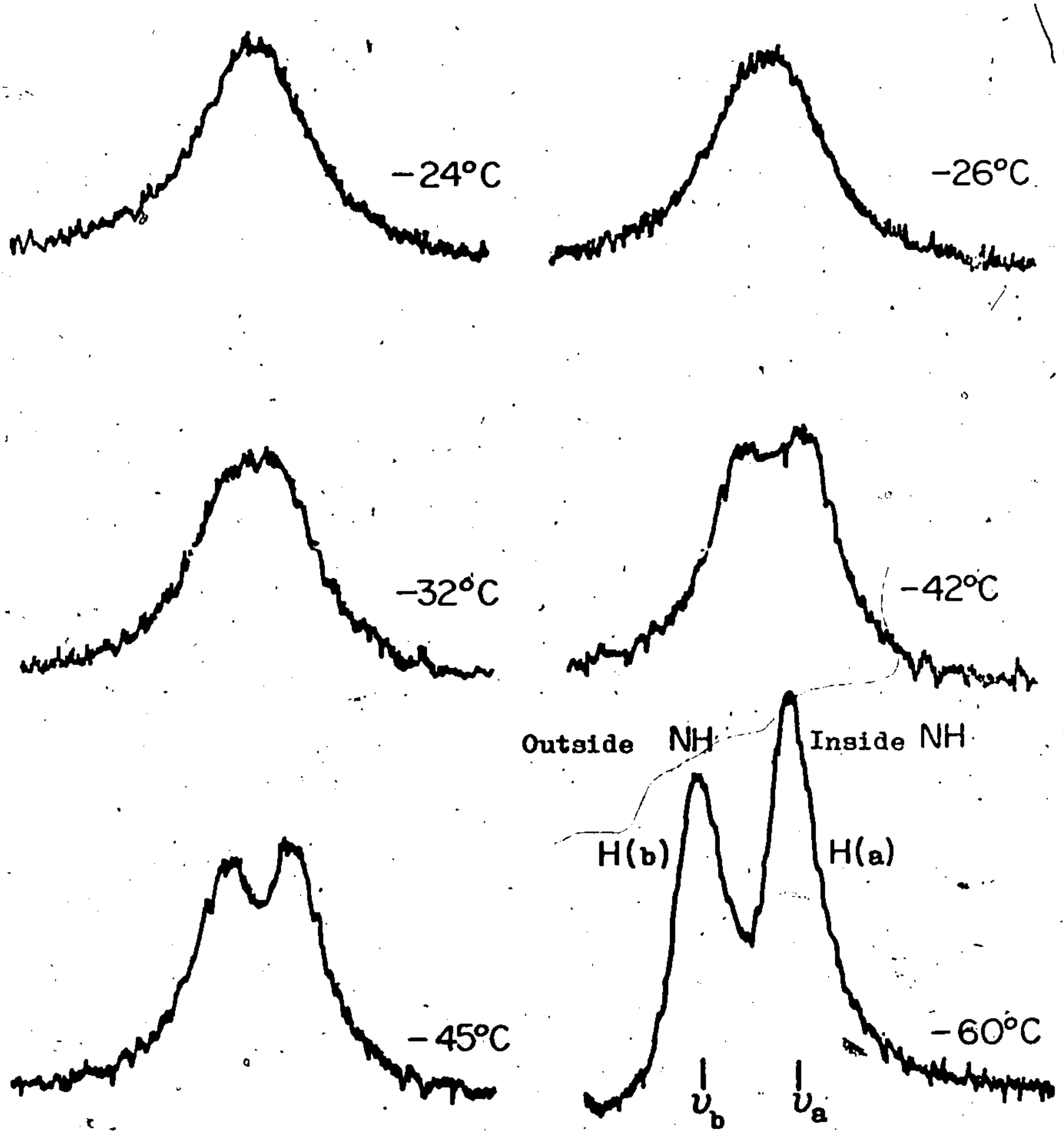


Fig.(3-4) ^{1}H NMR spectra of Thiourea at various temperatures frozen out, i.e. from the measurements of line widths of "inside" and "outside" resonances (Fig.3-4). The effective tranverse relaxation times T_2' at various temperatures (i.e. -18° to -38°C) are obtained from the measurements of the line widths of the average signal at these temperatures. For thiourea, the site populations p_A and p_B are equivalent as the intensities of both "inside" and "outside" NH resonances in the limiting spectrum are equal. By using the additional relations shown in the equation (2-11), the lifetimes of the exchanging protons (a) and (b) can be obtained for various temperatures. Plotting the variation of these lifetimes versus the reciprocal of the absolute temperature enables activation parameters for the hindered internal rotation of C-N bond to be found. In the case of substituted thioureas, however, the intensity of each NH resonance is not equal. In such cases, the site populations of H(a) and H(b) are obtained by taking the ratios of intensities of the signals. The activation energy is found to be 7 ± 2 k cal.mole^{-1}. Table (3-2) summarizes the results.

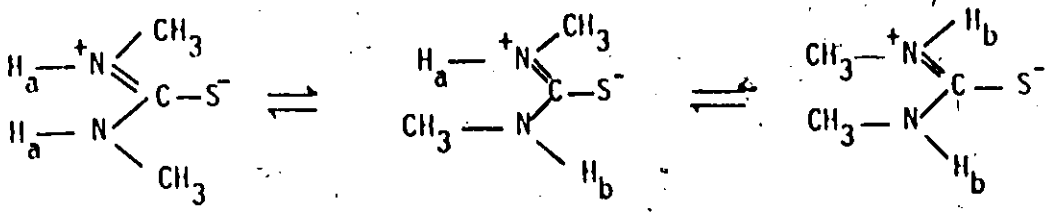
The barrier associated with the partial double bond character of C-N bond gives rise to at least two physically distinguishable isomers in substituted thioureas. Below - 50°C, the ^{1}H NMR spectra of both N,N'-dimethylthiourea and N,N'-diethylthiourea show two sets of NH resonances in the ratio of intensity of 1:2 and 1:3 respectively attributed to "outside" and "inside" protons arising from restricted rotation. Using equation (2-25) and following the procedure shown in the case of thiourea, kinetic parameters for the exchange of "inside" proton to "outside" proton

Table(3-2) Kinetic Parameters for Internal Rotation of C-N Bond in Thiourea

t°c	Linewidth of average NH	$P_A=P_B$	$4\tau = (\tau_A+\tau_B)$	$\tau_A=\tau_B=2\tau$	$K_1=\frac{1}{2\tau}$ sec^{-1}	$\ln\frac{1}{2\tau}$	$\frac{10^3}{T}$	E_a
27	-	0.5	-	-	5×10^2	6.20	3.33	
-18	20.1	0.5	35.6×10^{-3}	1[illegible].8x10^{-3}	71	4.02	3.92	
-24	23.5	0.5	50.6×10^{-3}	2[illegible].3x10^{-3}	40	3.68	4.01	7±2 Kcal mol^{-1}
-26	24.7	0.5	55.9×10^{-3}	21.9x10^{-3}	36	3.58	4.04	
-32	27.6	0.5	68.0×10^{-3}	3[illegible].0x10^{-3}	29	3.30	4.14	

$$\ln k_1 = \ln A - \frac{E_a}{RT}$$

can be calculated. Taking the example of N,N'-dimethlythiourea, the following possible equilibrium can be written for three different rotamers.



I II III

It is obvious that proton (a) differs from proton (b) in its magnetic environment. The relative energy of each rotamer will depend on the effect of hydrogen bonding by the solvent and 1,3-trans-trans steric interaction of CH_3 and the proton. The structure III is unlikely on steric ground and the most probable structure would be I. Therefore, the most important dynamic equilibrium that exists in solution should involve both structure I and II, where structure I would be in a larger proportion.

A plot of $\ln \frac{1}{\tau}$ versus $\frac{10^3}{T}$ provides the activation energy of interconversion (Fig. 3-5) and the results are summarized in Table (3-3).

(3-3) DISCUSSION

From the data in Table (3-4), it is apparent that the barriers to internal rotation increase in the order

$$Tu < Mtu \simeq Dmtu < Detu \ll Nptu$$

The numerical values agree quite well with the reported 9-12 K.Cal. of N-methylthiourea in different solvents.[118] It should be noted that the barrier for the "inside" to "outside" exchange differs from that for the "outside"

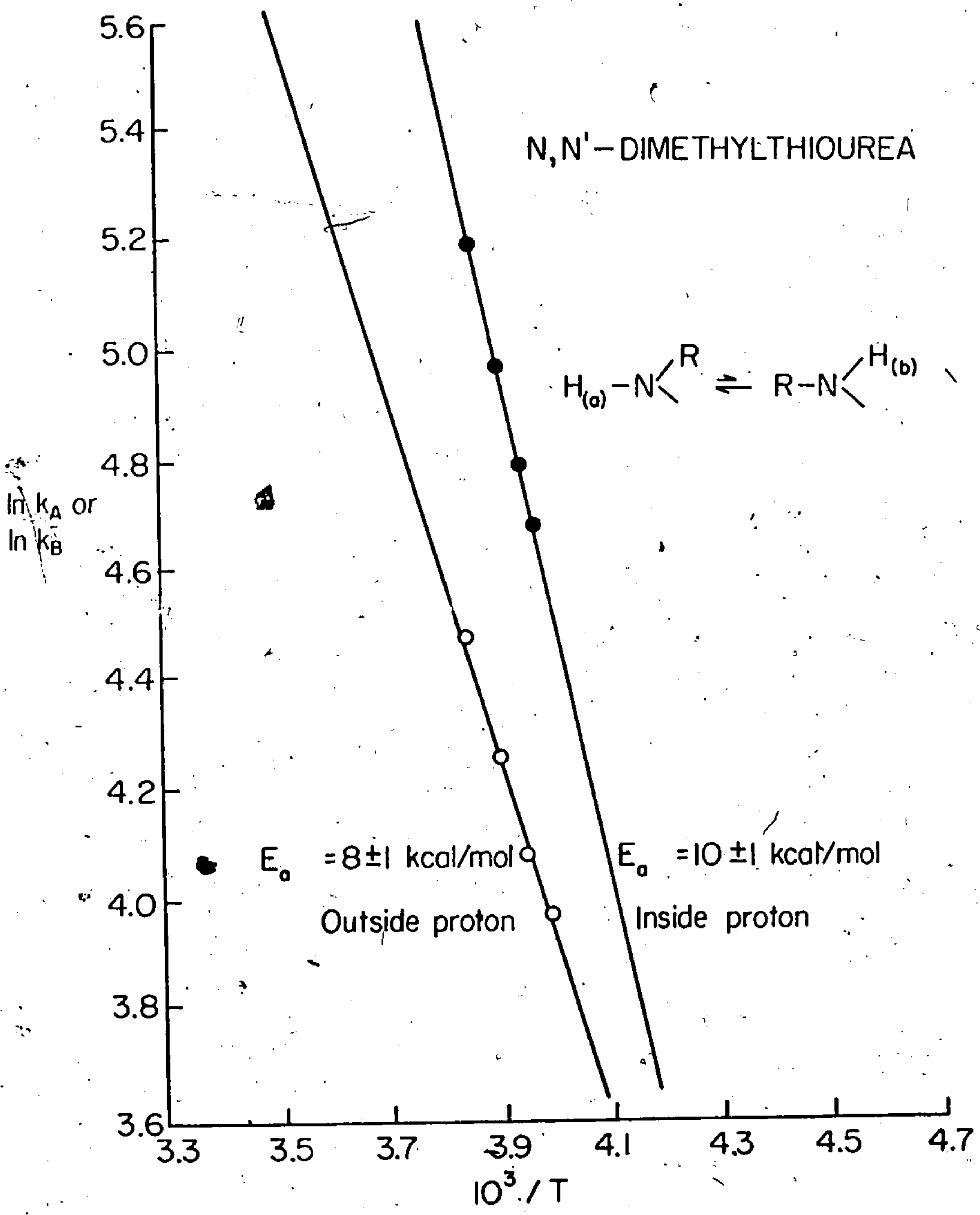


Figure (3-5): Plot o 'nk vs $\frac{10^3}{T}$ [Dmtu]

Table(3-3) Kinetic Parameters for Hindered Internal Rotation of C-N Bond in N,N'-dimethylthiourea

t°c	Linewidth of NH resonance 60MHZ	p_B	p_A	$\tau_A + \tau_B$	$p_B(\tau_A+\tau_B) = \tau_B$	$P_A(\tau_A+\tau_B) = \tau_A$	$k_B = \frac{1}{\tau_B}$	$k_A = \frac{1}{\tau_A}$	$E_{a(A)}$ Kcal mol^{-1}	$E_{a(B)}$ Kcal mol^{-1}
27^{*}	-	0.33	0.67	-	-	-				
-13	31	0.33	0.67	1.69×10^{-2}	5.57×10^{-3}	1.13×10^{-2}	180	53		
-17	34	0.33	0.67	2.11×10^{-2}	6.95×10^{-3}	1.41×10^{-2}	144	59	10±1	8±1
-20	37	0.33	0.67	2.53×10^{-2}	8.34×10^{-3}	1.69×10^{-2}	120	71		
-23	39	0.33	0.67	2.81×10^{-2}	9.27×10^{-3}	1.88×10^{-2}	108	88		

Table(3-4) Kinetic Parameters and Activation Parameters for Thiourea and Its Related Systems(+27°C)

Compound	Inside NH k_A sec^{-1}	Outside NH k_B sec^{-1}	Inside NH $E_a(A)$ $K.Cals.mol^{-1}$	Outside NH $E_b(B)$ $k.Cals.mol^{-1}$	Remark	cis to trans ratio	Coalescence Temps.
Thiourea (Tu)	5×10^2	5×10^2	7 ± 2	7 ± 2	$\Delta E \approx 0$	1	$-42^\circ \pm 3$
N-methyl-thiourea(Mtu)	$\approx 4 \times 10^2$	$\approx 7 \times 10^2$	9 ± 1	8 ± 1	$\Delta E \approx 1 \pm 1$	≈2	$-29^\circ \pm 3$
N,N'-dimethyl-thiourea(Dmtu)	4.10^2-6.10^2	7.10^2-11.10^2	10 ± 1	8 ± 1	$\Delta E \approx 2 \pm 1$	2	$-26^\circ \pm 3$
N,N'diethyl-thiourea(Detu)	3.10^2-9.10^2	9.10^2-24.10^2	12 ± 2	9 ± 2	$\Delta E \approx 3 \pm 2$	3	$-40^\circ \pm 3$
1-naphthyl-2-thiourea(Nptu)	slow	slow	high	high		≈ ∞	> +27°
Tetramethyl-thiourea(Tmtu)	-	-	-	-	Single line up to -90°	-	?

to "inside" process in unsymmetric thioureas. This reflects the difference in energy between the two distinguishable isomers. The values of around 2 k cals. mole^{-1} obtained for this difference seem quite reasonable. This difference is obviously much larger for the N-naphthylthiourea compound. It should be noted that the possibility that the observed rate process is a proton exchange involving adventitious water rather than a restricted rotation was considered and rejected. The acetone-d_6 used contains 0.2 - 0.5% of water (see Chapter IV) but the water resonance is separate from those of the NH protons and does not parallel the temperature dependence of the latter. The rotational nature of the process is further confirmed by the observation of exchange between CH_3 groups on N-methyl and N,N'-dimethlythioureas.

It is interesting to notice that the frequency factor (A) for hindered rotation in thiourea and its related compounds varies from 10^6 to 10^{11} sec.$^{-1}$ This figure is indeed comparable with those previously reported for dialkyl acetamide in the literature.[55,56] It is also noticeable that for alkylthioureas the frequency factor for "inside" and "outside" proton differs by $\sim 10^2$ sec.$^{-1}$ which is attributed to the difference in rate constants k_A and k_B.

CHAPTER IV

STRUCTURE AND LIGAND EXCHANGE OF Co(II) COMPLEXES OF THIOUREA AND SUBSTITUTED THIOUREAS

(4-1) INTRODUCTION

NMR studies of kinetics of ligand exchange processes in transition metal complexes have been an extensive field of investigation. The majority of these studies carried out so far have involved charged species in aqueous solutions.[4,71-75] A limited amount of work has been carried out on ligand substitution in "tetrahedral" divalent first-row transition metal complexes in non-aqueous solvents. These studies[87-91] include complexes of the type ML_2X_2 where M can be Fe(II), Co(II) and Ni(II) and the exchanging ligand L can be triarylphosphine, 2-picoline or hexamethylphosphoramide and X is a halogen. Studies of this sort are extremely important in the understanding of mechanisms of homogeneous catalysis, since such mechanisms involve a sequence of ligand exchange steps. Information on ligand lability can be obtained by NMR for systems in which the lifetime of a given species is in the time range 10^{-4} to 10^{2} sec. We have therefore undertaken a detailed examination of some thiourea complexes of Co(II) and Ni(II) in a non-aqueous solvent. The NMR line broadening technique has been employed to study the kinetics and mechanisms of such ligand exchange processes.

The major part of the present chapter is concerned with two topics. The first portion involves a structural study of Co(II) complexes of thiourea and its related systems in acetone-d_6. The effect of modification of the ligands is discussed. NMR parameters and thermodynamic data for ligand dissociation are presented. The second part considers the mechanisms and kinetics of rapid ligand exchange processes. Activation parameters are presented, and used as a basis for a quantitative discussion. These parameters will be compared with those of the corresponding Zn(II) systems which will be discussed in Chapter (VII).

(4-2) THIOUREA COMPLEXES

Thiourea (Tu) complexes of Co(II), Ni(II) and Zn(II) were apparently first studied by Rosenheim and Meyer.[121] Their work was extended by Cotton et al.[122] who reported $Co(Tu)_2X_2$(X=Cl,Br), $Co(Tu)_4(ClO_4)_2$, $Co(Tu)_3\ SO_4$ and $Co(Tu)_4(NO_3)_2$. All these complexes were studied spectroscopically and magnetically. $Co(Tu)_2Cl_2$ gives a non-conducting solution in nitromethane. The visible and near infrared spectra indicate that both $Co(Tu)_2Cl_2$ and $Co(Tu)_2Br_2$ are tetrahedral. $Co(Tu)_4(ClO_4)_2$ solutions contain the tetrahedral $Co(Tu)_4^{++}$ ion which tends to be solvolyzed in acetone. The visible and near-infrared spectrum of $Co(Tu)_4(ClO_4)_2$ with excess of free thiourea in acetone solution shows the presence of typical tetrahedral $Co(Tu)_4^{++}$ ion. The spectrum of solid $Co(Tu)_4(ClO_4)_2$ is very similar in the visible except for the increased widths of the absorption bands.

The magnetic and spectroscopic data for $Co(Tu)_3(SO_4)_2$ are strongly indicative of tetrahedral coordination of the cobalt ion.[123] The infrared spectrum indicates coordination of a sulphate ion through one oxygen atom. $Co(Tu)_4(NO_3)_2$ shows anomalous behaviour in its electronic and magnetic data. Electronic spectral data are quite consistent with the postulate of a tetrahedral $Co(Tu)_4^{++}$ ion. Although the compound is soluble in a number of organic solvents, there were colour changes indicative of reaction or solvolysis and the solution structure may therefore differ from the solid state structure. The observed magnetic moment 4.75 B.M. does not correspond with that for $Co(Tu)_4^{++}$ (4.5 B.M.); it is, however, quite consistent with the occurrence of an octahedral coordination group made up of four thiourea sulphur atoms and two nitrate oxygen atoms, $(Co(Tu)_4(ONO_2)_2)$. Infrared spectral data are inconclusive and do not provide any information regarding bonding of nitrate group. The corresponding $Ni(Tu)_6(NO_3)_2$ showed infrared absorptions for ionic nitrate ions, however.

Studies on the infrared spectra from 400 to 135 cm^{-1} of a number of metal complexes of thiourea have been made.[123] There are no skeletal vibrations within the ligand molecule[124] below 400 cm^{-1}. A considerable amount of structural information is available for these compounds and metal-sulphur stretching vibrations can be studied. Flint and Goodgame[123] reported $Co(Tu)_2I_2$ along with other analogues. They suggested $Co(Tu)_2X_2$(X=Cl,Br) retain in the solid state the tetrahedral structure they have in solution. The reflectance spectrum of $Co(Tu)_2I_2$ is so much like those of its analogues as to suggest a tetrahedral structure for this complex. Magnetic data for this compound corrected for temperature-dependent paramagnetism are in good agreement with this conclusion.

Further studies on Co(II) compounds with thiourea have been reported by Pakinam Askalani and Bailey[125] who studied a number of substituted thiourea complexes of Co(II). These complexes were $Co(L)_2X_2$ (X-Cl,Br),$Co(L)_4(ClO_4)_2$ and $Co(L)_3(NO_3)_2$ where L=Mtu,Dmtu(Mtu=N-methylthiourea,Dmtu=N,N'dimethylthiourea) respectively. They were characterized using infrared, visible spectroscopy, and magnetic susceptibility. It was again concluded that thiourea and its N-substituted forms tend to surround Co(II) ions in a tetrahedral geometry. Infrared evidence for sulphur bonding of thiourea and its related ligands was presented. $Co(Mtu)_2X_2$ and $Co(Dmtu)_2X_2$(X=Cl,Br) complexes are paramagnetic with three unpaired electrons. The chlorides are non-conducting in nitromethane and the anions are believed to be coordinated. The compounds $CoL_3(NO_3)_2$ were suggested to have one ionic nitrate group on the basis of infrared data. All perchlorate compounds are 1:2 electrolytes like the unsbstituted compounds in acetone. Optical spectra in acetone in the visible region indicate a typical tetrahedral species of CoL_4^{++} ion.

(4-3) EXPERIMENTAL SECTION

The following compounds were synthesized by literature methods.[122, 124,125]

$Co(Tu)_2Cl_2$	$Co(Mtu)_2Cl_2$
$Co(Tu)_2Br_2$	$Co(Mtu)_2Br_2$
$Co(Tu)_2I_2$	$Co(Mtu)_2I_2$

$Co(Dmtu)_2Cl_2$
$Co(Dmtu)_2Br_2$
$Co(Dmtu)_2I_2$

$Co(Tu)_4(NO_3)_2$
$Co(Tu)_4(ClO_4)_2$
$Co(Mtu)_4(ClO_4)_2$
$Co(Dmtu)_4(ClO_4)_2$

$Co(L)_2X_2$ (where L=Tu,Mtu,Dmtu and X=Cl,Br) were prepared by reacting stoichiometric quantities of metal salt and the ligand in hot organic solvents such as isopropanol for $Co(Tu)_2X_2$, $CHCl_3$-ethanol for $Co(Mtu)_2X_2$ and methanol for $Co(Dmtu)_2X_2$ respectively. For all perchlorate complexes, isopropanol was used when L=Tu and Mtu, and $CHCl_3$-ethanol when L=Dmtu. All hot solutions were heated for 30-60 mins., and cooling in ice with vigorous stirring to help initiate crystallization. They were then filtered to remove the unreacted materials. All solid products were recrystallized usually from the solvents used in the preparation. They were thoroughly washed with anhydrous ether for several times and dried in vacuum until pure.

All starting materials were purchased from Fischer Scientific Company, Alfa Inorganics, and Pfaltz and Bauer Inc. Products were characterized by their melting points and visible spectra, all of which agree well with data in the literature. They are shown in the Tables (4-1) and (4-2) respectively. $Co(Dmtu)_2Cl_2$ is very sparingly soluble in acetone and NMR data is not reported for this reason.

$Co(Mtu)_2I_2$ and $Co(Dmtu)_2I_2$ do not appear to have been reported previously. They were prepared by the similar procedure.

$Co(Mtu)_2I_2$

Stoichiometric quantities of $CoI_2.2H_2O$ and Mtu were dissolved in a mixture of chloroform and ethanol 1:3 by volume and the solution heated for 30-40 min. The hot solution was filtered and allowed to evaporate at room temperature for several days. The dark green oily liquid obtained was washed several times with ether and the remaining ether pumped off. The resulting dark green liquid was dried in vacuo over P_4O_{10} to give a crystalline solid. The melting point of the product was 80-82°. The visible spectrum shows the triplet of bands characteristic of tetrahedral Co complexes (14800, 13900, and 13050 cm^{-1}).

$Co(Dmtu)_2I_2$

The procedure was similar to the above except that ethyl alcohol was used as a solvent. Melting point of product was 113-115°C; absorption bands observed at 15500, 14500 and 13800 cm^{-1}. All compounds were dried over P_4O_{10} under vacuo before using. NMR spectra were obtained with a Varian DP 60 spectrometer operating at 56.4 or 60 MHz and equipped with a variable temperature probe. Acetone-h_6 was dried over a molecular sieve and redistilled. Tetramethyl-silane was used as an internal reference throughout.

Table (4-1)

Melting Points of Some Co-Tu,Mtu,Dmtu-Complexes

Compound	Observed* melting point(°C)	Literature melting point(°C)
$Co(Tu)_2Cl_2$	146-147	148
$Co(Tu)_2Br_2$	162	163
$Co(Tu)_2I_2$	170-172	172-174
$Co(Tu)_4(NO_3)_2$	127	127
$Co(Mtu)_2Cl_2$	123-124	125
$Co(Mtu)_2Br_2$	89	89
$Co(Mtu)_2I_2$	80-82	-
$Co(Dmtu)_2Cl_2$	220	222
$Co(Dmtu)_2Br_2$	178-179	179
$Co(Dmtu)_2I_2$	113-115	-

*obtained using Reiclart Hot Stage M.P. apparatus

Compound	Observed band positions cm^{-1}	Literature band positions cm^{-1}
$Co(Tu)_2Cl_2$	16207	16200[123]
	15037	15000
	14124	13800
$Co(Tu)_2Br_2$	15873	15600[123]
	14749	14600
	13966	13900
$Co(Tu)_2I_2$	14925	15100[123]
	13947	13800
	13071	13600
$Co(Tu)_4(NO_3)_2$	16129	16000[122]
	14705	14500
	13698	13700
$Co(Tu)_4(ClO_4)_2$	15625	15600[122]
	14705	14580
	13888	13890
$Co(Mtu)_2Cl_2$	16232	-
	15151	1500 [125]
	14084	-
$Co(Mtu)_2Br_2$	13927	-
	13157	14900[125]
	12500	-
$Co(Mtu)_2I_2$	14814	-
	13888	- ?
	13054	-
$Co(Mtu)_4(ClO_4)_2$	16129	-
	14598	15100[125]
	13698	-
$Co(Dmtu)_2Br_2$	15455	-
	14534	14600[125]
	13793	-
$Co(Dmtu)_2I_2$	15576	-
	14556	-
	13774	- ?
$Co(Dmtu)_4(ClO_4)_2$	15267	-
	14492	14400[125]
	13812	-

Table(4-2) Visible Absorption Spectra of Co(II) Complexes

(4-4) STRUCTURAL STUDIES IN SOLUTION

Some twelve Co(II) complexes have been examined. All these complexes are paramagnetic. Two structural conclusions have been drawn from the magnetic and spectroscopic studies reported in the literature. It has been concluded, mostly from infrared data, that they are all bonded through the sulphur atom. They are also thought to have tetrahedral or distorted tetrahedral geometry about the metal atom. The only cases where this has been challenged are $Co(Tu)_4(NO_3)_2$ for which six coordination was suggested[122] and some complexes of stoichiometry $Co(Tu)_3X_2$ for which five coordination was postulated.[126] However, later workers[123,127] concluded that these compounds are also tetrahedral or distorted tetrahedral in solution. Spectroscopic studies have also shown that in solvents such as acetone, these compounds are partly dissociated although no quantitative results have been reported. In compounds such as $Co(Tu)_2Cl_2$ where there is a choice of dissociating ligands, conductivity studies indicate that it is the thiourea which dissociates. The present results are entirely compatible with all these conclusions.

Figure (4-1) and (4-2) show some representative NMR spectra of Co(II) thiourea complexes. As anticipated for paramagnetic compounds, the shifts are much larger than those of the diamagnetic zinc complexes. In all cases, there is a doubling of the resonance attributable as before to restricted rotation about the C-N bond. There is no collapse of any of these doublets up to the boiling point of acetone. The large chemical shifts greatly facilitate quantitative measurements on the dissociation

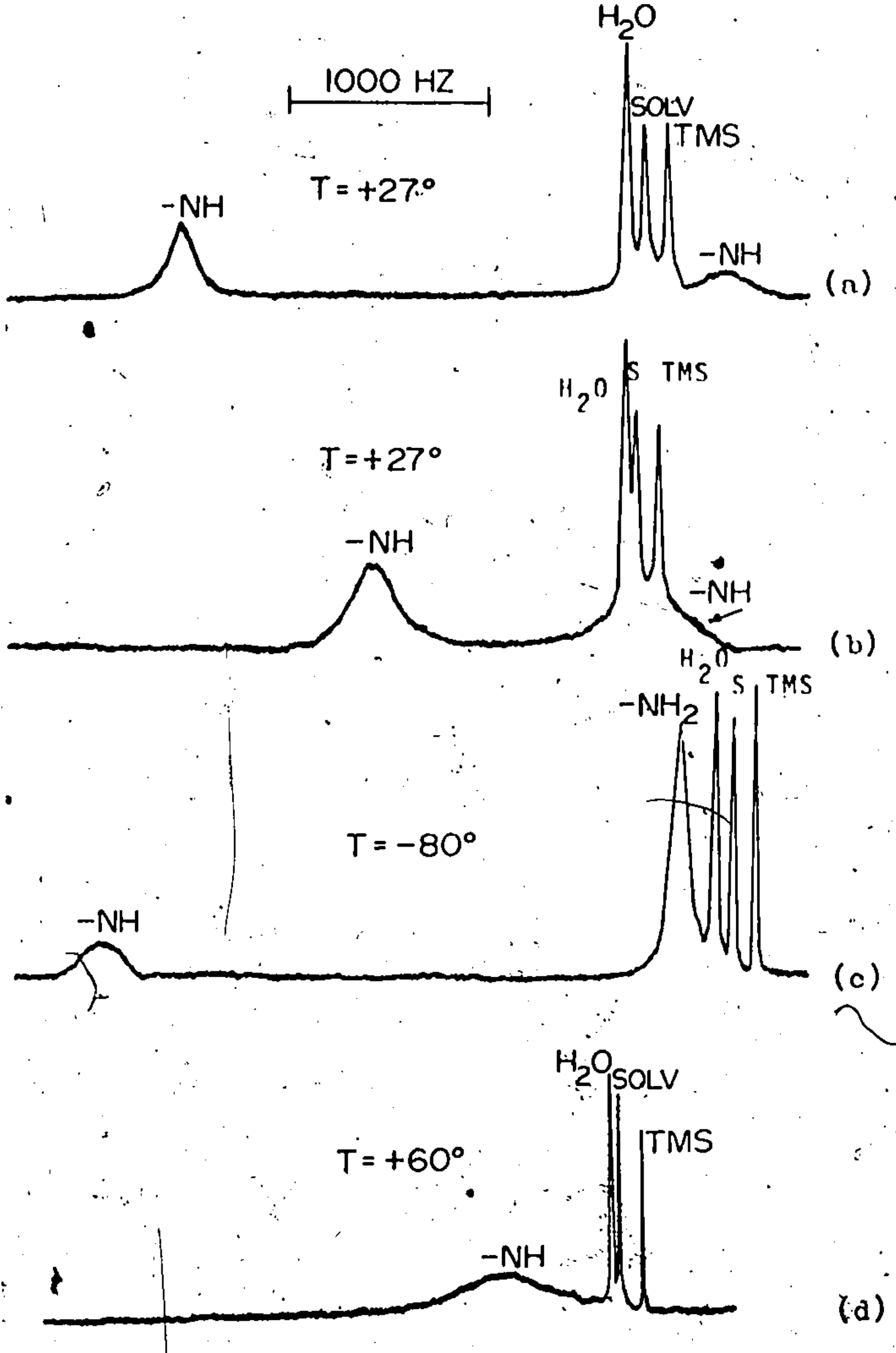


Figure (4-1) ^1H NMR spectra of $Co(Tu)_2Cl_2$ at 56.4 MHz.
(a) = ^1H NMR spectrum at 27°
(b,c,d) = with excess ligand at various temps. ((b,d) = fast exchange, (c) = slow exchange)

and ligand exchange equilibria of these compounds. Addition of free ligand to these solutions at room temperature leads to a single set of resonances at an average position demonstrating fast exchange. This is illustrated in Fig. (4-1(b)). Cooling a solution containing complex and free ligand leads to the appearance of both contact shifted and free ligand lines (Fig.4-1(c)). The ligand exchange process has become slow. Heating such a solution averages the two N-H lines (Fig.4-1(d)). Ligand dissociation has been followed by rotation about the C-N bond. The frequencies of the resonances are concentration dependent demonstrating dissociation of the thiourea. The quantitative behaviour of the N-methylthiourea and N,N'-dimethylthiourea complexes is similar. Room temperature spectra are shown in Fig. (4-2).

Before proceeding with any quantitative analysis of these spectra, we must first deal with two possible difficulties. Firstly it may be noted that all the spectra show a small resonance attributable to water present in the acetone-d_6. Since water is itself a potential ligand, it could play an important role in the system. Addition of water enhances this resonance but does not affect the line due to acetone-d_5. Therefore, there is no fast proton exchange between water and acetone under the conditions of these experiments. The amount of water in the original solvent can therefore be estimated from the integrated intensities of the resonances obtained by adding measured increments of water. Values of between 1 and 2% were obtained. Acetone-h_6 can be obtained somewhat drier without too much difficulty and a sample was shown to have 0.3% water by comparative integration of the acetone ^{13}C satellites. In acetone-h_6, resonances in

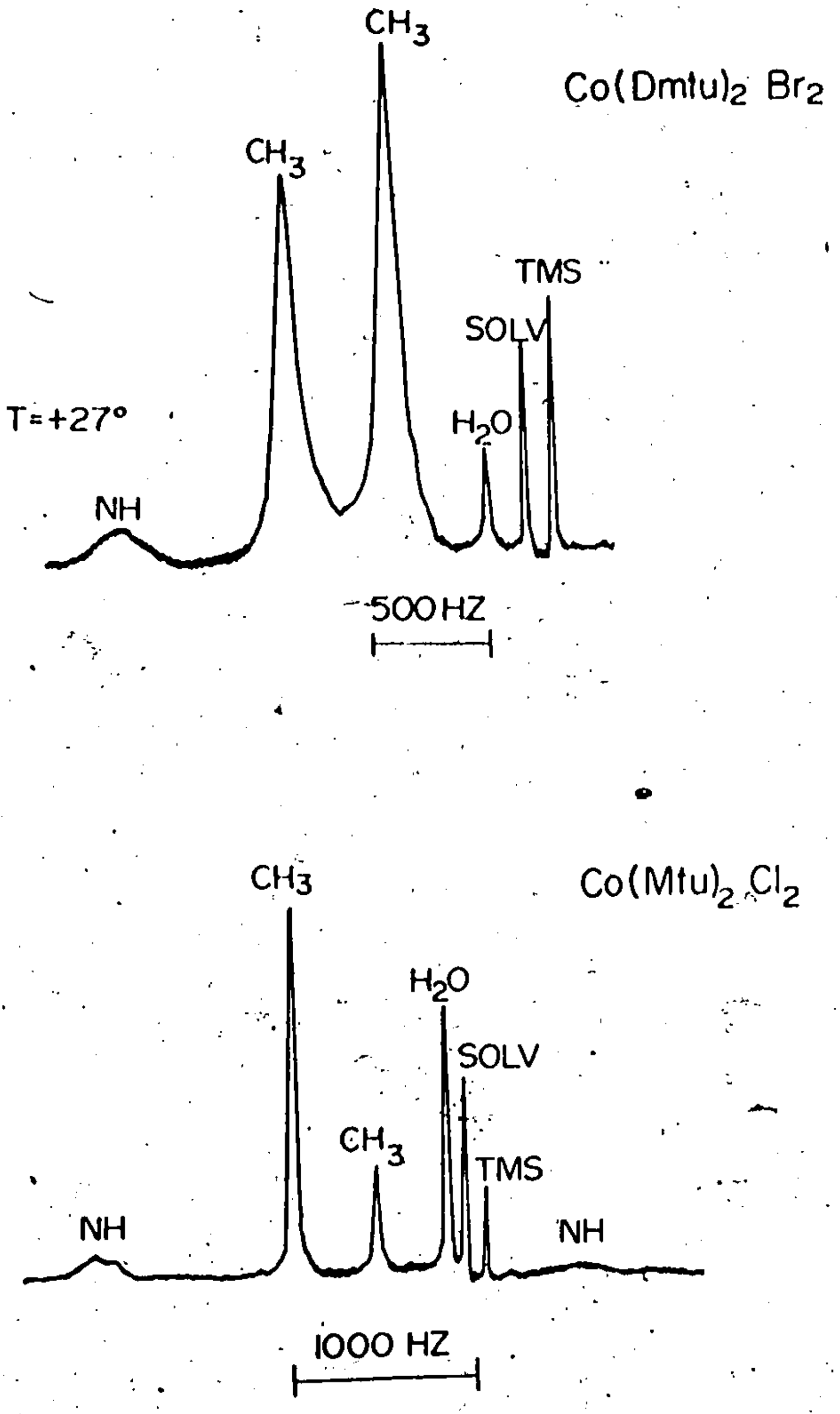


Figure (4-2): ^{1}H NMR spectra of Co(Dmtu)$_2$Br$_2$ and Co(Mtu)$_2$Cl$_2$ at 27°C the diamagnetic region are largely obscured by the solvent but it was shown that the isotropically shifted peaks of cobalt thiourea complexes occurred in the same positions in this solvent as in the acetone-d_6. The effect of adding increasing amounts of water on the thiourea and water resonances of $Co(Tu)_2Cl_2$ and $Co(Tu)_4(ClO_4)_2$ has been investigated. The thiourea resonance is not affected initially but then moves towards its diamagnetic position when a large amount of water is added. The water resonance initially occurs at its diamagnetic position but is shifted to low field if a large excess of water is added. Fast exchange of both water and thiourea between coordinated and free environments is indicated. On a mole fraction basis, a 40-fold excess of water is needed to displace half the thiourea of $Co(Tu)_4(ClO_4)_2$. At -80°C, both exchange equilibria are slow and the coordinated water appears as a broad line at about -7000 Hz from TMS. This is consistent with literature values for the shift of water complexes to Co^{2+} in other solvents.[128] These results are not consistent with an equilibrium of the type

$$Co(Tu)_2Cl_2 + H_2O \rightleftharpoons Co(Tu)(H_2O)Cl_2 + Tu \quad \ldots \quad (4\text{-}1)$$

with an equilibrium constant independent of solvent composition. For such a situation of excess of one of the ligands must always lead to a decrease in the average shift for that ligand whereas the water shift is increased by addition of water. The situation is rather that the complexing abilities of thiourea and water depend strongly on the nature of the solvent system. A similar conclusion has been reached by Shul'man et al.[129] from electro-chemical studies. At low condentrations of water, the water is a very poor ligand and does not compete with thiourea. At higher concentrations, it competes much more favorably. At the 1-2% level, the observed shift from the diamagnetic position is less than 5 Hz and since the full contact shift of water at room temperature is ~5000 Hz and there is fast exchange, a negligible amount of water is complexed. We can, therefore, neglect the equilibrium (4-1) under these conditions. A plausible rationalization of these observations is that if the cobalt is formally neutral, i.e. if the chloride ion is not dissociated from $Co(Tu)_2Cl_2$, water is a poor ligand. With increasing dielectric constant, there is some ionization and water becomes a better ligand. Water obviously competes somewhat more favorably in the perchlorate complex which is charged. In any event, we can safely disregard small percentages of water provided its resonance occurs within a few Hz of its diamagnetic position.

The second point which deserves some preliminary consideration concerns the coordination number of the cobalt. The consensus as we have noted above, is that only four coordinated tetrahedral species are present in solutions of cobalt thiourea complexes. Swaminathan and Irving[130], however, have studied cobalt perchlorate thiourea in 95% ethanol and concluded that $Co(Tu)_6^{2+}$ is an important species. If this were the case in acetone, it would invalidate the analysis of the data given in Table (4-3). The coordination number of the cobalt in solutions containing excess thiourea can be obtained in the following manner. The limiting shift for thiourea fully complexed to cobalt can be obtained directly at low

Table (4-3) Coordination numbers of Co complexes

$Co(Tu)_2Cl_2$			$Co(Tu)_4(ClO_4)_2$		
Total conc. Tu(mg/ml)	Observed shift(Hz)*	Calcd. coord.No	Total conc. Tu(mg/ml)	Observed shift(Hz)*	Calcd. coord.No.
3.61	-2079	3.9	7.74	-1353	3.6
4.61	-1620	3.8	8.74	-1224	3.3
5.61	-1291	3.8	9.94	-1125	3.5
6.61	-1186	3.9	1094	- 964	3.3
7.61	- 923	3.7	11.94	- 862	3.2
			12.94	- 797	3.2

*Shifts are measured relative to the free ligand temperatures, where the exchange is slow, and indirectly at higher temperatures. Given this limiting shift, the fraction of thiourea complexed in any fast exchanging solution is readily obtained from the observed contact shift. Knowing the total thiourea concentration, the number of moles complexed can be compared with the number of moles of cobalt present and a coordination number obtained. A series of results for $Co(Tu)_2Cl_2$ and $Co(Tu)_4(ClO_4)_2$ each in the presence of excess thiourea is given in Table (4-3). In all cases, the total coordination number remains somewhat below four. There is, however, a possible flaw in this argument. If the limiting shift of a five or six coordinated species was substantially less than that of the four coordinated species, low apparent coordination numbers would be obtained. If this were so, though, at low temperatures, we would obtain a different (smaller) limiting shift in the presence of excess thiourea. Experiment shows that this does not occur and that at 80°C excess ligand merely increases the free ligand resonance without shifting the complexed resonance. We therefore agree with the conclusions of Cotton and co-workers,[122] Hall and Horrocks,[127] and Manecces et al.,[131] that five or higher coordination numbers are not important for these compounds in solution. This does not preclude the presence of small concentrations of such species which might act as intermediates in the exchange process. We will also express some reservations later about the situation at very low temperatures for one compound. However, it seems reasonable to attempt initial analysis of the data on the basis of four coordination.

On this assumption, the principle equilibrium present is

$$Co(Tu)_2X_2 + S \rightleftharpoons Co(Tu)SX_2 + Tu \ldots \qquad (4\text{-}2)$$

where S represents a solvent molecule. In some cases it may also be necessary to consider the further dissociation

$$\mathrm{Co(Tu)SX_2 + S \rightleftharpoons CoS_2X_2 + Tu} \quad \ldots \qquad (4\text{-}3)$$

In the fast exchange situation, if the degree of dissociation is small, the shift of the undissociated compound may be obtained by plotting the observed shifts against the reciprocal of the square root of the concentration. Rewriting the equation (4-2) in a simple form,

$$\begin{array}{ccc} \mathrm{Co(Tu)_2X_2} & \rightleftharpoons & \mathrm{Co(Tu)X_2} + \mathrm{Tu} \\ c(1-\alpha) & & \alpha c \qquad \alpha c \end{array}$$

where c and α are the concentration and degree of dissociation of the complex, so that the following expressions will hold

number of moles of complexed Tu $= 2c(1-\alpha) + \alpha c$

number of moles of free Tu $= \alpha c$

total number of moles of Tu $= 2c(1-\alpha) + \alpha c + \alpha c$

fraction complexed $= \dfrac{\text{number of moles of complexed Tu}}{\text{total number of moles of Tu}}$

$$= \frac{2c(1-\alpha) + \alpha c}{2c(1-\alpha) + \alpha c + \alpha c}$$

$$= (1 - \alpha/2)$$

The observed contact shift Δv_o of the complex can be related to the fraction complexed:

$$\Delta v_o = \text{fraction complexed} \times \Delta v_L$$

where Δv_L is the limiting shift of the complex. Therefore,

$$\Delta v_o = (1 - \alpha/2)\,\Delta v_L \quad \ldots \quad (4\text{-a})$$

The dissociation constant K of the above equilibrium can be shown as

$$K = \frac{c\alpha^2}{(1 - \alpha)} \quad \ldots \quad (4\text{-b})$$

Since α is very small, $(1 - \alpha) = 1$ and $\alpha = (K/c)^{1/2}$ so that

$$\Delta v_o = \Delta v_L\{1 - (1/2)(k/c)^{1/2}\}$$

Generally, for a complex of type $Co(L)_nX_2$, the observed shift Δv_o can be written as

$$\Delta v_o = \Delta v_L\{1 - (1/n)(K/c)^{1/2}\} \quad \ldots \quad (4\text{-c})$$

such that if $(1/c)^{1/2} \to 0$, $\Delta v_o \to \Delta v_L$.

A typical plot is shown in Figure (4-3). In the slow exchange situation at low temperatures, the limiting shift is obtained directly. If this analysis is correct, the limiting shifts should plot against 1/T throughout the temperature range. Figure (4-4) shows these plots for $Co(Tu)_2X_2$ where X=Cl,Br,I.

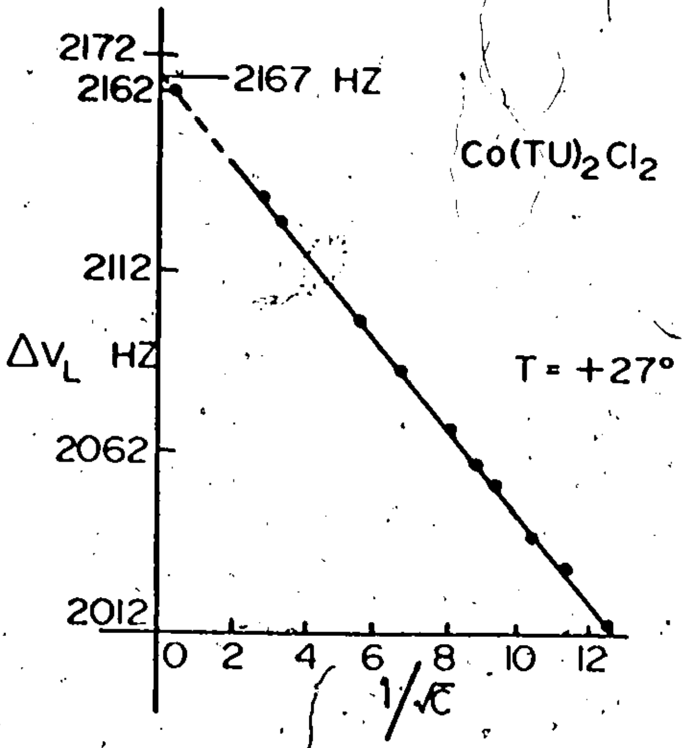


Figure (4-3): Observed shift versus $1/\sqrt{C}$ ····[$Co(Tu)_2Cl_2$]

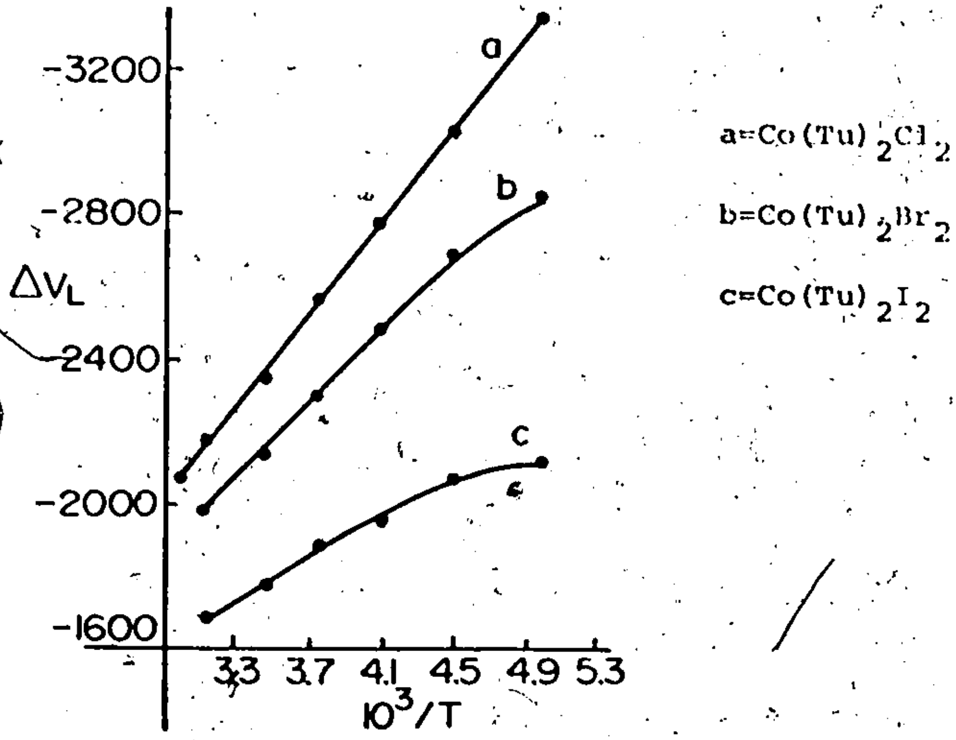


Figure (4-4): Limiting Shifts versus $10^3/T$ ····[$Co(Tu)_2X_2$]

It may be noted that there is some indication of non-linearity at the lowest temperatures for the bromide and iodide. The perchlorate and nitrate complexes show similar behaviour. With one exception, the Mtu and Dmtu complexes closely parallel the Tu complexes. The exception is $Co(Mtu)_2I_2$ which appears to be anomalous in both the concentration and temperature dependence of the shifts. It is believed that this discrepancy arises from poor experimental data resulting from overlap of different resonances at certain concentrations and temperatures. It is possible that the slightly anomalous shifts at low temperature indicate the formation of new and different complexes. More probably, they simply represent a "normal" deviation from Curie law behaviour. However, the general consistency of the high and low temperature data leads us to believe that the values obtained for the limiting shifts are reliable.

Given this reassurance, we may then use the limiting shifts to calculate the degrees of dissociation and equilibrium constants for reaction (4-2) for all cases where we have fast exchange. The temperature dependence of the equilibrium constant gives values of ΔH and ΔS for reaction (4-2). Some experimental data for the cobalt complexes is given in Table (4-4). Limiting shifts, equilibrium constants at room temperature, and values of ΔH and ΔS for all the compounds examined are given in Table (4-5). The data at low concentrations was then re-examined to investigate the effect of the second dissociation (Eq. 4-3). In all cases, very small values (10^{-9} - 10^{-10}) were obtained for the second dissociation constants. Differences between the values for different compounds are probably not significant.

(4-5) DISCUSSION OF STRUCTURAL DATA

(4-5a) THE NUCLEAR MAGNETIC RESONANCE SPECTRA

The chemical shift data for these complexes is collected in Table (4-4). All the NMR data can be readily interpreted on the assumption that thiourea is bonded to the metal through sulphur and rotation about the C-N bond is completely restricted. The high field resonance is significantly broader than the low field resonance. Since the predominant relaxation mechanism is likely to be dipolar interaction with the unpaired electrons on the cobalt, the hydrogen closer to the metal will be broader. A model gives distances of 5.88 and 4.62 A° for the "inside" and "outside" hydrogens, respectively. The high field line is therefore assigned to the "outside" position. For all Dmtu complexes, two hydrogens and two methyls are observed. Both methyls are shifted to low field but the less shifted line is broader. This is therefore assigned to the outer position. $Co(Mtu)_2Cl_2$ and $Co(Mtu)_4(ClO_4)_2$ both show two methyl resonances and three hydrogens, two to low field and one to high field, under appropriate conditions. Presumably we are distinguishing between hydrogens H_a and H_b in structure (3-2). The relative intensities of the various lines suggest that isomers with "outside" methyl groups are preferred as might be anticipated on steric grounds. The enhanced barrier to rotation on complexing the thiourea suggests that ionic structures such as (3-2) make a greater contribution when the thiourea interacts with a positively charged metal ion. This seems not unreasonable. The origin of the isotropic shifts is not unambiguous. The choice lies between a dipolar mechanism which requires the complex to be magnetically anisotropic, a contact mechanism which requires delocalization of spin density to the ligand or a combination of the two. Since the ground state of tetrahedral Co(II) is orbitally non-degenerate, the magnetic anisotropy might be expected to be small and the dipolar shifts correspondingly not important[6]. This argument is, however, far from water-tight since there are low-lying excited states. We are more impressed by the observation that octahedral $Ni(Tu)_6(ClO_4)_2$ shows a large splitting between "inside" and "outside" NH protons. In this case, significant dipolar shifts are very unlikely and the difference must arise from differing contact interaction. Thus although it is tempting to postulatd that the difference in shift of the "inside" and "outside" hydrogens arises from differences in the $(3 \cos^2\theta - 1)/r^3$ term in the expression for dipolar shifts, this explanation will not hold for nickel complexes and therefore seems less likely for cobalt complexes. We prefer the possibility that the difference reflects the difference in electronic environments resulting from differing hydrogen bonding interactions of the two hydrogens. Effects of this type do not appear to have been reported previously. It is interesting to note that Piovesana and Furlani[132] have recently suggested that the infrared spectra of these complexes provide evidence for intra-molecular hydrogen bonding between an "outside" hydrogen and a halide ligand. There are possibilities of delocalizing spin into both the σ and π orbitals of the ligand. Since both high and low field shifts are observed, both types of delocalization may be contributing. It is quite plausible that the relative contributions should depend critically on the energy of the NH bonding orbital relative to that of the molecular orbital containing the unpaired electron and hence on the hydrogen bonding. It is also interesting that the contact shifts change smoothly in the series Cl, Br, and I with the low field shifts decreasing and the high field shifts increasing. Attempts have been made to explain similar trends observed in Co(II) pyridine and hexamethylphosphoramide complexes in terms of changes in the metal ligand bonding.[133a] The significance of this correlation has however been challenged[133b] and an alternative explanation based on steric factors put forward. Either type of explanation could be applied to the present case and we do not feel that we can add much towards the resolution of this particular controversy.

(4-5b) LIGAND DISSOCIATION

The equilibrium constants of Table (4-5) show that the degree of dissociation of all three series of complexes depends on the anion present and increases in the order Cl < Br < I < ClO_4. The differences between corresponding compounds of Tu, Mtu, and Dmtu are relatively small but indicate that the Dmtu perchlorate is least dissociated followed by Mtu and Tu in that order. The data of Table (4-5) also show that the entropy term is at least as important as the enthalpy term in determining the amount of dissociation. The indicated errors are obtained by least squares analysis of the data. The results with aqueous acetone have indicated that thiourea becomes a poor ligand if the positive charge on the cobalt atom becomes large. Presumably back donation to the π^* orbital makes a significant contribution to the bond strength. The significantly lower values of ΔH for

Table (4-4) Observed isotropic shifts for Co(II) complexes*

Compound	Isotropic shift			
	Inside NH -	Outside NH -	Inside N - CH_3	Outside N - CH_3
$Co(Tu)_2Cl_2$	-2460	+ 200	---	---
$Co(Tu)_2Br_2$	-2275	+ 820	---	---
$Co(Tu)_2I_2$	-1980	+1500	---	---
$Co(Tu)_4(NO_3)_2$	-1674	+ 244	---	---
$Co(Tu)_4(ClO_4)_2$	-1746	+1333	---	---
$Co(Mtu)_2Cl_2$	-2171	---	-1026	-565
$Co(Mtu)_2Br_2$	-1868	+1144	-1131	-736
$Co(Mtu)_2I_2$	-1552	+1868	-1223	-789
$Co(Mtu)_4(ClO_4)_2$	-1378 -1175	+1459	-1750	-851
$Co(Dmtu)_2Br_2$	-1831	---	-1115	-726
$Co(Dmtu)_2I_2$	---	+2540	-1276	-734
$Co(Dmtu)_4(ClO_4)_2$	-1078	+1723	-1697	-802

*Shifts in Hz at 56.4 M Hz from TMS. All solutions 0.02 M in acetone-d_6, temperature 27 °C.

Table (4-5) Limiting shifts and thermodynamic data for Cobalt complexes

Compound	$\Delta\nu_L$*	$K_D \times 10^{-4}$ (27°C)†	ΔH(Kcal/mol)	ΔS(cal.°K⁻¹mole⁻¹)
$Co(Tu)_2Cl_2$	-2167	1.46	+3.5 ± 0.4	-5.8 ± 1.5
$Co(Tu)_2Br_2$	-1982	2.82	+4.0 ± 0.4	-2.5 ± 1.6
$Co(Tu)_2I_2$	-1684	3.86	+6.1 ± 0.8	+4.9 ± 2.8
$Co(Tu)_4(NO_3)_2$	-1362	14.4	+4.6 ± 0.2	+2.6 ± 0.9
$Co(Tu)_4(ClO_4)_2$	-1496	53.5	+2.9 ± 0.4	+0.1 ± 1.6
$Co(Mtu)_2Cl_2$	-1925	1.21	+3.2 ± 0.5	-6.6 ± 2.1
$Co(Mtu)_2Br_2$	-1646	1.29	+3.9 ± 0.2	-4.5 ± 0.9
$Co(Mtu)_2I_2$	-1047‡	4.09	§	§
$Co(Mtu)_4(ClO_4)_2$	-1638‡	31.7	+2.9 ± 0.2	-1.7 ± 0.6
$Co(Dmtu)_2Br_2$	- 997‡	2.06	+2.3 ± 0.1	-8.9 ± 0.5
$Co(Dmtu)_2I_2$	-1220‡	3.66	+3.3 ± 0.9	-5.1 ± 3.6
$Co(Dmtu)_4(ClO_4)_2$	-1585‡	29.4	+2.7 ± 0.4	-2.2 ± 1.6

*$\Delta\nu_L$ is limiting shift in Hz at 56.4 M Hz measured from free ligand

†K_D obtained from equations $\alpha = n(1 - \Delta\nu_o/\Delta\nu_L)$, $K_D = \alpha^2 C/(1-\alpha)$; where α = fraction of complex dissociated, n = number of thiourea molecules in complex, $\Delta\nu_o$ = observed shift, $\Delta\nu_L$ = limiting shift

‡Limiting shift of CH_3 resonance. Other limiting shifts refer to NH

§Line overlap leads to questionable temperature data the ionic perchlorates is consistent with this picture. We tentatively ascribe differences in ΔS to variations in the hydrogen bonding interactions which determine the structure of the second coordination sphere.

(4-5c) MECHANISM OF LIGAND EXCHANGE PROCESS

Some deductions regarding mechanism from the variation of the line widths with concentration have been discussed in Section (2-8), Chapter II. If the mechanism of ligand exchange is associative, i.e.

$$Co(Tu)_nX_2 + Tu^* \rightleftharpoons Co(\overset{*}{Tu})_{n+1}X_2 \rightleftharpoons Co(\overset{*}{Tu})_nX_2 + Tu$$

it can be readily shown that

$$\tau_c^{-1} = k[Tu]$$

$$\tau_L^{-1} = k[(Co(Tu)_nX_2]$$

where τ_c and τ_L are the lifetimes of complexed and free ligand and τ_c^{-1} and τ_L^{-1} are a measure of the respective line widths under conditions such that separate lines are observed for the two environments. However, if we have a dissociative mechanism, it follows that

$$\tau_c^{-1} = k$$

$$\tau_L^{-1} = k[Co(Tu)_nX_2][Tu]^{-1}$$

We cannot distinguish between a dissociative mechanism involving a lower coordination number for cobalt and one in which the coordination number is maintained by substituting solvent molecules. The latter is much more likely and the observation of the second type of kinetics most probably indicates that the rate determining step for thiourea ligand exchange is

$$Co(Tu)_nX_2 + S \rightleftharpoons [Co(Tu)_{n-1}(S)X_2] + Tu$$

This is then followed by fast reaction of the solvent containing complex with free thiourea. It is apparent that the key experiment is to determine the behaviour of the line widths as a function of free ligand concentration at low temperature. The results of Fig. (4-5a) show very clearly that both types of mechanism must be considered. Thus, the lines A and A' for $Co(Tu)_2Cl_2$ show that the line width of the complexed thiourea resonance is independent of free thiourea concentration whereas that of the free thiourea decreases with added ligand. On the other hand, B, C, and C' clearly demonstrated that the line-widths of complexed Mtu and Dmtu increase with added ligand. For Tu complexes, a dissociative mechanism predominates, for Mtu and Dmtu complexes, an associative mechanism is more important. Most probably both processes occur for all complexes and only their relative contributions are changing.

Finally we draw attention to the spectra of $Co(Dmtu)_4(ClO_4)_2$ shown in Fig. (4-5b). These spectra were obtained at -80°C and the sharp resonances at the free ligand positions show that free ligand is not involved in fast exchange with the complex. However, addition of free ligand clearly shifts the positions of the complexed ligand lines. A fast equilibrium between complexed ligand and ligand in a fifth coordination position or an outer

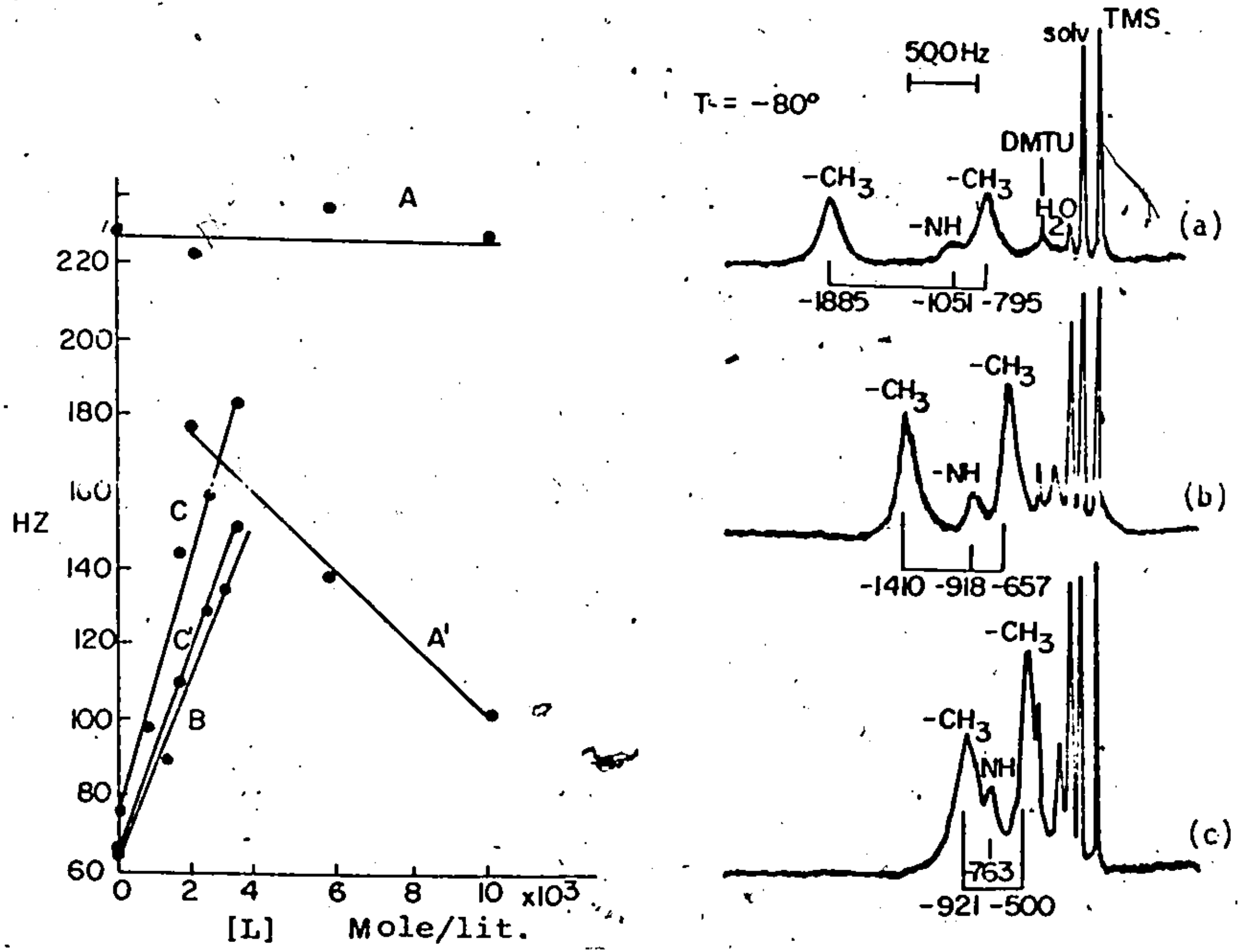


Figure (4-5): Dependence of line widths in free ligand concentration and low temperature NMR spectra of $Co(Dmtu)_4(ClO_4)_2$ in the presence of excess ligand (a , b , c represent increasing amount of ligand).

A,A' = Line widths of complexed and free $Tu[Co(Tu)_2Cl_2]$.

B,C,C' = Line widths of complexed Mtu and Dmtu $[Co(Mtu)_2Cl_2$ and $Co(Dmtu)_2Br_2]$.

sphere site is indicated. We cannot distinguish between these possibilities in the present case. This is the only complex in the present series which shows this type of behavior with thiourea as the competing ligand but we shall report in the Appendix more substantial evidence for the existence of such type of complex in exchange reactions between diacetamide complexes and free ligand.

(4-6) KINETICS OF LIGAND EXCHANGE IN COBALT (II) COMPLEXES OF THIOUREA

Ligand exchange is a process fundamental to all of coordination chemistry and as such has been the subject of intensive investigation. A large proportion of this area has been reviewed previously and the reader is referred to Chapter I. Since ligand exchange is pertinent to the understanding of the mechanism of homogeneous catalysis, our interest lies in labile complexes of thiourea and substituted thiourea with first-row transition metal ion. The relevant theory associated with it has been discussed in Chapter II. We are particularly interested in enquiring how the ligand exchange rates vary with changes in transition metal ion, in geometry, in oxidation state, in substituent on the exchanging ligand, and in the nature of non-exchanging ligands. The present chapter is concerned with quantitative measurements on the ligand exchange reactions of Co(II) complexes. In the subsequent chapters, ligand exchange in these complexes will be compared with those in thiourea complexes of nickel and zinc.

Ligand exchange studies have been previously made for three series of tetrahedral cobalt complexes to obtain rate data. Pignolet and Horrocks[87,89] have examined the ligand exchange reactions of CoL_2X_2 complexes where L is a phosphine and X a halide ion. They found a second order (associative) exchange mechanism and report enthalpies of activation in the range 5-10 kcal. mole^{-1} and entropies of activation in the range -20 to -30 cal·K^{-1} mole^{-1} We will compare these results with those obtained with analogous thiourea complexes later in the present section. Zumdahl and Drago[88,91] have studied a similar series of hexamethyl phosphoramide complexes. Measurements on these compounds were restricted by the narrow temperature range accessible for study. However, they were able to demonstrate both a second order exchange process with an activation energy of around 5 kcal. mole^{-1} and a first order process with a higher activation energy of around 15 kcal. mole^{-1} They considered that this second process indicated a dissociative mechanism involving a three-coordinated cobalt intermediate. The same authors[88,91] have also studied the kinetics of ligand exchange in CoL_2Cl_2 (L = 2-picoline) and found an associative process with ΔH = 4.8 kcal. mole^{-1}, ΔS = -14.5 cal·K^{-1} mole^{-1} Thus it appears from these studies, that associative kinetics predominate with rather small enthalpies of activation and rather large negative entropies of activation but that there is a possibility of a first order exchange process.

(4-6a) LIMIT OF EXPERIMENT AND MEASUREMENTS OF RELAXATION TIMES

All Co complexes are paramagnetic and they have tetrahedral or distorted tetrahedral geometry. They show very large chemical shifts and their isotropically shifted resonances are inherently broad relative to a free ligand line. As a result, measurements of their line widths in the intermediate ligand exchange region are impractical and are therefore, restricted to the use of the low temperature (slow exchange) and high temperature (fast exchange) regions. The high temperature region is preferable as has been discussed previously and reasonable approximations relating the life-times in the different environments to the observed line width are given by equations (2-11) and (2-25) in Chapter II. These equations are applicable in the temperature range -30°C to +10°C. Below -30°C, the exchange broadening is too excessive for accurate measurements. Above +10°C, the effects of additional line broadening due to the onset of free rotation about the C-N bond of the uncomplexed ligand become significant. Thus, -30°C to +10°C is the preferred temperature range for quantitative measurements since both the quality of spectra in terms of signal to noise ratio and the accuracy of the temperature controls are superior to those in the slow exchange region. The strategy is therefore to obtain qualitative mechanistic data at low temperatures and quantitative rate data at high temperatures. However, there remains the problem of obtaining values of T_{2A} and T_{2B} for use in equation (2-25). We may obtain values of these relaxation times directly from the line widths at the extreme low temperature end of the measurements where the ligand exchange is too slow to affect the line widths. There remains the problem, though, as to how these line widths vary with temperature. This problem is not too serious for the free ligand line width, T_{2B}, since the range of free ligand line width is relatively small compared with the line widths for the ligand exchange situation and they can in any event be obtained by direct measurements on thiourea solutions over the temperature range in question. The values for complexed ligand T_{2A} present more of a problem. Theoretically, the situation is rather complicated. Some previous investigators have assumed that the line widths of complexed ligands will decrease with increasing temperature according to the relationship[88,91]

$$\log \Delta\nu_{1/2} \propto \frac{1}{T} \qquad (4\text{-}f)$$

Such a relationship will hold if the line width depends on the rotational correlation time of the molecules in solution which is the case for most relaxation processes. However, for cobalt (II) complexes, it has been shown that T_2 is determined by the electron spin relaxation time (T_{1e}) of the metal rather than by molecular tumbling. T_{1e} may however, itself depend on the correlation time for tumbling in solution. Specifically for tetrahedral cobalt (II) La Mar[134] has shown that the electron spin relaxation time is determined by coupling of the zero-field splitting with the molecular motion according to the equations

$$\frac{1}{T_{1e}} = \frac{32\pi^2}{5} \left(\frac{D^2}{h^2}\right) \left[\frac{\tau}{1 + \omega_s^2 \tau^2} + \frac{\tau}{1 + 4\omega_s^2 \tau^2}\right] \qquad (4\text{-}g)$$

In this equation D is the usual zero-field splitting parameter, τ is the molecular tumbling time and ω_s is the Larmor frequency in radians per second for the electron spin measured at the magnetic field used in the NMR experiment. Obviously if $\omega_s^2 \tau^2 >> 1$, $\frac{1}{T_{1e}} \propto \frac{1}{\tau}$ and if $\omega_s^2 \tau^2 << 1$, $\frac{1}{T_{1e}} \propto \tau$. Since the nuclear spin relaxation time becomes shorter as the electron spin relaxation time becomes larger, and τ becomes smaller with increasing temperature in the first case, the NMR line should become narrower with increasing temperature and in the second case, it should become broader. LaMar estimated $\omega_s^2 \tau^2 =$ 20 for a specific case but this value is sufficiently close to unity to make the generalization to other cobalt complexes in different solvents somewhat hazardous. Indeed, Frankel[135] has found that for solutions of Co^{2+} in water $1/T_2$ for the protons is virtually independent of viscosity implying no dependence on rotational correlation time and Zumdahl and Drago[91] have reached a similar conclusion with regard to the ligand protons of cobalt-hexamethylplosphoramide complexes. In this laboratory, we have observed that the line widths of some β-diketone complexes of V(III)vary very little over a wide range of temperatures.[136] The relaxation situation for these octahedral V(III)complexes should be quite similar to that for tetrahedral Co(II). For measurements involving the NH_2 protons of thiourea, there is an additional complication in that relaxation processes arising from interaction with the quadrupole moment of the nitrogen can also contribute to the line width. Transition from a sharp singlet at low temperatures to a broad singlet at higher temperatures and eventually to a resolved triplet is expected.[137]

In the light of the above discussion, it did not seem desirable to obtain the line widths of the complexed thiourea by extrapolation from higher or lower temperatures as has been done by previous investigators. Neither is it possible to obtain this data by direct measurement of the thiourea line widths of solutions to which no excess thiourea ligand has been added since the dissociative equilibrium (4-2) has been demonstrated. Equilibrium constants for this reaction are however, relatively small and the chemical shifts of complexed thiourea have been obtained by plotting observed shifts against $(1/\sqrt{c})$ where c is the concentration of cobalt complex. When $1/\sqrt{c} = 0$, the concentration of free ligand is zero and equation (2-25) indicates that $\frac{1}{T_2} = \frac{1}{T_{2A}}$. The line widths for complexed thiourea can therefore be obtained by plotting the observed line widths for solutions without added excess thiourea against $(1/\nu_c)$ and extrapolating to $(1/\nu_c = 0)$. Essentially, therefore, we have replaced the temperature extrapolation used by previous investigators to obtain the limiting line widths with a concentration extrapolation and regard this as the more reliable method since it is based on an experimentally established equilibrium rather than a theoretical consideration regarding the relaxation mechanism.

(4-6b) LIGAND EXCHANGE KINETICS

A solution containing paramagnetic metal ion Co complexed by L(Tu,Mtu,Dmtu) and with excess of free ligand L^*, undergoes the exchange reaction

$$\underset{\tau_A}{CoL_n + L^*} \rightleftharpoons \underset{\tau_B}{CoL_n^* + L}$$

The NMR spectrum of L will show the effects of this rapid exchange. Analysis of the NMR data gives the lifetimes τ_A and τ_B for complexed and free ligand molecules. These parameters must be related to the rates of specific reactions. From qualitative measurements in the previous section (4-5c), at slow exchange region, it has been previously demonstrated that two mechanisms must be considered. The first of these is exchange via a solvated intermediate and the second of these is direct exchange by an associative mechanism, i.e.

$$\mathrm{Co(L)_2X_2} + \mathrm{S} \rightleftharpoons \mathrm{Co(L)(S)X_2} + \mathrm{L}$$

$$\mathrm{Co(L)_2X_2} + \mathrm{L} \rightleftharpoons \mathrm{Co(L)(L)X_2} + \mathrm{L}$$

The first reaction can be broken down into various steps in order to produce the relation involving kinetic parameters. Thus,

$$\underset{\mathrm{A}}{\mathrm{Co(L)_2X_2}} + \mathrm{S} \underset{k_{-1}}{\xrightarrow{k_1}} \mathrm{Co(L)_2(S)X_2} \underset{k_{-2}}{\xrightarrow{k_2}} \underset{\mathrm{B}}{\mathrm{Co(L)(S)X_2}} + \mathrm{L} \qquad (4\text{-}4)$$

$$\text{Forward rate} \quad = \quad k_1[\mathrm{Co(L)_2X_2}][\mathrm{S}]$$

$$\tau_A = \frac{[\mathrm{Co(L)_2X_2}]}{k_1[\mathrm{Co(L)_2X_2}][\mathrm{S}]} = 1/k_1[\mathrm{S}]$$

$$\text{and} \quad \tau_A^{-1} = k_1[\mathrm{S}]$$

$$\text{Backward rate} \quad = \quad k_{-2}[\mathrm{Co(L)(S)X_2}][\mathrm{L}]$$

$$\tau_B = \frac{[\mathrm{L}]}{k_{-2}[\mathrm{Co(L)(S)X_2}][\mathrm{L}]} = 1/k_{-2}[\mathrm{Co(L)(S)X_2}]$$

$$\tau_B^{-1} = k_{-2}[\mathrm{Co(L)(S)X_2}] \qquad (4\text{-}h)$$

If K is the equilibrium constant for the reaction, then

$$K = \frac{[\mathrm{Co(L)(S)X_2}][\mathrm{L}]}{[\mathrm{Co(L)_2X_2}][\mathrm{S}]}$$

$$[Co(L)(S)X_2] = \frac{K[Co(L)_2X_2][S]}{[L]}$$

Therefore, $\tau_B^{-1} = K\,k_{-2}\,\frac{[Co(L)_2X_2][S]}{[L]}$ **(4-i)**

The direct replacement reaction of L with L^* can be shown as

$$\underset{A}{Co(L)_2X_2} + L^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co(L)_2(\overset{*}{L})X_2 \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} \underset{B}{Co(L)(\overset{*}{L})X_2} + L \qquad (4\text{-}5)$$

Forward rate $= K_3[Co(L)_2X_2][L^*]$

Therefore, $\tau_A = \frac{[Co(L)_2X_2]}{k_3[Co(L)X_2][L^*]}$, and $1/\tau_A = k_3[L^*]$

$$\tau_B = \frac{[L]}{k_3[Co(\overset{*}{L})_2X_2][L]}, \text{ and } 1/\tau_B = k_3[Co(\overset{*}{L})_2X_2]$$

Thus, the total τ_A^{-1} and τ_B^{-1} can be written as

$$\tau_A^{-1} = k_1[S] + k_3[L]$$

$$\tau_B^{-1} = K\,k_{-2}\frac{[Co(L)_2X_2][S]}{[L]} + k_3[Co(L)_2X_2]$$

i.e., $\tau_B^{-1} = [Co(L)_2X_2]\left[\frac{K\,k_{-2}[S]}{[L]} + k_3\right]$ **(4-j)**

Since there is no evidence for any experimentally measurable concentrations of five coordinated complexes, it is assumed in both cases that the overall rate of ligand exchange is determined by the rate of formation of the five-coordinated intermediate. In the above relations, K_1, k_{-2} and k_3 are second order rate constants and K is the equilibirum constant for the overall reaction (4-4). k_1 and k_3 may therefore be obtained from the intercept and slope respectively of a plot of τ_A^{-1} versus [L]. From equation (4-j), k_{-2} and k_3 are obtained as the slope and intercept of a plot of τ_B^{-1} versus $[L]^{-1}$. The equilibrium constant K is known from previous results. The two values of k_3 obtained by this analysis provide an indication of the likely systematic errors in experiments of this type. Free energies of activation of the reaction may be calculated from equation (2-34). Enthalpies and entropies of activation are obtained by plotting $\Delta G^{\ddagger}$ against temperature.

(4-6c) RESULTS

Measurements have been made on eight complexes of the type CoL_2X_2 in which L = thiourea, N-methylthiourea and N,N'-dimethyl-thiourea and X = Cl,Br,I. Limited solubility in acetone prevented us from obtaining data for the compound with L = N,N'-dimethyl-thiourea and X = Cl. In each case, the primary data collected comprised of a set of line widths and line positions obtained for seven concentrations of metal complex to each of which was added free ligand at five different concentrations. Measurements were carried out over the temperature range -30°C to +10°C. For the thiourea complexes, measurements were made on the low field (-1000 to -2500 Hz from TMS at -60 MHz) line associated with the inside NH proton. For the methyl and dimethyl ligands, the lower field CH_3 resonance was used.

The data was analysed using equation (2-25). As indicated above,

Table (4-6)

Co(Tu)$_2$Cl$_2$ (+8°C) ν_A = 2460 - 2480 Hz ν_B = 405 Hz T_{2A}^{-1} = (60)π T_{2B}^{-1} = (40)π

(a) Contact Shift (Tu)	(b) Line Width $\Delta\nu_{\frac{1}{2}}$	(c) Conc. of Tu mole lit^{-1}	(d) P_A	(e) P_B	(f) $\frac{P_A}{T_{2A}}$	(g) $\frac{P_B}{T_{2B}}$	(h) $\frac{P_A}{T_{2A}}+\frac{P_B}{T_{2B}}$	(i) = (b) - (h)	(j) $4\pi P_A P_B^2 \times (\nu_A-\nu_B)^2 \times (\tau_A+\tau_B)$ $(\tau_A+\tau_B) \times$	(k) $\tau_A+\tau_B$	(l) $\tau_A=P_A(\tau_A+\tau_B)$	(m) $\tau_B=P_B(\tau_A+\tau_B)$	(n) $k_A=\tau_A^{-1}$	(o) $k_B=\tau_B^{-1}$	(p) $[Tu]^{-1}$
2240	201	8.7×10^{-3}	0.91	0.09	54.63	3.58	58.21	142.79	503721	2.8×10^{-4}	2.5×10^{-4}	2.5×10^{-5}	4.0×10^{3}	4.0×10^{4}	120
2183	230	12.5×10^{-3}	0.88	0.12	53.24	4.50	57.74	172.26	758684	2.3×10^{-4}	2.0×10^{-4}	3.2×10^{-5}	5.0×10^{3}	3.1×10^{4}	80
2110	272	17.5×10^{-3}	0.86	0.14	51.45	5.69	57.14	214.86	1130127	1.9×10^{-4}	1.6×10^{-4}	2.7×10^{-5}	6.3×10^{3}	3.7×10^{4}	57
2068	301	20.0×10^{-3}	0.84	0.16	50.44	6.37	56.81	244.19	1363244	1.8×10^{-4}	1.5×10^{-4}	2.9×10^{-5}	6.7×10^{3}	3.4×10^{4}	50
1953	343	25.0×10^{-3}	0.79	0.21	47.64	8.24	55.88	287.12	2033458	1.4×10^{-4}	1.1×10^{-4}	2.9×10^{-5}	9.1×10^{3}	3.4×10^{4}	40
1867	383	31.2×10^{-3}	0.76	0.24	45.54	9.64	55.18	327.82	2543182	1.3×10^{-4}	9.8×10^{-4}	3.1×10^{-5}	10.0×10^{3}	3.2×10^{4}	32

Co(Tu)$_2$Cl$_2$ (-8°C) ν_A = 2660 Hz ν_B = 404 Hz T_{2A}^{-1} = (84)π T_{2B}^{-1} = (40)π

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i) = (b) - (h)	(j) $\times(\tau_A+\tau_B)$	(k) $=(\tau_A+\tau_B)$	(l) $=\tau_A$	(m) $=\tau_B$	(n) $=\tau_A^{-1}$	(o) $=\tau_B^{-1}$	(p)
2525	186	4.6×10^{-3}	0.95	0.05	79.74	2.03	81.77	104.23	205862	5.1×10^{-4}	4.8×10^{-4}	2.5×10^{-5}	2.1×10^{3}	4.0×10^{4}	220
2439	271	9.2×10^{-3}	0.92	0.08	77.03	3.32	80.35	190.65	514811	3.7×10^{-4}	3.3×10^{-4}	3.1×10^{-5}	3.0×10^{3}	3.2×10^{4}	110
2367	357	13.8×10^{-3}	0.89	0.11	74.75	4.40	79.15	277.85	853119	3.3×10^{-4}	2.9×10^{-4}	3.6×10^{-5}	3.4×10^{3}	2.8×10^{4}	73
2324	400	16.5×10^{-3}	0.87	0.13	73.39	5.05	78.44	321.56	134403	2.4×10^{-4}	2.1×10^{-4}	3.0×10^{-5}	4.8×10^{3}	3.3×10^{4}	61
2224	457	20.2×10^{-3}	0.84	0.16	70.23	6.56	76.79	380.10	1068888	2.3×10^{-4}	1.9×10^{-4}	3.8×10^{-5}	5.3×10^{3}	5.3×10^{3}	50
2124	500	25.7×10^{-3}	0.80	0.20	67.07	8.06	75.13	424.86	2300662	1.8×10^{-4}	1.4×10^{-4}	4.0×10^{-5}	7.1×10^{3}	2.5×10^{4}	39

Co(Tu)$_2$Cl$_2$ (-20°C) ν_A = 2825 Hz ν_B = 405 Hz T_{2A}^{-1} = (108)π T_{2B}^{-1} = (40)π

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i) = (b) - (h)	(j) $\times(\tau_A+\tau_B)$	(k) $=(\tau_A+\tau_B)$	(l) $=\tau_A$	(m) $=\tau_B$	(n) $=\tau_A^{-1}$	(o) $=\tau_B^{-1}$	(p)
2703	243	4.6×10^{-3}	0.96	0.04	103.34	1.72	105.07	137.93	170496	8.1×10^{-4}	7.7×10^{-4}	3.4×10^{-5}	1.3×10^{3}	2.9×10^{4}	220
2653	314	9.2×10^{-3}	0.94	0.06	101.43	2.43	103.86	210.14	326851	6.4×10^{-4}	6.0×10^{-4}	3.9×10^{-5}	1.7×10^{3}	2.6×10^{4}	110
2596	400	13.8×10^{-3}	0.92	0.08	99.25	3.24	102.49	297.51	555428	5.4×10^{-4}	4.9×10^{-4}	4.3×10^{-5}	2.0×10^{3}	2.3×10^{4}	73
2553	457	16.5×10^{-3}	0.90	0.10	97.61	3.85	101.46	355.54	757742	4.7×10^{-4}	4.2×10^{-4}	4.5×10^{-5}	2.4×10^{3}	2.2×10^{4}	61
2510	486	20.2×10^{-3}	0.89	0.11	95.96	4.42	100.38	385.62	963764	3.9×10^{-4}	3.5×10^{-4}	4.3×10^{-5}	2.9×10^{3}	2.3×10^{4}	50
2470	543	25.7×10^{-3}	0.87	0.13	94.44	5.02	99.46	443.54	1208999	3.7×10^{-4}	3.2×10^{-4}	4.6×10^{-5}	3.1×10^{3}	2.2×10^{4}	39

All shifts measured at 60 MHz relative to free ligand

From τ_A										
t°c	Intercept k_A sec^{-1}	$k_1 = \frac{k_A}{[S]}$ $mol^{-1} sec^{-1}$	$\Delta H_1^{\ddagger}$ K.cal mol^{-1}	$\Delta S_1^{\ddagger}$ e.u.	Slope k_3 mol^{-1} sec^{-1}	$\Delta H_3^{\ddagger}$ K.cal. mol^{-1}	$\Delta S_3^{\ddagger}$ e.u.	ΔH K.cal. mol^{-1}	ΔS e.u.	K_{eq}
+ 27°	2.4×10^3	1.8×10^2	3.6 ± 0.6	-36 ± 2	3.5×10^5	1.3 ± 0.6	-29 ± 2	3.5 ± 0.4	-5.8 ± 1.5	1.46×10^{-4}
+ 9°	1.6×10^3	1.2×10^2			2.8×10^5					1.1×10^{-4}
- 8°	9.6×10^2	7.1×10			2.1×10^5					8.0×10^{-5}
- 20°	7.0×10^2	5.2×10			1.0×10^5					6.1×10^{-5}

From τ_B										
t°c	Slope= [compd.]x $K_{eq}k_{-2}[S]$	K_{eq}x [compd.]	k_2 $mol^{-1} sec^{-1}$	$\Delta H_{-2}^{\ddagger}$ K.cal. mol^{-1}	$\Delta S_{-2}^{\ddagger}$ e.u.	Intercept k_B = k_3[compd.]	k_3 mol^{-1} sec^{-1}	$\Delta H_3^{\ddagger}$ K.cal.mol^{-1}	$\Delta S_3^{\ddagger}$ e.u.	$\ln \frac{KT}{h}$
+ 27°	-	8.2×10^{-6}	3.4×10^7	0.9 ± 0.6	-21 ± 2	-	5.6×10^5	1.3 ± 0.6	-28 ± 2	29.4634
+ 9°	180	6.3×10^{-6}	2.9×10^7			2.66×10^4	4.7×10^5			29.4051
- 8°	120	4.6×10^{-6}	2.6×10^7			2.06×10^4	3.6×10^5			29.3393
- 20°	80	3.5×10^{-6}	2.3×10^7			1.84×10^4	3.2×10^5			29.2934

$[Co(Tu)_2Cl_2] = 5.7 \times 10^{-2}$ mol.lit^{-1} $\quad k = \frac{KT}{h} e^{-\Delta G^{\ddagger}/RT}$

$[Acetone] = [S] = 13.45$ mole.lit^{-1} $\quad \Delta G^{\ddagger} = -RT(\ln k - \ln \frac{KT}{h})$

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T.\Delta S^{\ddagger}.$

Table (4-6): Kinetic and Activation Parameters from τ_A and τ_B $[Co(Tu)_2Cl_2]$

$1/T_{2A}$ was found by extrapolating the line width to ($1/v_c^- = 0$) at each temperature. Several of these plots are shown in Fig. (4-6). We note that the NH line width decreases from approximately 100 Hz at -20°C to 60 Hz at +10°C. The width of the complexed thiourea at -80°C is 100 Hz. On the other hand, above 10°C, the limiting line width again increases. It is obvious that the temperature dependence is by no means simple exponential. Over the -30°C to +10°C temperature range, the width of the CH_3 resonances are in the 15 to 40 Hz range. Free ligand line widths were measured directly at the different temperatures and vary from 20 Hz to 40 Hz. It may be noted that the experimental line widths $1/T_2'$ vary from 200 to 400 Hz for the NH and from 60 to 200 Hz for the CH_3 resonances. The $1/T_{2A}$ and $1/T_{2B}$ terms in equation (2-25) therefore contribute between 10% and 50% of the total width depending on temperature and concentration. The chemical shifts of the complexed ligands and of the free ligands are known. We may therefore calculate the fraction of ligand complexed (p_A) and the fraction free (p_B) directly from the observed average shifts. Equations (2-11) and (2-25) now give τ_A and τ_B. A typical set of data is shown in Table (4-6). Typical plots of τ_A^{-1} and τ_B^{-1} used to obtain the rate constants k_1, k_{-2} and k_3 are shown in Figures (4-7) and (4-8). Figure (4-9) shows some examples of the plots of $\Delta G^{\ddagger}$ versus T (absolute) used to find the activation parameters. Finally, rate constants at room temperature and activation parameters for the three ligand replacement reactions for all eight complexes are gathered together in Table (4-7).

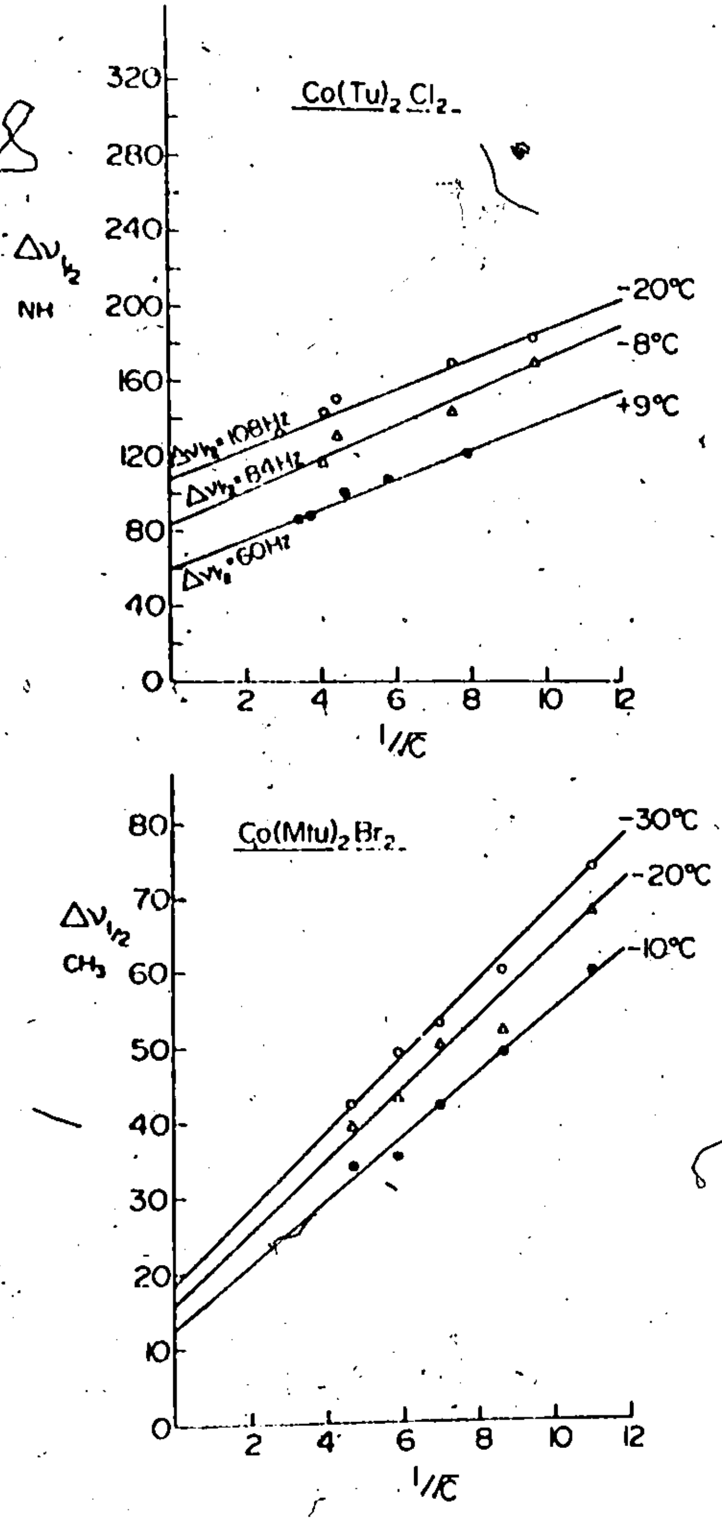


Figure (4-6): Plots of line widths ($\Delta v_{1/2}$) versus $\frac{1}{\sqrt{C}}$ [Co(Tu)$_2$Cl$_2$ and Co(Mtu)$_2$Br$_2$]

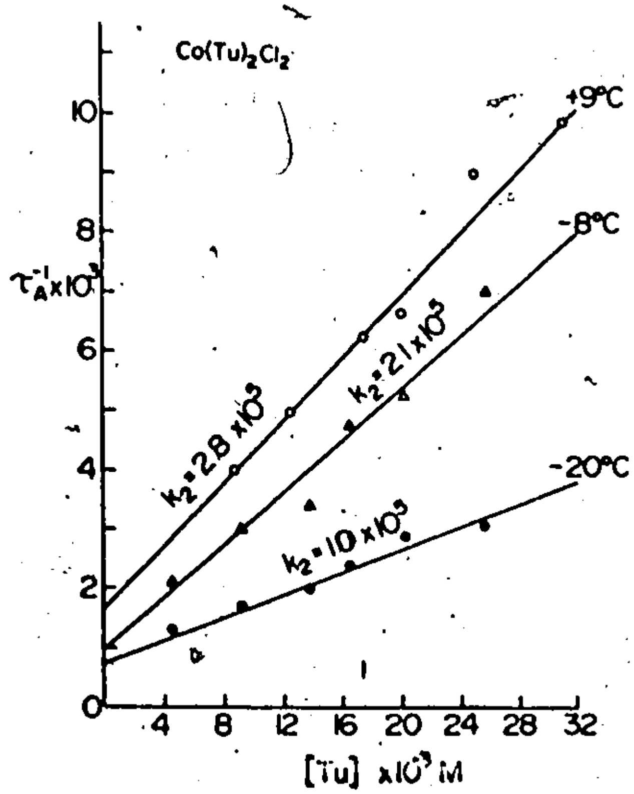


Fig. (4-7)

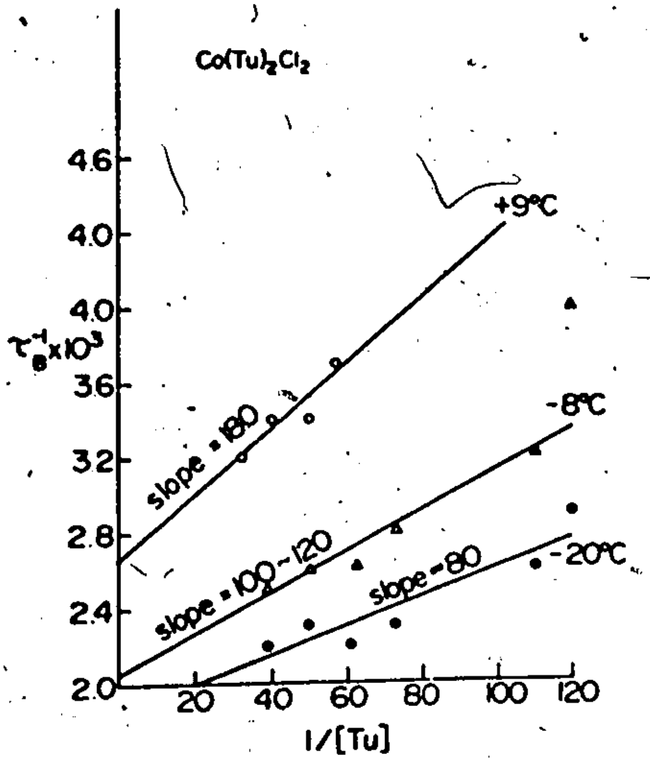


Fig. (4-8)

Plots of τ_A^{-1} and τ_B^{-1} versus [Tu] and $[Tu]^{-1}$ for Co(Tu)$_2$Cl$_2$

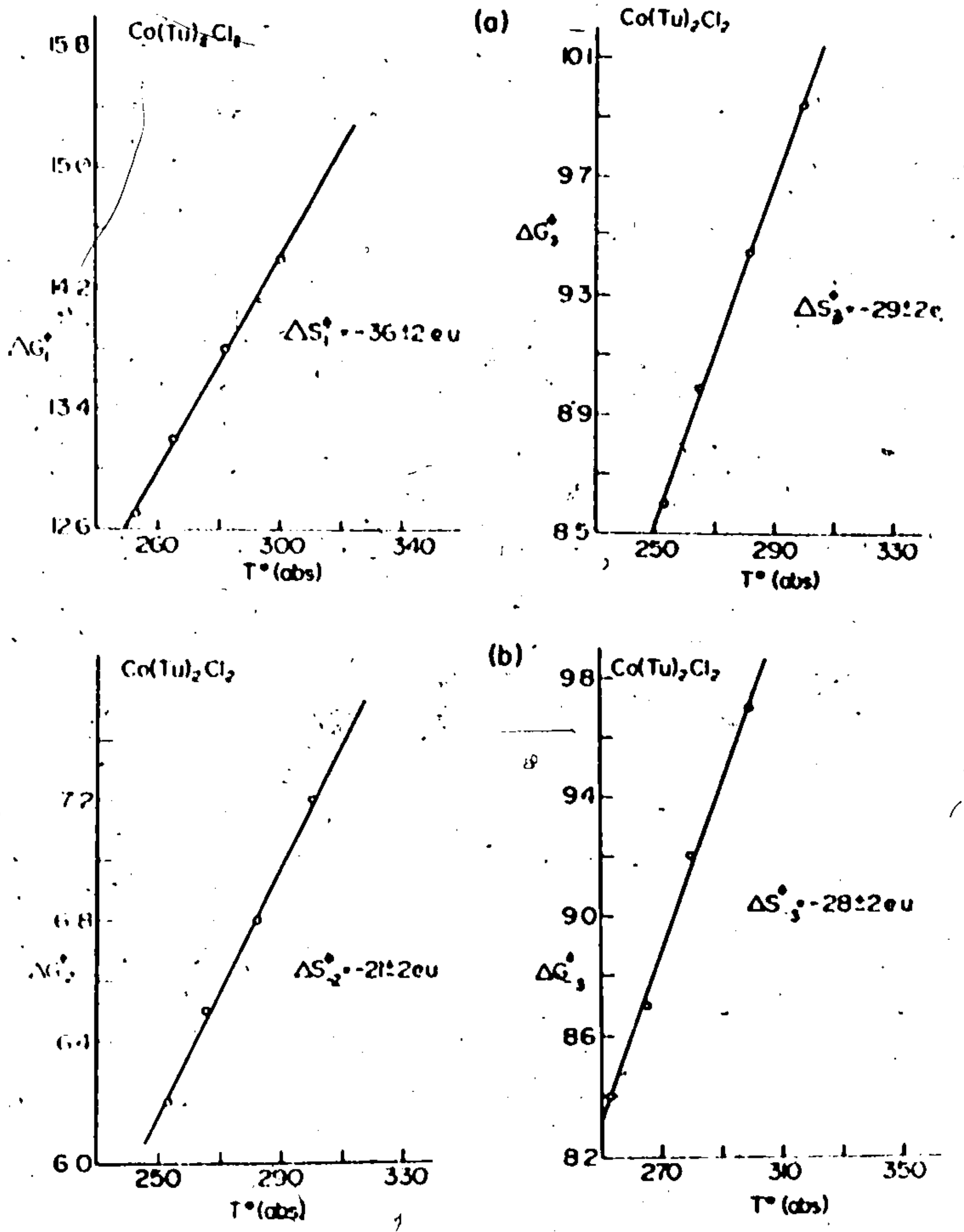


Figure (4-9): Plots of $\Delta G^{\ddagger}$'s versus T (Absolute) ...[$Co(Tu)_2Cl_2$]

(4-6d) DISCUSSION OF KINETIC DATA

The data of Table (4-7) shows a number of interesting factors. We note first that two term expressions for the rate of substitution of square-planar complexes of platinum are quite common. One mechanism involves substitution by a solvent molecule followed by replacement of the solvent by incoming ligand and the second term is a simple bimolecular ligand exchange. This situation has not been previously reported for tetrahedral Co(II) complexes. The first order term reported for Co(II) hexamethylphosphoramides was considered to represent a dissociative mechanism. We consider that the "first order" term observed in the present work almost certainly involves prior solvent substitution and this conclusion is strongly supported by the large negative entropy of activation for the process. A dissociative process should lead to a positive entropy of activation and this is indeed found to be the case for octahedral Ni(II) thiourea complexes. The rate constants for this process have accordingly been reported as second order constants to allow direct comparison with the other rate processes. The three different reactions for which data are available are:

(a) $Co(Tu)_2X_2 + S \longrightarrow Co(Tu)_2SX_2$ $k_1 \sim 10^2$ $mole^{-1} sec.^{-1}$

(b) $Co(Tu)_2X_2 + Tu \longrightarrow Co(Tu)_3X_2$ $k_3 \sim 10^5$ $mole^{-1} sec.^{-1}$

(c) $Co(Tu)SX_2 + Tu \longrightarrow Co(Tu)_2SX_2$ $k_{-2} \sim 10^7$ $mole^{-1} sec.^{-1}$

The three reactions have very different rate constants. These rates

Table (4-7): Kinetic and Activation Parameters for Ligand Exchange in CoL_2X_2(27°C)

Compound	k_1 mol^{-1} sec^{-1}	$\Delta H_1^{\ddagger}$ K.cal. mol^{-1}	$\Delta S_1^{\ddagger}$ e.u.	k_3 mol^{-1} sec^{-1}	$\Delta H_3^{\ddagger}$ K.cal. mol^{-1}	$\Delta S_3^{\ddagger}$ e.u.	k_{-2} mol^{-1} sec^{-1}	$\Delta H_{-2}^{\ddagger}$ K.cal. mol^{-1}	$\Delta S_{-2}^{\ddagger}$ e.u.	k_3 $mol^{-1} sec^{-1}$
$Co(Tu)_2Cl_2$	$1.8x10^2$	3.6±0.6	-36±2	$3.5x10^5$	1.3±0.6	-29±2	$3.4x10^7$	0.9±0.6	-21±2	$5.6x10^5$
$Co(Tu)_2Br_2$	$1.3x10^2$	3.5±0.6	-37±2	$2.6x10^5$	2.9±0.6	-24±2	$2.3x10^7$	0.6±0.6	-23±2	$6.5x10^5$
$Co(Tu)_2I_2$	$1.1x10^2$	3.4±0.6	-38±2	$1.6x10^5$	3.2±0.6	-24±2	$4.4x10^6$	-0.2±0.6	-29±2	$3.4x10^5$
$Co(Mtu)_2Cl_2$	$1.5x10^2$	4.4±0.9	-34±3	$2.9x10^5$	2.3±0.9	-26±3	$2.5x10^7$	0.5±0.6	-23±2	$6.8x10^5$
$Co(Mtu)_2Br_2$	$1.2x10^2$	4.1±0.9	-35±3	$2.3x10^5$	3.1±0.6	-25±2	$2.4x10^7$	0.2±0.6	-26±2	$3.7x10^5$
$Co(Mtu)_2I_2$	$3.7x10^1$	4.0±0.6	-38±2	$6.1x10^4$	3.8±0.6	-23±2	$2.2x10^7$	0.00±0.6	-25±2	$1.3x10^5$
$Co(Dmtu)_2Br_2$	$4.3x10^1$	3.6±0.6	-39±2	$8.9x10^4$	3.5±0.4	-24±2	$1.9x10^7$	1.7±0.4	-20±2	[illegible]
$Co(Dmtu)_2I_2$	$2.5x10^1$	3.8±0.6	-40±2	$8.5x10^4$	4.8±0.6	-20±2	$1.7x10^7$	0.7±0.4	-24±2	$1.0x10^4$

e.u.= $Cal.K^{-1}.mol^{-1}$.

may be compared with the second order rate constants for square-planar platinum complexes (10^{0} - 10^{-4}mole^{-1}sec.$^{-1}$)and those for Co(II) hexamethylphosphoramide complexes ($\sim 10^{2}$) and Co(II) phosphines ($\sim 10^{3}$). Since the previous tetrahedral cobalt data refers to analogues of reaction (b), it is apparent that the thiouea complexes are the most labile yet studied. We note at this point that the two sets of values for k_3 agree well in order of magnitude and in relative values for different compounds. There is a disagreement of approximately a factor of 2 in absolute magnitude which in all probability reflects systematic errors in the equilibrium constants and line widths used in the calculations.

We turn now to a consideration of the activation parameters. The entropies of activation all fall in the range -20 to -40 cal °K^{-1} mole^{-1} which is very similar to the values found for associative exchange for Pt(II), Pd(II), Ni(II), and Co(II) complexes reported in the literature. The greater lability of the present compounds is due very largely to lower enthalpies of activation. We also note that for all series of compounds of Co(II) and Ni(II) of stoichiometry ML_2X_2, the exchange rates fall in the order Cl > Br > I. This order has been found for all the CoL_2X_2 series thus far examined. The rationalization originally suggested for the phosphine complexes[138] was that stronger π bonding resulting from dπ to dπ electron donation to the phosphine was to be expected because I^- was a better π donor than Cl^-. This would lead to greater difficulty in breaking the phosphorus-cobalt bond. Pignolet and Horrocks[87] questioned this interpretation since they found the rates depended more on $\Delta S^{\ddagger}$ than $\Delta H^{\ddagger}$. In the present compound, the $\Delta H^{\ddagger}$ values do indeed increase in the right order but since the rate determining step is formation of the five-coordinated complex rather than loss of ligand, this earlier interpretation does not appear to be correct. Again in agreement with the phosphine results, substitution on the exchanging ligand has relatively little effect on the rates. Exchange is somewhat slower for the methyl substituted thioureas and this is mainly due to larger enthalpies of activation.

Perhaps the most interesting comparison is between the activation parameters for the three reactions (a), (b) and (c). The average enthalpies of activation for the eight examples of each reaction are 3.8 kcal mole^{-1}, 3.1 kcal mole^{-1}, and 0.5 kcal mole^{-1} for (a), (b) and (c) respectively. The corresponding average entropies of activation are -32 cal °K^{-1} mole^{-1}, -24 cal °K^{-1} mole^{-1} and -23 cal °K^{-1} mole^{-1}. Reaction of acetone with $Co(Tu)_2X_2$ is slower than reaction of thiourea with $Co(Tu)_2X_2$ largely because of the less favourable entropy of activation. On the other hand, reaction of thiourea with $Co(Tu)_2X_2$ is slower than reaction of thiourea with $Co(Tu)SX_2$ almost entirely because of the very low (practically zero) enthalpy of activation in the latter case. Thus it seems that the enthalpy of activation is predominantly determined by the nature of the metal complex but the entropy is determined by the nature of the incoming ligand.

Finally, it is interesting that the values of ΔH (from Table (4-5)) are quite similar to those $\Delta H^{\ddagger}$ for the same reactants. The values of ΔS on the other hand are quite small and may be either positive or negative whereas the $\Delta S^{\ddagger}$'s are all large and negative. Thus almost the entire activation barrier arises from the entropy term (i.e. the enthalpy of the transition state is virtually the same as that of the product). This observation is of course consistent with the very small $\Delta H^{\ddagger}$'s observed for the reverse reaction (c).

CHAPTER V

STRUCTURE AND LIGAND EXCHANGE OF NICKEL COMPLEXES

(5-1) INTRODUCTION

Recent studies[139-143] have led to the preparation and characterization of a considerable number of complexes of Ni(II) with thiourea and substituted thioureas. Most of the complexes of Ni(II) with thiourea so far reported involve six coordinated Ni(II). These complexes are of the type $Ni(Tu)_6X_2(X=ClO_4,NO_3,Br,I)$, $Ni(Tu)_4Cl_2$ and $(Ni(Tu)_2(NCS)_2)_n$. In the case of substituted thiourea complexes, a variety of solid-state structures with octahedral, square planar and tetrahedral geometries have been reported.[140] It appears that the energy separation of the different structural forms is often quite small and that stereochemical changes can be brought about by slight changes in the nature of ligands. It has also been reported that the Ni(II) ion attains different stereochemical arrangements depending on the nature of the anion and the preparative conditions.[144] In the present study, Ni(II) complexes of several thioureas with halide, perchlorate, tetrafluoroborate and nitrate anions have been examined in solution. NMR has been used as the principal experimental tool. These complexes, like the corresponding systems of Co(II) exhibit rapid ligand exchange in solution. The situation is ~~more~~ complicated for the nickel compounds, although in that, complexes of different geometries may co-exist in solution. As a result, the observed NMR shifts may involve the averaging of different metal complex environments as well as the free ligand. First we shall make use of these shifts to extract the structural information on these systems participating in structural and spin equilibria. Second we shall investigate the ligand dissociation and finally, the kinetics of ligand exchange processes in solution.

(5-2) PREVIOUS STUDIES OF NICKEL THIOUREA COMPLEXES

Nardelli and co-workers[142,143] showed that $Ni(Tu)_4Cl_2$ is octahedral with trans chlorine atoms in the inner sphere. Oliff[145] studied the infrared spectra of $Ni(Tu)_6X_2$($X=ClO_4, NO_3, Br$), $Ni(Tu)_4X_2$($X=Cl, Br$) and $Ni(Tu)_2(NCS)_2$. He reported that bands in the 3200-3500 cm^{-1} region are associated with N-H bonds in these complexes. They do not seem to be shifted significantly on coordination. By analogy with urea complexes, where both N- and O-coordination are found, this region of the spectrum can be used to determine the donor atoms in a given complex . Coordination by oxygen introduces little change in the spectrum with respect to that of free urea, but N-coordination causes a splitting of these bands and a decrease in their intensity. The latter does not appear to happen for thiourea complexes, so that bonding through sulphur can be inferred in all cases.

The sharpening of these bands noticed by Yamaguchi et al.[146] for $Ni(Tu)_2(NCS)_2$ appears to be restricted to that compound. The broadening of these bands in pure thiourea is attributed to a considerable amount of hydrogen bonding,[142,145] which is absent in $Ni(Tu)_2(CNS)_2$. The generally broad nature of these bands for the hexa- and tetra-thiourea, nickel (II) complexes is very similar to that observed in free thiourea, so that considerable hydrogen bonding must also be present in these compounds. It is not clear whether intramolecular or intermolecular interactions are involved. Piovesana and Furlani[132] have claimed to have demonstrated intramolecular hydrogen bonding in $Co(Tu)_2Cl_2$ and there could be similar possibilities in the nickel complexes[##]. The structure of $Ni(Tu)_2(NCS)_2$, with its planar $Ni(Tu)_2$ unit allows very little scope for such hydrogen bonding.

The B_1 N-C-N stretching mode, found at 1476 cm^{-1}, in free thiourea, should be sensitive to coordination through sulphur, because of the increased double-bond character of the C-N bond. This is clearly seen in the series: free thiourea, 1476 cm^{-1}; mono-coordinate thiourea, $Ni(Tu)_6(NO_3)_2$, 1488 cm^{-1}; $Ni(Tu)_4Cl_2$, 1500 cm^{-1}; bridging thiourea, $Ni(Tu)_2(NCS)_2$, 1518 cm^{-1}.

Three A_1 modes (C-S stretching, C-N stretching and NH_2 rocking) give rise to absorption in free thiourea at 1416, 1090 and 733 cm^{-1}. Coordination will lead to a decrease in the C-S stretching frequency, and an increase in the C-N stretching frequency. The experimental frequencies result from "hybrids" of these three modes, and the effect of coordination on the frequency depend on their relative weightings in each "hybrid". Therefore, the bands at about 1100 cm^{-1} show an increase on coordination ($1090 \rightarrow 1100 \rightarrow 1115$ cm^{-1}), indicating that the C-N stretching mode contributed more than the C-S stretching mode. In the 700 cm^{-1} region, the reverse is the case ($733 \rightarrow 718 \rightarrow 702$ cm^{-1}). The 1400 cm^{-1} band was also lowered on coordination.

The bands at 1350 and 832 cm^{-1} for $Ni(Tu)_6(NO_3)_2$ were associated with the nitrate group. As they were not shifted from the positions for

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[##] Infrared study shows the evidence of intramolecular hydrogen bonding but it is still doubtful in the X-ray studies.

normal ionic nitrates[147] this group was not coordinated to the metal. This conclusion had also been reached by Cotton et al.[122]

Coordination of thiourea to nickel caused shifts of certain infrared absorption frequencies, notably at about 1400, 1100, and 700 cm^{-1}, which could be correlated with changes in double-bond character of the C-S and C-N bounds. Such changes imply increased importance of charged resonance-contributions of the type $\overset{+}{N}H_2{=}C(S^-)\text{-}NH_2$, and hence an effective movement of electron density towards the sulphur-nickel bonds.

Magnetic moments, infrared, and electronic spectra indicate that in solid, all complexes of type $Ni(Tu)_4Cl_2$,$Ni(Tu)_6X_2$(X=Br,I) and $Ni(L)_6X_2$ (L=Tu,Dmtu,Detu and X=ClO_4,BF_4, and NO_3) are octahedral and the type $Ni(Dptu)_2X_2$(X=Br,I) in tetrahedral geometry. These results reported are sensitive to the medium in which they are examined due to solute-solvent interactions. Therefore, previous studies were carried in solid and the spectra of solid compounds were taken as the true electronic spectra of the complexes.

Octahedral Ni(II) complexes are magnetically isotropic having an orbital singlet ground term, and the isotropic shifts shown by such compounds arise from contact interactions. Tetrahedral Ni(II) complexes have orbitally degenerate ground terms, and hence it is to be expected that there will be a dipolar contribution to their shifts. This orbital degeneracy is removed in complexes of less than tetrahedral geometry (as in the Ni(II) complexes) and this usually results in predominantly contact interactions. The theory of this case has been discussed in the literature.[149]

The magnetic features of Ni(II) complexes have been studied extensively.[149] It has been shown that with a few exceptions, all octahedral Ni(II) complexes with two unpaired electrons exhibit moments ranging from 2.9 to 3.4 BM depending on the magnitude of the orbital contribution. By elongating one of the axes of an octahedral complex, the limiting structure of the complex will be a square-planar configuration. Simple considerations suggest that this structure automatically would produce a diamagnetic Ni(II) complex. However, Ballhausen[150] had shown that a very weak square-planar crystal field will still produce a paramagnetic complex depending on whether the energy of separation of the uppermost d orbitals containing two unpaired electrons is greater or less than the energy necessary to cause electron pairing. This separation is determined by the nature of the two ligands and by the degree to which surrounding molecules - either solvent or other in a crystal lattice. Magnetic measurements indicate a lowering of the moment ($0 < \mu < 2.7$ BM) under such a situation. The last structure of Ni(II) which deserves consideration is the tetrahedral configuration. All Ni(II) complexes with tetrahedral configuration possess magnetic moments varying from 3.3 to 3.8 BM depending on the orbital contribution. A regular tetrahedral complex with four ligands should have a moment between 3.5 to 4.2 BM and would have an orbitally degenerate ground state. Any deviation from a perfect symmetry may cause a lowering of the magnetic moment. For over a decade, [illegible] NMR technique has been successfully applied[149] for structural equilibria involving species of different geometries and therefore we shall be adopting it to investigate the solution chemistry of some thiourea complexes of Ni(II) in the following sections.

(5-3) EXPERIMENTAL SECTION

The following compounds were synthesized by the literature methods. A mixture of stoichiometric amountsof thiourea or alkyl-thiourea and the appropriate Ni(II) salt in n-butanol was concentrated on a water bath until the presence of a solid was noticeable. The light green products were separated upon cooling. The solid was then collected on a filter, washed with ether and dried under vacuum. All compounds were recrystallized from the solvent used in the preparation.[122,140,141,144,145]

$Ni(Tu)_4Cl_2$
$Ni(Tu)_6Br_2$
$Ni(Tu)_6I_2$
$Ni(Nptu)_2Br_2$
$Ni(Nptu)_2I_2$
$Ni(Tu)_6(ClO_4)_2$
$Ni(Dmtu)_6(ClO_4)_2$
$Ni(Detu)_6(ClO_4)_2$
$Ni(Etu)_6(ClO_4)_2$
$Ni(Tu)_6(BF_4)_2$
$Ni(Detu)_6(BF_4)_2$
$Ni(Tu)_6(NO_3)_2$
$Ni(Dmtu)_6(NO_3)_2$
$Ni(Detu)_6(NO_3)_2$

Starting materials were purchased from the companies listed in the chapter IV, section (4-3). Products were characterized by their melting point and visible spectra, all of which agree well with data in the literature. All compounds were dried over P_4O_{10} under vacuo before using. NMR spectra were obtained with a Varian DP-60 spectrometer operating at 56.4 MHz and equipped with a variable temperature probe. Acetone-d_6 was used as purchased. TMS was used as an internal reference throughout.

Magnetic measurements were made in dried acetone-h_6 following the literature methods.[151] The solvent was placed in a capillary tube which was placed coaxially inside a normal NMR tube containing a dilute complex solution of known concentration. The tubes were spun as is usual during NMR measurements. Under these circumstances for a dilute solution, the susceptibility of the paramagnetic solute is

$$X = \frac{3}{2\pi m} \cdot \frac{\Delta f}{f} + X_0$$

where f is the frequency of the proton resonance, Δf is the frequency difference (Hz) between solvent and solution lines, m, the mass of solute and X_0 is the solvent susceptibility. Diamagnetic corrections were made following the standard texts,[151,152] and effective magnetic moments (spin-only) calculated by the equation

$$\mu_{eff.} = 2.828\ (X_c.T)^{1/2}$$

where X_c is the corrected molar susceptibility and T the absolute temperature. The acetone resonance does not shift relative to TMS on the addition of Ni(II) thiourea complexes and may therefore, be safely used for susceptibility determinations.

Conductivity measurements at 25°C and -78°C were made in a glass cell with electrodes which gave a cell constant of approximately 29 cm^{-1}. The conductivity cell was immersed in an oil thermostat maintained at 25°C or in dry ice-acetone mixture maintained at -78°C. The solvent used was dried acetone and the conductance of solutions were measured with a Wayne-Kerr Universal Bridge operating at 1000 cps. A detailed procedure is described in the Ph.D. Thesis "The Fluoro-Sulfuric Acid Solvent System" submitted by John B. Milne.[153]

(5-4) GEOMETRIES OF THIOUREA AND SUBSTITUTED THIOUREA COMPLEXES OF Ni(II) SALTS IN SOLUTION

Nickel (II) forms many complexes with octahedral, square planar, and tetrahedral geometries and a smaller number of five-coordinated compounds[154] with other stereochemical arrangements. It is generally considered that a combination of steric and electronic factors determines which of the three common geometries is assumed by a given compound. Steric factors clearly operate in the sense that bulky ligands are most favourable to tetrahedral geometry and least favourable to octahedral geometry. The mode of operation of electronic effects is much less clear in spite of extensive discussion of the subject.[155] The present studies of thiourea complexes have thrown some light on this question.

(5-4a) GEOMETRY OF COMPLEXES OF Ni(II) HALIDES

Complexes of a variety of thiourea ligands associated with Ni(II) halides have been examined. All these compounds are paramagnetic. The ^{1}H NMR spectra of the ligands have been discussed in Chapter III. Evidence from infrared data indicates that coordinated ligands are bonded through the sulphur atom. In the solid, $Ni(Tu)_4Cl_2$ and $Ni(Tu)_6X_2$ (X=Br,I) are thought to have an octahedral geometry, while $Ni(Nptu)_2X_2$ (X=Br,I) has a tetrahedral geometry. Solutions of $Ni(Tu)_4Cl_2$ in acetone are non-conducting at all temperatures. This indicates dissociation of thiourea and retention of chloride ion. The magnetic moment of a solution of $Ni(Tu)_4Cl_2$ has been determined by an NMR method.[151] It is found that the moment varies from 3.5 (+ 27°) to 3.8 BM (-90°) indicating a tetrahedral complex $Ni(Tu)_2Cl_2$ in solution. The ^{1}H NMR spectra of this complex in acetone-d_6 show two sets of resonances attributed to "inside" and "outside" protons of coordinated thiourea. Both resonances appear to low field of TMS. The extreme low field line is assigned to "inside" protons while the other line close to the diamagnetic free ligand signal is assigned to "outside" protons following the arguments put forward in Chapter IV. Both are temperature-dependent. Figure (5-4a-1) shows some representative spectra of $Ni(Tu)_4Cl_2$. The shifts are much larger than those of the diamagnetic Zn(II) complexes. All these shifts could arise from the isotropic contact interaction. A plot of the shifts versus the reciprocal of the absolute temperature yields a straight line indicating the presence of a single species at all temperatures which must be tetrahedral. The ^{1}H NMR spectrum of this compound in acetone-d_6 shows averaged complex and ligand resonances at + 27°, but at -90°, the chemical shift of the extreme low field line is too large to permit averaging with the ligand resonance. The second peak, which has a smaller chemical shift remains as an averaged resonance (see Fig. 5-4a-1). There is no change in colour of the solution on cooling it from room temperature to -90°. The solubility of $Ni(Tu)_4Cl_2$ is extremely low in acetone and a saturated solution of indefinite concentration has to be used in all the experiments. A study of ligand exchange with the excess of free thiourea is impractical since insoluble $Ni(Tu)_4Cl_2$ is precipitated upon addition of free ligand solution. Thus the situation for this complex is relatively simple and all the data are consistent with the presence of only tetrahedral $Ni(Tu)_2Cl_2$.

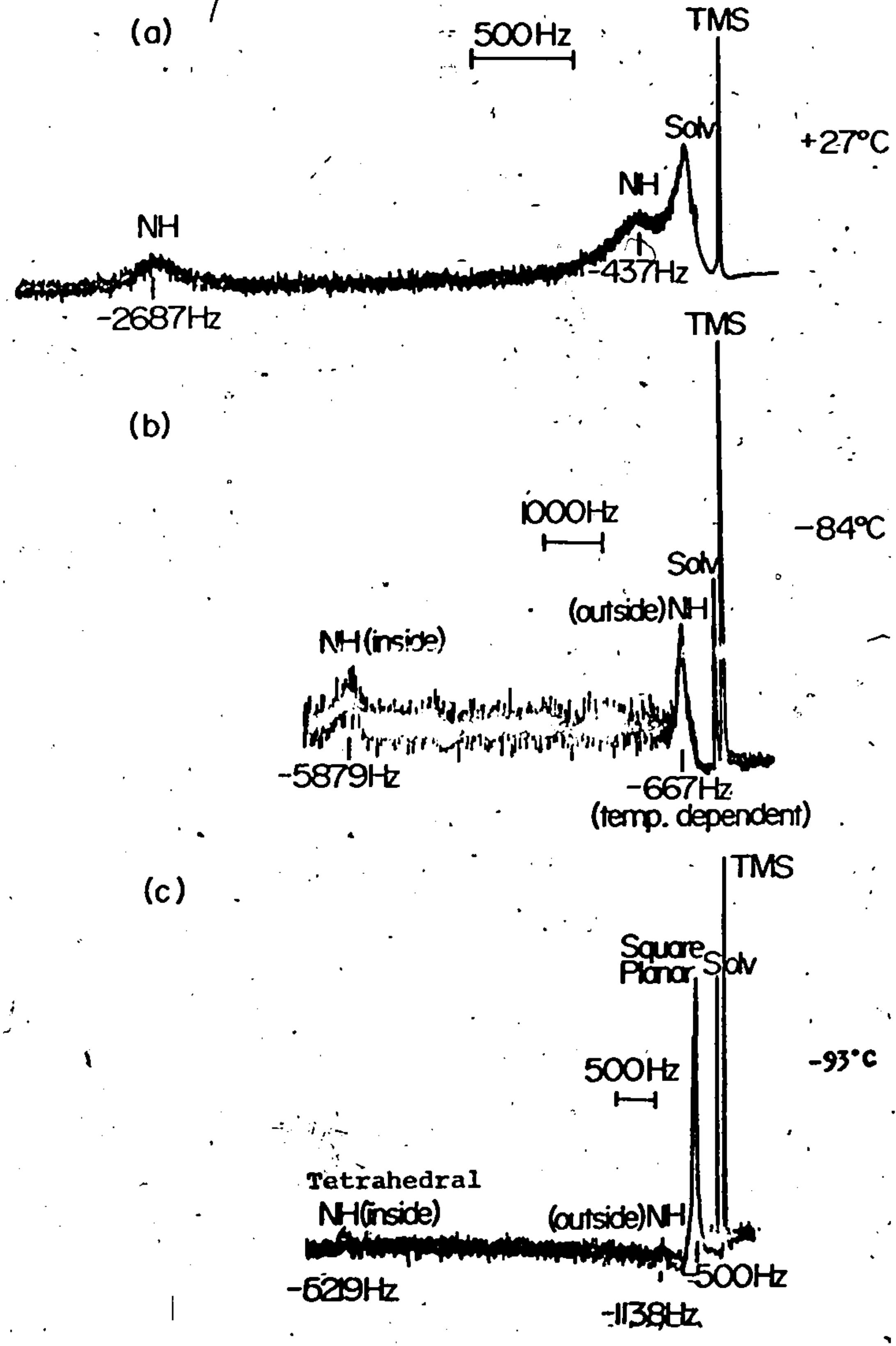


Figure (5-4a-1): ^{1}H NMR Spectra of Ni(Tu)$_2$Cl$_2$ at various Temps [a= +27°, b=-84°], ^{1}H NMR Spectrum of Ni(Tu)$_2$Br$_2$ and Ni(Tu)$_3$Br$^+$ [c]

$Ni(Tu)_6Br_2$ is fairly soluble in acetone. It has a moment varying from 3.6 BM at +27° to 1.2 at -94°. Solutions of $Ni(Tu)_6Br_2$ have a small conductivity at room temperature which increases at low temperature. At room temperature, the NMR spectrum is very similar to that of the chloride. However, the ^1H NMR spectrum at -93° has four resonances [Fig. 5-4a-1]. Two show contact shifts (-6219 ± 20 Hz and -1138 ± 20 Hz) respectively attributable to "inside" and "outside" protons of paramagnetic complex. The third resonance is a doublet consisting of two lines of equal intensity at -500 ± 20 Hz assignable to a diamagnetic complex. All shifts were measured from TMS at 56.4 MHz. The diamagnetic complex must be ionic since its formation is accompanied by an increase in conductivity. On adding free ligand the ^1H NMR spectra show averaging of "inside" and "outside" hydrogens of thiourea at room temperature. This observation indicates that ligand exchange is extremely fast since rotation about the C-N bond only occurs in the free ligand. However, slow exchange occurs at -90°. Addition of free ligand to a solution at -90°C leads to the appearance of a new NH resonance at the correct frequency for free ligand. The lines assigned to the diamagnetic complex remain sharp and distinct for the free ligand peaks. These two species are therefore not in fast exchange. The paramagnetic peaks at ~ - 6000 Hz and -1100 Hz which are relatively weak are further broadened. Fast exchange with this compound therefore occurs but since free ligand is present in large excess, the exchange has relatively little effect on the free ligand line width.

At room temperature, the solution is only very slightly conducting. The magnetic moment is 3.6 BM and the NMR spectrum is similar to that of the chloride. Therefore, we deduce that tetrahedral $Ni(Tu)_2Br_2$ is the principal species. At low temperatures, a diamagnetic species appears. The concentration of this species is decreased by adding Me_4NBr indicating that the formation involves ionization of Br^- as is also indicated by the increased conductivity. This diamagnetic complex could therefore be either $Ni(Tu)_3Br^+$ or $Ni(Tu)_4^{+2}$. But we shall show below from studies of $Ni(Tu)_6(ClO_4)_2$ that in the presence of excess Tu, $Ni(Tu)_4^{+2}$ is completely converted to octahedral $Ni(Tu)_6^{+2}$ at -90°C. The present diamagnetic species must therefore be $Ni(Tu)_3Br^+$. There remains the question of assigning the lines observed at -6219 Hz and -1138 Hz at -90°C. These are quite similar to those of $Ni(Tu)_2Cl_2$ at this temperature and can therefore be reasonably assigned to a small amount of tetrahedral $Ni(Tu)_2Br_2$.

$Ni(Tu)_6I_2$ has a moment of 3.15 BM at 27° which falls to 0.8 BM at -75° and rises again to 1.36 BM at -94°. Its conductivity increases at lower temperature and is greater than that of the bromide at all temperatures. The contact shift shown by the "inside" proton appears at -1641 Hz from TMS at room temperature. On cooling the complex solution to -5°, the resonances disappear. On further cooling, they reappear again but slowly moving towards the diamagnetic free ligand position. This reflects an increase in the concentration of a square-planar species as the temperature of the solution is decreased. At -90°, a change in colour (brown to blue) is observed. A plot of contact shifts versus the reciprocal of absolute temperature gives a non-linear curve (Fig. 5-4a-4). This is also true in $Ni(Tu)_6Br_2$ and indicates the presence of $Ni(Tu)_3X^+$ at low temperatures. Figure (5-4a-2) shows the effect of temperature on the position of "inside" NH proton of the iodide compound. A summary of results are shown in Table (5-4a). These results

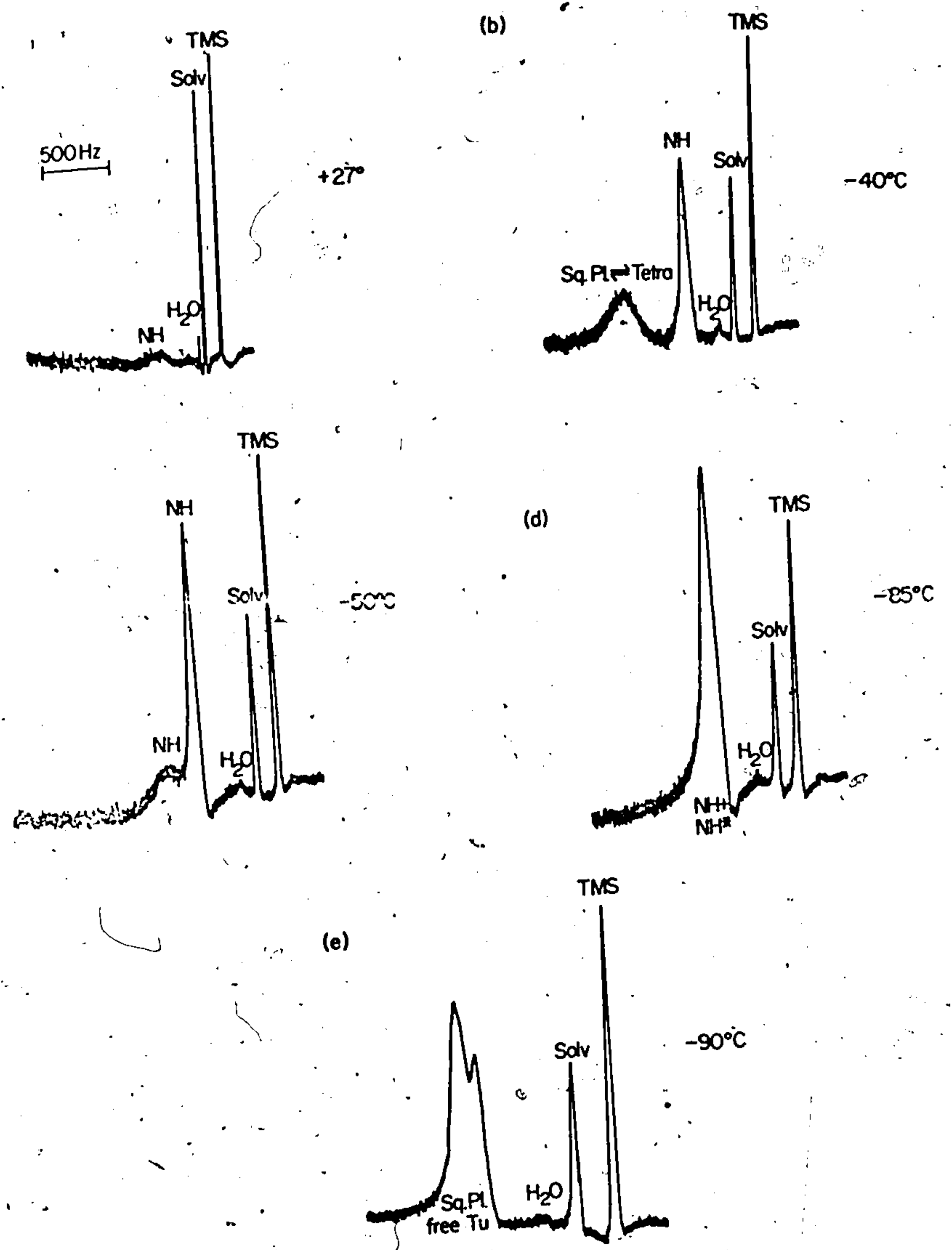


Figure (5-4a-2): ^{1}H NMR spectra of Ni$(Tu)_6I_2$ at various temperatures.

Table(5-4a) :Contact Shift and Magnetic Data for Complexes of Ni(II) Halides

Compound	Contact shifts of			Moment		Triplet ⇌ Singlet	
	Temp	"Inside" NH	"Outside" NH	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Tu)_4Cl_2$	27°	-2307	-57	37°	3.5		
	-20	-3020	-95	-14°	3.6		
	-35°	-3651	-75	-25°	3.6		
	-50°	-4214	-180	-37°	3.6		
	-65°	-5057	-245	-45°	3.7	-	-
	-75°	-5308	-245	-50°	3.7		
	-84°	-5499	-287	-61°	3.7		
	-92°	-5529	-286	-75°	3.9		
				-79°	3.9		
				-94°	3.8		

all shifts measured from free ligand

ΔH expressed in kcals $mole^{-1}$ and ΔS in cal $°K^{-1}$ $mole^{-1}$

Table (5-4a)

Compound	Contact shifts of			Moment		Triplet ⇌ Singlet	
	Temp	"inside" NH	"outside" NH	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Nptu)_2Br_2$	27°	-3911	-628	37°	3.1	+2.4±0.4	+13±2
	-10°	-624 -4341	-628	-12°	3.3		
	-20°	-668 -4498	?	-25°	3.3		
	-30°	-1061 -4522	-601	-34°	3.3		
	-40°	-1155 -4614	-666	-44°	3.4		
	-50°	-1259 -4854	-667	-57°	3.3		
	-70°	-1357 -5695	-695	-60°	3.2		
				-68°	3.0		
				-86°	2.7		
				-93°	2.5		

Compound	Contact shifts of			Moment		Triplet ⇌ Singlet	
	Temp	"Inside" NH	"Outside" NH	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Nptu)_2I_2$	27°	-3141	-600	37°	2.8	+2.5±0.4	+12±2
	0°	-1214 -3947	-561	-11°	3.1		
	-20°	-1169 -4014	601	-29°	3.1		
	-30°	-1013 -4349	-614	-37°	3.1		
	-40°	-1013 -4960	-764	-52°	2.9		
				-60°	2.8		
				-73°	2.5		
				-79°	2.4		
				-84°	2.4		
				-94°	2.39		

Table (5-4a)

Compound	Contact Shifts of			Moment		Triplet ⇌ Singlet.	
	Temp	"Inside" NH	"Outside" NH	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Tu)_6Br_2$	27°	-1557	-192	36°	3.6		
	-22°	-2020	-170	-15°	3.7		
	-35°	-?	-178	-36°	3.7		
	-50°	-?	-184	-46°	3.5	+5.0±0.4	+25±2
	-62°	-5239	-144	-56°	3.4		
	-75°	-5320 -470	-120	-63°	3.1		
	-84°	-5669 -644	-120	-77°	2.4		
	-93°	-5839 -758	-145 -120	-80°	2.4		
				-87°	2.0		
				-95°	1.2		

Compound	Contact Shifts of			Moment		Triplet ⇌ Singlet	
	Temp	"Inside" NH	"Outside" NH	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Tu)_6I_2$	27°	-1261	-95	31°	3.5		
	- 5°	-1307	-95	-14°	3.0		
	-25°	-977	-110	-39°	2.5		
	-40°	-509	-98	-42°	2.3		
	-50°	-438	-95	-55°	1.6	+5.9±0.4	+24±2
	-65°	-242	-89	-64°	0.9		
	-85°	-120	-80	-77°	0.8		
	-90°	-114	-51	-80°	0.6		
				-87°	1.1		
				-94°	1.4		

indicate that at room temperature, the solutions contain a mixture of tetrahedral $Ni(Tu)_2I_2$ and square-planar $Ni(Tu)_3I^+$. As the temperature is lowered the proportion of the square-planar compound increases as does the conductivity. An experiment adding $(CH_3)_4NI$ to the solution at -50°C decreased the diamagnetic fraction. At the very lowest temperatures, the moment again increases. We believe this indicates the formation of octahedral $Ni(Tu)_6^{+2}$. No contact shifted resonances are observed at -90°c. This is consistent with the results reported below for $Ni(Tu)_6(ClO_4)_2$.

Steric considerations are extremely important in favouring tetrahedral geometry. We have synthesized[140] $Ni(Nptu)_2X_2$, (where X=Br,I and Nptu=1-(1-naphthyl)-2-thiourea) where a large naphthyl group is present to provide such an effect. Holt and Carlin[140] proposed that these compounds have a tetrahedral geometry in solution on the basis of optical and magnetic data. We have extended their study by using NMR as an experimental tool. In acetone-d_6, both compounds show isotropic shifts attributable to "inside" and "outside" protons of thiourea. The observed shifts agree well with those found for tetrahedral $Ni(Tu)_2X_2$. There are only two NH resonances and one naphthyl group at room temperature (Fig. 5-4a-3). However, at low temperatures, three NH resonances of which two due to "inside" and one "outside" protons are observed as in the case of tetrahedral $Co(Mtu)_2X_2$ in the Chapter IV. All these signals are temperature-dependent and plots of the contact shifts versus the reciprocals of absolute temperature provide a straight line up to -80°C, indicating the presence of only a tetrahedral species. The magnetic data by NMR confirm this postulate. Both contact shift and magnetic data, however indicate the presence of a small amount of square-planar

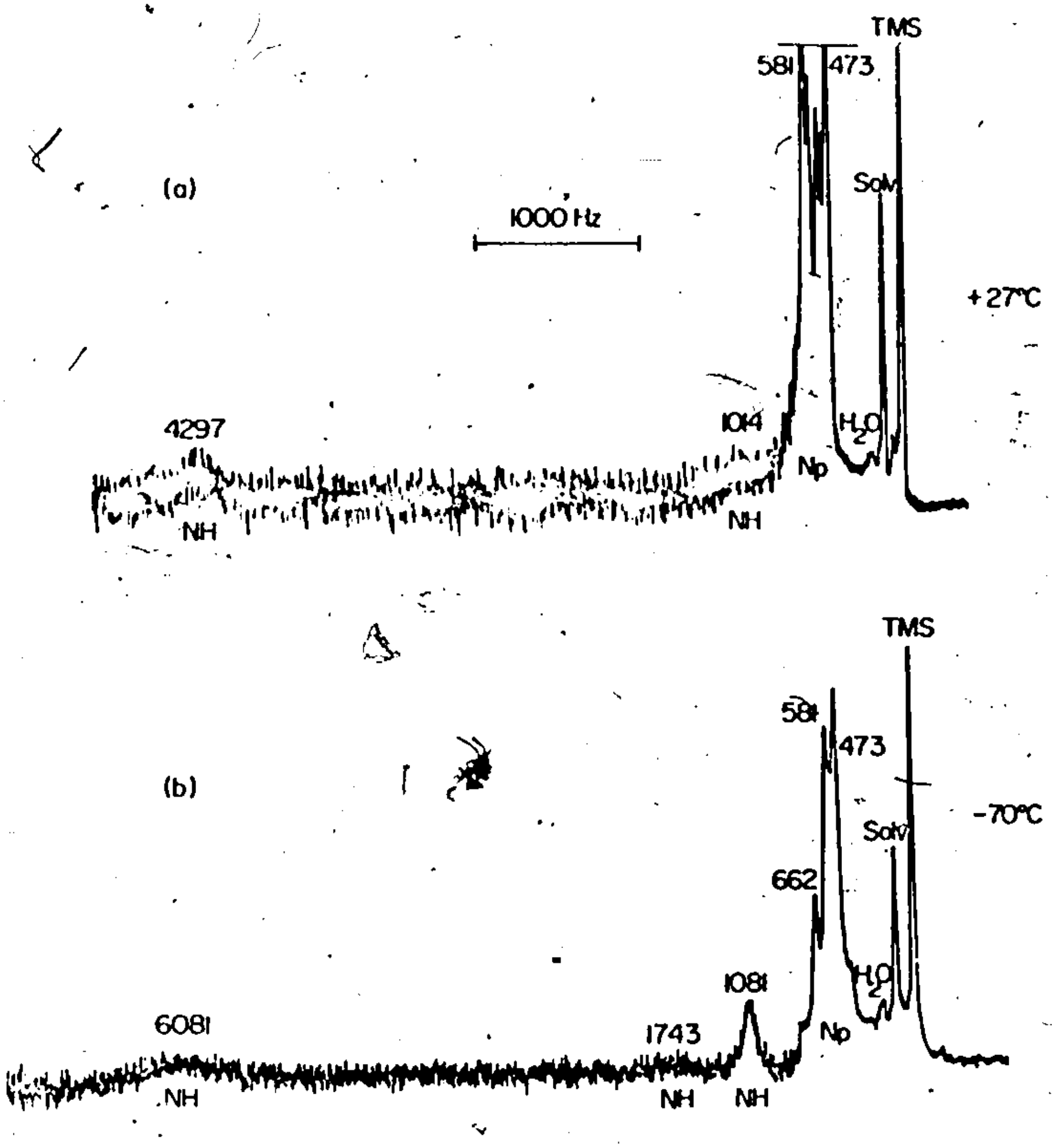
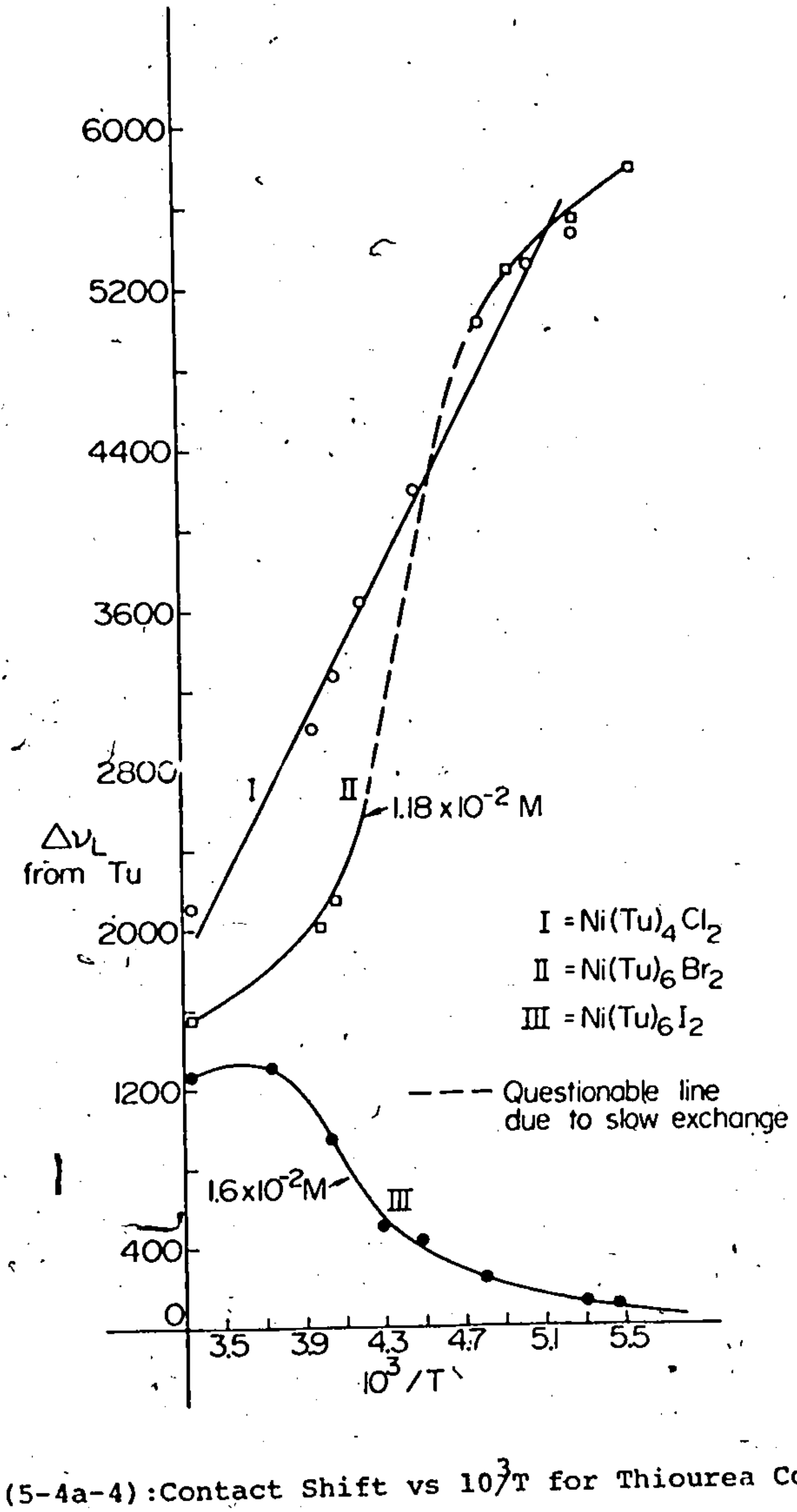


Figure (5-4a-3): ^{1}H NMR spectra of $Ni(Nptu)_2Br_2$ at various temperatures.



Figure(5-4a-4):Contact Shift vs $10^3/T$ for Thiourea Complexes of Ni(II) halides complex is greatest for the iodide. The results are shown in Table (5-4a).

In all of these cases, there is some displacement of thiourea by solvent acetone (particularly at high temperatures) which can be conveniently monitored by NMR, but this is not pertinent to determing the geometry. We have made similar investigations with $Ni(Dmtu)_4X_2$ which gives similar results to confirm the above pattern. It is also expected that other N-substituted thiourea complexes would exhibit similar behaviour.

(5-4b) GEOMETRY OF COMPLEXES OF Ni(II) PERCHLORATE AND TETRAFLUOROBORATE

Previous investigators,[140,144] have reported that complexes of type $Ni(L)_6X_2$ (where L=Tu,Dmtu,Detu,Etu and $X=ClO_4$, and L=Tu,Detu and $X=BF_4$) in acetone are 1:2 electrolytes. The electronic spectral, magnetic and infrared data indicate that they are all sulphur-bonded complexes. However, most of the data was obtained in the solid state and the structure may not be the same in solution. They all have a light green colour. Magnetic moments and electronic spectra clearly classify them as octahedral complexes in solid. Their infrared spectra show that the anions are in the ionic form.[144] They dissolve in acetone yielding deep green conducting solutions forming 1:2 electrolytes. The spectral and conductivity data have been interpreted[140,144] in terms of the following equilibria:

$$\begin{aligned} Ni(L)_6(X)_2 &\rightleftharpoons NiL_6^{+2} + 2X^- \\ NiL_6^{+2} &\rightleftharpoons NiL_4^{+2} + 2L \\ NiL_4^{+2} + yS &\rightleftharpoons NiL_xS_y^{+2} + (4-x)\,L \end{aligned} \qquad (5\text{-}4b)$$

where x + y = 6.

The species NiL_4^{+2} is a square-planar compound which absorbs at 17000-18000 cm^{-1} in the optical spectrum[156] No tetrahedral species is reported in solution. In solvents which are better ligands than acetone, they yield only solvolyzed six-coordinated species. The present work deals with the study of geometry of these compounds in solution as a function of temperature. It is of prime importance to solve this problem before proceeding to a study of ligand exchange processes which will be discussed in the last section of this chapter.

The ^{I}H NMR spectrum of $Ni(Tu)_6(ClO_4)_2$ in acetone-d_6 shows a single broad line at -880 Hz from TMS (Fig. 5-4b-a). Averaging of free and complexed ligand obviously occurs but there is also the possibility of a rapid exchange between paramagnetic octahedral $Ni(Tu)_6^{+2}$ and diamagnetic square-planar $Ni(Tu)_4^{+2}$. A value of 2.3 BM is found for the magnetic moment in acetone at room temperature which is lower than expected value for an octahedral species. This directly confirms the previous postulate of the equilibrium (5-4b) at room temperature. On cooling the solution to -30°C, the moment is found to increase. This is the opposite behaviour to that found for the halides. The ^{I}H NMR spectrum at that temperature reveals two sets of resonance at -1552 Hz and -394 Hz respectively from TMS in the low field attributable to "inside" and "outside" protons of coordinated thiourea in fast exchange (Fig. 5-4b-b). On further cooling, a intermediate exchange situation results and both lines are hardly seen down to -96°C. This indicates the formation of $Ni(Tu)_6^{+2}$ at low temperature. Similar observations are made for the corresponding tetrafluoroborate compound. Thus, from the ^{I}H NMR and magnetic data, it can be concluded that both octahedral and square-planar species are present in rapid equilibrium at high temperature and only octahedral molecules are present at low temperatures. The magnetic data provides no evidence for a tetrahedral species. We would anticipate a high moment (3.8 BM) for such a species. $Ni(Tu)_2Cl_2$ has a moment of 3.8 BM, $Ni(Tu)_4^{++}$ would have a structure closer to a perfect tetrahedron than $Ni(Tu)_2Cl_2$. Since the high moment is associated with the orbital degeneracy of a symmetric tetrahedron $Ni(Tu)_4^{++}$ should have a moment of at least 3.8 BM. This is not so in perchlorate solutions and the moment at -96°C is 3.1 BM which is a typical value for a NiL_6^{+2}.

Ligand exchange is slower and direct observation of resonances of "inside" and "outside" methyl protons is possible for $Ni(Dmtu)_6(ClO_4)_2$ at low temperature (Fig. 5-4b-d). These resonances are found at -1063 Hz and -713 Hz from TMS at -104°C. At this temperature, ligand exchange is completely frozen out and separate resonances observed for free and complexed N,N-diemthylthiourea. The moment of the resulting solution at that temperature is 3.3 BM indicating octahedral $Ni(Dmtu)_6^{+2}$. These two lines arise from the restricted rotation about the C-N bond of coordinated ligand. There is, however, only one line observable for protons bonded to nitrogen. This is assigned to the "inside" position. Normally, an "inside" proton appears at low field and an "outside" proton appears at higher field. We cannot detect the "outside" proton in this case. It could possibly be overlapped by the two methyl resonances or be too broad to be observable. The corresponding tetrafluoroborate cannot be isolated and we therefore do not report its NMR spectra. All the perchlorate and tetrafluoroborate compounds exhibit a rapid equilibrium between octahedral and square-planar species at high temperature. However, at low temperatures (i.e., below -60°C) they all form a single paramagnetic species NiL_6^{+2}. The ligand exchange in $Ni(Tu)_6^{+2}$ leads

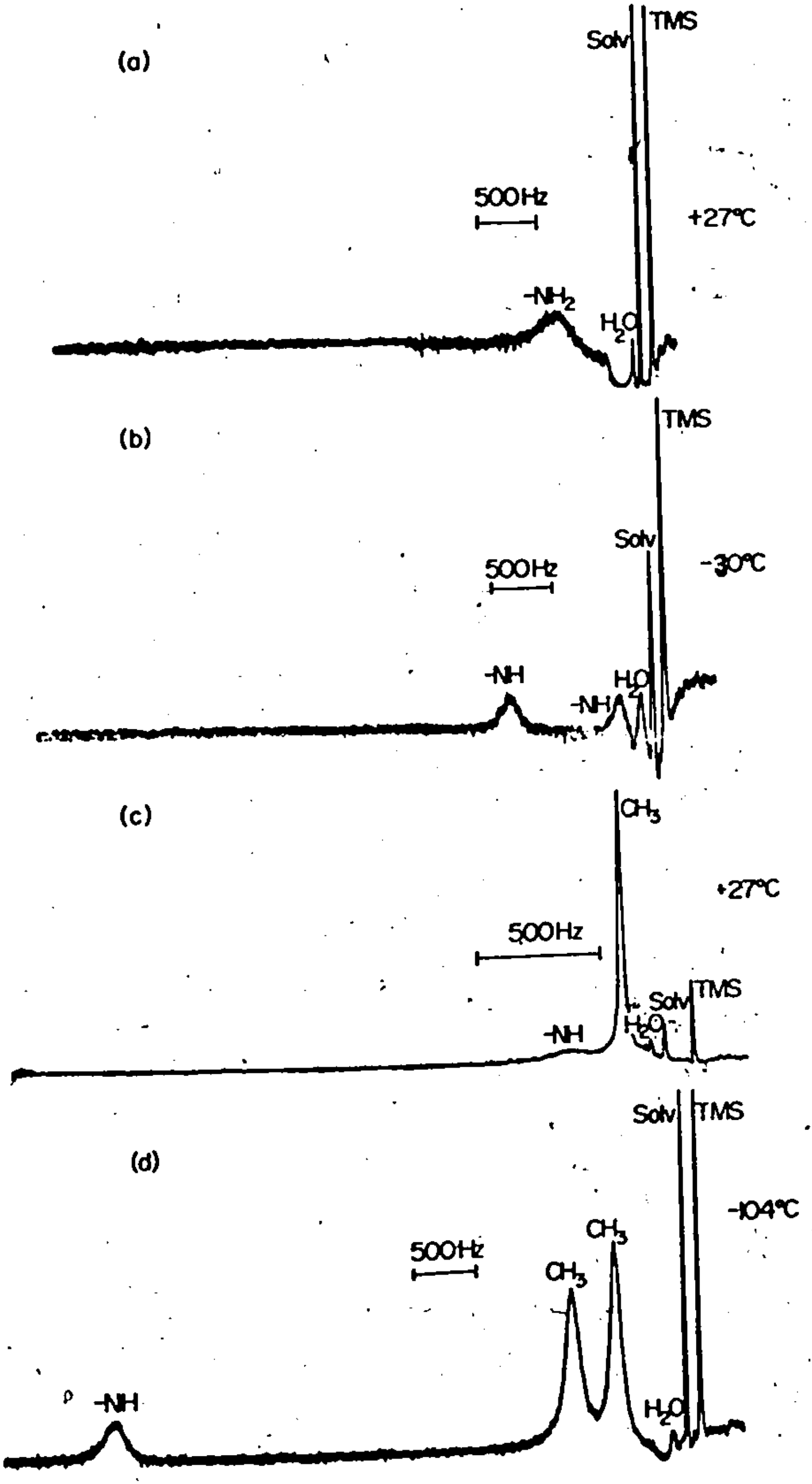


Figure (5-4b-a) and (5-4b-b): ^{1}H NMR spectra of Ni(Tu)$_6$(ClO$_4$)$_2$; Figure (5-4b-c) and (5-4b-d): ^{1}H NMR spectra of Ni(Dmtu)$_6$(ClO$_4$)$_2$ at various temperatures. (solvent: acetone-d$_6$)

to line broadening but is too fast to allow observations in the slow exchange region. However, other alkyl substituted derivatives show an exchange process which is completely frozen out. The shifts are summarized in Table (5-4b).

The shifts observed for octahedral species NiL_6^{+2} arise form isotropic contact interaction. A normal straight line is expected if the shifts are plotted versus the reciprocals of absolute temperature provided that there is a single paramagnetic species, and there is no change in geometry. Experimentally observed shifts are plotted against the receiprocals of absolute temperature and are shown in Fig. (5-4b-1). It is obvious that there is non-linearity in each plot indicating a change of geometry due to the square-planar octahedral equilibrium.

In the case of thiourea complexes of Ni(II) halide, we have considered the possibility that the diamagnetic compounds may not be four-coordinated. One might argue that they could be diamagnetic, five-coordinated $Ni(Tu)_5^{+2}$ or $Ni(Tu)_4X^+$. We consider these assignments less likely for several reasons. At room temperature, optical spectra consistent with square-planar $Ni(Tu)_4^{+2}$ have been reported in the solutions containing $Ni(Tu)_6(ClO_4)_2$.[139,140] The susceptibility and NMR data show that diamagnetic $Ni(Tu)_5^{+2}$ is not formed at low temperatures in these solutions. At -90°C the relative intensities of the "free ligand" NMR peaks of $Ni(Tu)_6Br_2$ agree better with the ratios expected for $Ni(Tu)_3X^+$ than they do for $Ni(Tu)_4X^+$. We also find that this complex exchanges ligands by an associative process. A dissociative mechanism might have been expected for a five-coordinated compound. Although not conclusive, these arguments incline us against postulating five-coordinated complexes.

Table(5-4b):Contact Shift and Magnetic Data for $Ni(L)_6(ClO_4)$

Compound	Contact Shift ([illegible])			Magnetic Moment		Thermodynamic Data	
	Temp	"Inside"	"Outside"	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Tu)_6(ClO_4)_2$	27°	-498	-66	49°	2.3		
	-17°	-1033	-60	32°	2.3		
	-31°	-1173	-14	9°	2.1		
	-46°	-1528	-15	-4°	2.1		
	-62°	-1928	-15	-11°	2.1		
	-80°	-	-	-38°	2.3	-2.6±0.6	-15±3
	-90°	-	-	-50°	2.4		
	-100°	-	-	-62°	2.7		
				-71°	2.8		
				-90°	3.1		
				-49°	3.2		

Compound	Contact Shift([illegible])				Magnetic Moment		Thermodynamic Data	
	Temp	"Inside" NH	"Inside" CH_3	"Outside" CH_3	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Dmtu)_6(ClO_4)_2$	27°	-345	Average 132		37°	2.0		
	-18°	-372	-210	-102	27°	2.1		
	-28°	-474	-178	-114	-11°	2.2		
	-33°	-643	-	-129	-19°	2.6		
	-35°	-645	-136	-117	-35°	2.8		
	-43°	-886	-180	-148	-42°	2.9	-3.4±0.6	-17±3
	-57°	-1247	-243	-180	-51°	3.0		
	-66°	-	-578	-406	-57°	3.0		
	-85°	-4179	-781	-434	-64°	3.1		
	-95°	-4328	-858	-511	-71°	3.2		
	-104°	-4477	-690	-344	-88°	3.3		

Table (5-4b)

Compound	Contact Shift(Detu)				Magnetic Data		Thermodynamic Data	
	Temp	"Inside" NH	CH_2	CH_3	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Detu)_6(ClO_4)_2$	27°	-1272	-101	-42	37°	1.7		
	-10°	-2542	-101	-38	-16°	1.7		
	-20°	-2728	-107	-45	-23°	1.6		
	-40°	-4216	-105	-40	-33°	2.4		
	-50°	-1353	-105	-42	-41°	2.8	-4.4	-22±3
	-60°	-4570	-238	-40	-49°	2.9		
	-90°	-4710	-240	-40	-58°	3.1		
					-64°	3.2		
					-77°	3.2		
					-84°	3.3		
					-102°	3.3		

Compound	Contact Shift(from etu)				Magnetic Moment		Thermodynamic Data	
	Temp	"Inside NH	"Outside" NH	CH_2	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Etu)_6(ClO_4)_2$	-	-	-	-	47°	2.0		
	-	-	-	-	35°	2.1		
	-	-	-	-	30°	2.2		
	-	-	-	-	13°	2.5		
	-	-	-	-	- 7°	2.6		
	-	-	-	-	-23°	2.8		
	-	-	-	-	-31°	2.9	-3.4±0.4	-16±2
	-	-	-	-	-52°	3.1		
	-	-	-	-	-74°	3.1		
	-	-	-	-	-83°	3.2		
	-	-	-	-	-89°	3.3		
	-	-	-	-	-102°	3.3		

Table (5-4b)

Compound	Contact Shift(tms)			Magnetic Moment		Thermodynamic Data	
	Temp	"Inside" NH	"Outside" NH	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Tu)_6(BF_4)_2$	27°	-624	-	30°	2.1		
	-1°	-1067	-500	4°	2.1		
	-8°	-1173	-395	-9°	2.1		
	-15°	-1265	-368	-16°	2.0		
	-22°	-1409	-355	-25°	2.1		
	-30°	-1528	-355	-34°	2.2	-2.0±0.4	-10±2
	-37°	-1765	-355	-42°	2.4		
	-45°	-1988	-355	-50°	2.6		
	-52°	-2291	-355	-58°	2.7		
	-59°	-2581	-355	-66°	2.8		
	-63°	-2712	-355	-81°	3.0		
				-89°	3.1		

Compound	Contact Shift(from Detu)				Magnetic Moment		Thermodynamic Data	
	Temp	Inside NH	CH_2	CH_3	Temp	μ_{eff} BM	ΔH	ΔS
$Ni(Detu)_6(BF_4)_2$	27°	-960	-148	-28	37°	1.5		
	-16°	-1651	-154	-15	9°	1.5		
	-26°	-2313	-144	-14	-4°	2.0		
	-48°	-3228	-133	-15	-17°	2.0		
	-63°	-4164	-128	-16	-24°	2.7		
	-70°	-4264	-150	-17	-33°	2.8		
	-82°	-4373	-186	-17	-53°	2.9	-3.4±0.4	-18±2
	-94°	-4432	-201	-17	-62°	3.0		
					-68°	3.1		
					-72°	3.3		
					-81°	3.3		
					-87°	3.2		
					-93°	3.3		

#Contact shifts measured in Hz relative to L or TMS at 56.4 MHz. Solvent, acetone-d_6

#ΔH in kcal mole^{-1} and ΔS in cal. °K^{-1} mole^{-1}

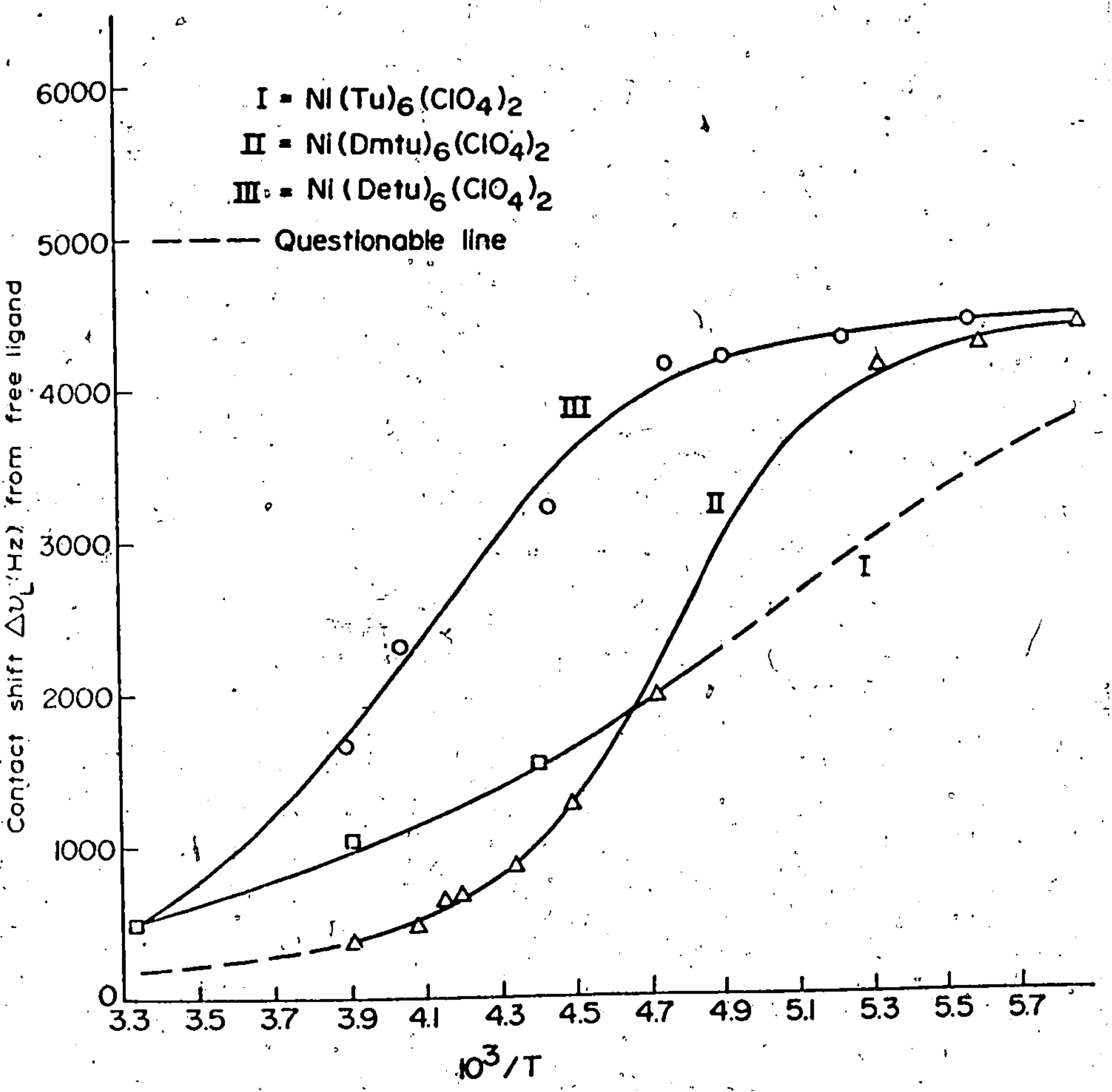


Figure (5-4b-1) Isotropic shifts of NH resonance versus $\frac{10^3}{T}$ [Ni(L)$_6$(ClO$_4$)$_2$].

We believe that the significant generalization from the results on all the Ni thiourea complexes is under identical conditions (solvent acetone, -90°C excess ligand present) the neutral complexes are tetrahedral $Ni(Tu)_2X_2$, the monopositive ions are square-planar $Ni(Tu)_3X^+$, and the di-positive ions tend to be octahedral $Ni(Tu)_6^{+2}$. We suggest that the geometry is determined by a competition involving energy gained by forming more or stronger bonds versus energy lost through interelectron replusion between bonding electrons. Bond energy is maximized in the series octahedral > square-planar > tetrahedral. Interelectron repulsion is minimized in the series tetrahedral < square-planar < octahedral. Increasing the positive charge on the metal increases bonding energy for either ionic or covalent bonding and this gradually becomes the dominant factor. Competition between d electron repulsion and ligand field stabilization energy is, of course, the dominant theme in crystal field theory. The role of interelectron repulsion between bonding (and lone pair) electrons in determining molecular geometry has long been advocated.[157] It seems reasonable that similar factors should play a part in the sterochemistry of nickel. It is noteworthy that in cases where there is an equilibrium between square-planar and tetrahedral complexes (e.g., aminotroponeiminates) electron-withdrawing substitutents, which will increase the positive charge on the metal, always favour the square-planar .[148] A summary of all the results is presented in the Table (5-4a).

(5-4c) GEOMETRY OF COMPLEXES OF Ni(II) NITRATE

Nitrate compounds of thiourea and substituted thioureas of stoichometry $Ni(L)_6(NO_3)_2$ have been investigated by optical and infrared spectra[122,144]. The results of these studies show that in the solid they are all sulphur-bonded and nitrate groups are not involved in the coordination. However, they form non-conducting solutions in acetone indicating dissociation of thiourea and retention of nitrate ion in the coordination sphere.

At 27°C, the ^1H NMR spectrum of $Ni(Tu)_6(NO_3)_2$ in acetone-d_6 (Fig. 5-4c-a) exhibits a broad line at -1419 Hz from TMS. The solution moment measured by NMR shows $\mu_{eff.}$ = 2.8 BM indicating the presence of an octahedral species. On cooling the solution to -17°C, ^1H NMR spectra shows two sets of resonance (-1954 Hz and -890 Hz from TMS) attributed to "inside" and "outside" protons of coordinated thiourea. The solution moment increases to 3.0 BM. At -31°C, the low field line starts broadening but the high field line still remains sharp, indicating a slow exchange. The situation is again normal to -60°C where the low field line reappears at -4538 Hz from TMS (Fig. 5-4c-b). The magnetic moment ($\mu_{eff.}$ = 3.3 BM) at -80°C, indicates that it is a typical octahedral species of either $Ni(Tu)_4(NO_3)_2$ or $Ni(Tu)_x(S)_y(NO_3)_2$ (where $x + y = 4$) in solution. The low field line is temperature dependent (-4718 Hz at -80°C) and the shifts are predominantly contact in origin (Fig. 5-4c-c). Data arising from contact shifts are summarized in Table (5-4c). The solubility of $Ni(Tu)_6(NO_3)_2$ is limited. Separation of solid-crystal results upon addition of free ligand. However, the solubility increases as the size of substitutent R increases.

$$Ni(Tu)_6(NO_3)_2 < Ni(Dmtu)_6(NO_3)_2 < Ni(Detu)_6(NO_3)_2$$

^1H NMR spectrum of $Ni(Dmtu)_6(NO_3)_2$ at room temperature indicates a fast exchange in solution. It shows a sharp methyl resonance at -333 Hz from

TMS. There is no observable N-H resonance in the low field. The solution moment ($\mu_{eff.}$ = 2.8 BM) indicates the presence of an octahedral species of either $Ni(Dmtu)_4(NO_3)_2$ or $Ni(Dmtu)_x(S)_y(NO_3)_2$. AT -25°C, a broad line attributable to NH resonance is observed at -1688 Hz. The average methyl resonance is shifted to -480 Hz from TMS. All the shifts are measured at 56.4 MHz. At -98°C, a limiting spectrum consisting of three lines (-5764 Hz, -5125 Hz and -3819 Hz) attributed to three different -NH protons and three lines (-1375 Hz, -1175 Hz and -736 Hz) attributable to methyl groups of coordinated ligand (Fig. 5-4c-d) ($\mu_{eff.}$ = 3.3 BM). The ligand exchange and rotation about the C-N bond are both known at this temperature. We therefore expect to see separate resonances from the "inside" and "outside" groups. There is also the possibility of cis and trans isomers of $Ni(L)_4(NO_3)_2$. Addition of excess of free ligand brings about the collapse of some lines giving a ^1H NMR spectrum which is a typical spectrum of $Ni(Dmtu)_6^{+2}$ at low temperatures (Fig. 5-4c-3). It could be possibly due to the formation of $Ni(Dmtu)_6^{+2}$ by the replacement of both NO_3^- ions with excess Dmtu. Following this observation, the assignment of the lines in ^1H NMR spectra of $Ni(Detu)_6(NO_3)_2$ comes out naturally. There are two sets of NH resonance in the low field (at -94°, -5053 Hz and -4671 Hz from TMS) and a group of CH_2- and CH_3- lines of which CH_2 lines are shifted relatively larger than the corresponding CH_3 lines. Addition of free ligand yields a spectrum which shows a typical pattern of the corresponding perchlorate or tetrafluoroborate compound under similar condition.

All nitrate compounds show solution moments (2.8 BM at room temperature and 3.3 BM at -90°C) which indicate the formation of an octahedral species. Contact shift data can be interpreted similarly [Fig. 5-4c-1)].

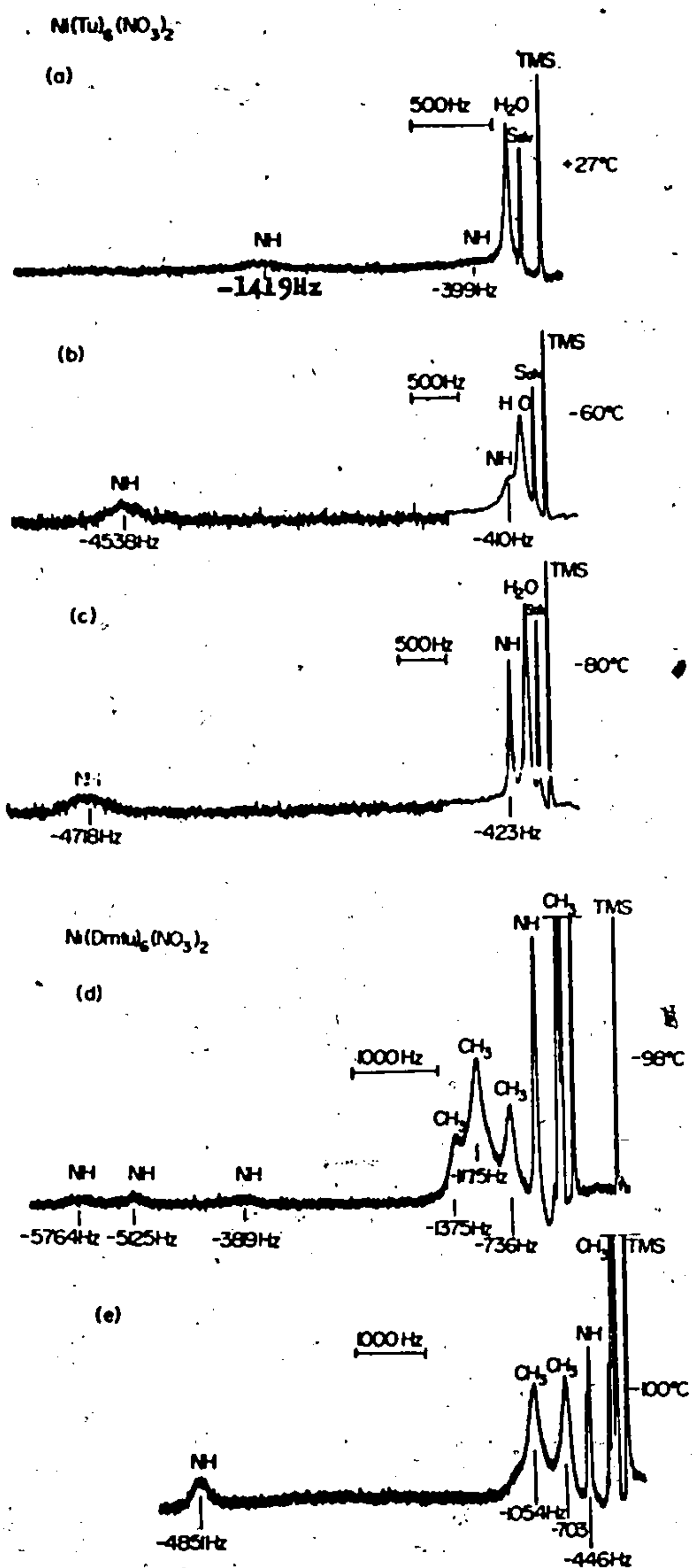


Figure (5-4c-a,b,c): ^{1}H NMR spectra of Ni(Tu)$_6$(NO$_3$)$_2$ and Figure (5-4c-d,e) ^{1}H NMR spectra of Ni(Dmtu)$_6$(NO$_3$)$_2$ at various temperatures. (Solvent: acetone-d$_6$)

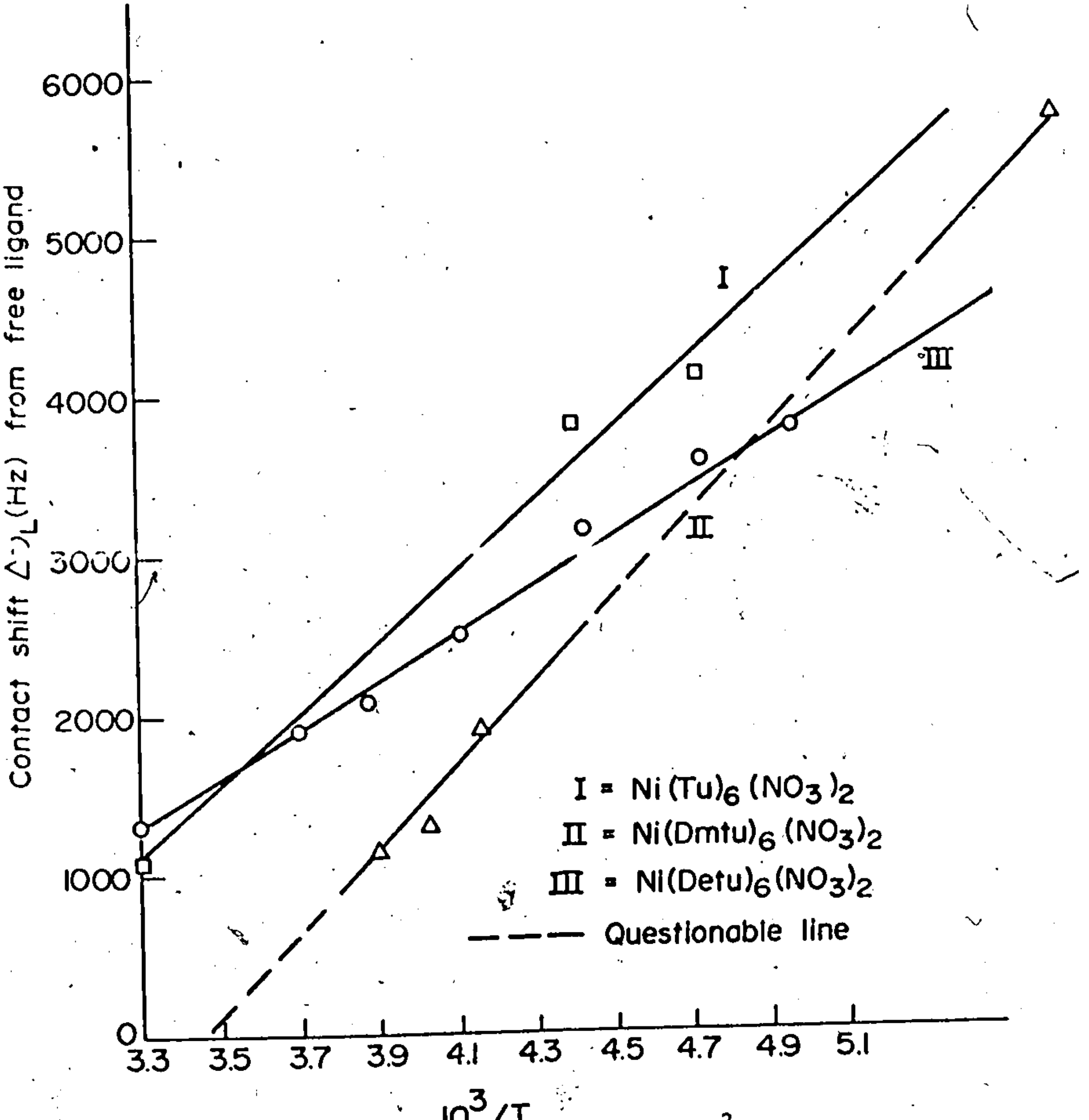


Figure (5-4c-1) Isotropic contact shifts versus $\frac{10^3}{T}$ ..[Ni(L)$_6$(NO$_3$)]

Table (5-4c): ^{1}H NMR data for Ni(II) nitrate complexes

Complex	Temperatures and contact shifts					
$Ni(Tu)_6(NO_3)_2$ Saturated Soln.	Temperature °C	27°C	-17°C	-46°C	-74°C	-93°C
	Contact shift of NH from Tu (Hz)	-1039	-1579	-3843	-4330	-4883
$Ni(Dmtu)_6(NO_3)$ Saturated Soln.	Temperature °C	27°C	-17°C	-33°C	-62°C	-98°C
	Contact shift of NH from Dmtu (Hz)	?	-1186	-1909	?	-5366 -4727 -3427
$Ni(Detu)_6(NO_3)_2$ 0.06 M	Temperature °C	27°C	-15°C	-47°C	-80°C	-94°C
	Contact shift of NH from Detu (Hz)	-1255	-2502	-3189	-3890	-4663 -4281

Conductivity data indicate the dissociation of L and retention of NO_3^-. Combinations of these data give a direct evidence of an octahedral species in solution at all temperatures. The results are summarized in Table (5-4c).

(5-5) STRUCTURAL EQUILIBRIA

The isotropic shifts[68,69] described above may be used to obtain information on the equilibrium between the diamagnetic and paramagnetic species present in solution. The temperature dependence of the shift is given by the expression of the form[158]

$$\frac{\hat{\Delta} H}{H_o} = \frac{A\, g_e^2\, \beta_e^2}{g_N\, \beta_N} \cdot \frac{S(S+1)}{3kT}\, \mathrm{Exp.}[(\Delta G/RT + 1)]^{-1} \qquad (5\text{-}5\text{-}1)$$

where ΔG is the free energy difference between the two species. ΔG can be found from the temperature dependence of the contact shift or alternatively solution susceptibilities, i.e.:

$$\Delta G = RT \ln\left(\frac{\mu_\infty^2}{\mu_{eff.}^2} - 1\right), \text{ and } \Delta G = - RT \ln K_{eq.} \qquad (5\text{-}5\text{-}2)$$

where μ_∞ is the moment for a fully paramagnetic species and $\mu_{eff.}$ the observed magnetic moment. Some confusion has arisen in this area from the use of an incorrect form of equation (5-5-1)[149] resulting in ΔG values too high by RT ln 3 and ΔS values too low by R ln 3 = 2.2 cal K^{-1} mole^{-1}; fortunately the spin densities obtained are unaffected by this error.[158]

As indicated above, there is evidence for equilibria between octahedral, square-planar and tetrahedral species in these nickel thiourea complexes in acetone solutions. Equation (5-5-2) is used to obtain thermodynamic parameters from the magnetic susceptibility data. For the perchlorates and tetrafluoroborates, the relevant equilibria involve octahedral and square-planar molecules. For the halides, we are concerned with equilibria between tetrahedral and square-planar species. For the iodides, the octahedral species becomes significant below -80°C. Data obtained at temperatures > -80°C was used to obtain the thermodynamic parameters for the tetrahedral square-planar equilibrium [Table (5-4a)]. Data for square-planar octahedral equilibirum is given in Table (5-4b).

It is found that the data for the tetrahedral square-planar equilibria are comparable with those of Ni(II) aminotroponeimineates[149]. For the latter compounds, ΔH varies from +2 to +4 k cal/mole and ΔS from +8 to +12 cal. K^{-1} mole^{-1} respectively. For the present compounds, ΔH and ΔS are all positive as was the case for aminotroponeimineates. The values obtained for the halides (ΔH = +2 to +6 k cal /mole and ΔS = +12 to +25 cal K^{-1} mole^{-1}) are somewhat higher than those found for aminotroponeimineates and this would be due to association, solvation and formation of charged species. However, $Ni(Nptu)_2X_2$ exhibits values closely parallel to those of some Ni(II) aminotroponeimineates in $CDCl_3$.[149] In comparison, all perchlorate compounds exhibiting an equilibrium between a diamagnetic square-planar species and a paramagnetic octahedral speices yield negative ΔH and ΔS values (ΔH = -2 to-4 k cal /mole, ΔS = -15 to -22 cal K^{-1} mole^{-1}) reflecting the formation of new bonds with two ligands (thioureas). This is accompanied by a release of energy and decrease of entropy of the system [Table (5-4b)]. The significant lower value of ΔH for these ionic compounds is consistent with the back donation to the π^* orbital which makes a contribution to the bond strength upon coordination of of the two ligands. We tentatively ascribe differences in ΔS to variations in the hydrogen bonding interaction which determines the second coordination sphere.

Ni(II) chelates of β-diketones containing bulky substituents are found to show, in solution, temperature dependent magnetic moments which can be understood on the basis of an equilibrium involving monomeric (square-planar, diamagnetic) and trimeric[160] or tetrameric[159] (octahedral, paramagnetic) species. It is interesting to note that the size and magnitude of the thermodynamic parameters for the trimeric Ni(II) complexes which have been obtained[160] are similar to those exhibited by nickel thiourea perchlorates. The ^{1}H NMR studies of the solution equilibria of Ni(II) complexes with Schiff bases formed from salicylaldehydes and N,N-substituted ethylenediamines have indicated that large negative and positive contact shifts observed are associated with a similar square-planar octahedral equilibrium in solution.[161] Direct estimation of ΔG values by using equation (5-5-1) for the equilibrium show all ΔG's to be negative and to increase in magnitude as the temperature decreases in agreement with the displacement of the equilibrium towards the octahedral from low temperatures. The existence of such an associative equilibrium is readily comparable with the present thiourea complexes, and is simiarly reflected in the anomalous magnetic properties of the solutions.

The estimation of population difference between two spin states for the haldide compounds at 27°C has been made from the equation (5-5-2) and the results indicate that about 6-12% of the total Ni present exists as a diamagnetic square-planar species. At low temperature, -90°C, for $Ni(Tu)_2Cl_2$, the ligand exchange has been frozen out. We may therefore calculate the room temperature shifts for this compound if Curie Law dependence is assumed. This calculation indicates relatively little replacement of thiourea by solvent in this compound. The room temperature observed shifts decrease in the order Cl > Br > I indicating greater replacement of thiourea by solvent for the iodide. This parallels the results found for the anologous Co complexes.

A direct measurement of the equilibrium constant for the replacement of thiourea by solvent in the octahedral complex from the concentration dependent shifts is not possible as a square-planar species NiL_4^{+2} is additionally present in solution. However, data is available to estimate the equilibrium constants for the square-planar octahedral equilibrium. At low temperatures, the solutions become fully paramagnetic and the moments are found to vary from 3.1 BM to 3.3 BM. Using this data, the molar susceptilbility of a fully paramagnetic species at room temperature can be calculated. By using this calculated value for fully paramagnetic NiL_6^{+2} the observed solution susceptibility, the fraction of paramagnetic and diamagnetic square-planar species at room temperature can be estimated. The results are not accurate but they are sufficient for a qualitative study. They are summarized in Table (5-5d-1). It is obvious that within experimental error, the equilibrium constants for perchlorate and tetrafluoroborate complexes of thiourea and N,N'-dimethylthiourea vary from 6×10^{-4} to 9×10^{-4} while the corresponding substituted complexes show slightly greater values demonstrating a larger dissociation. In short, a relatively larger proportion of square-planar species is formed in the substituted compounds This could possibly arise from steric effect. Thus, the degree of dissociation of all perchlorates and tetrafluoroborates largely depends on the

Complex	Conc. (M)	Fully Paramag. $X'_M \times 10^{-6}$ (27°C)	Observed $X'_M \times 10^{-6}$ (27°C)	Fraction of Paramag. Species	Fraction of diamag. Species	K_{eq}
$Ni(Tu)_6(ClO_4)_2$	3.2×10^{-2}	4232	2205	0.5210	0.4789	8.7×10^{-4}
$Ni(Tu)_6(BF_4)_2$	2.0×10^{-2}	3972	1825	0.4589	0.5410	5.5×10^{-4}
$Ni(Dmtu)_6(ClO_4)_2$	1.9×10^{-2}	4501	1822	0.4048	0.5952	7.5×10^{-4}
$Ni(Detu)_6(ClO_4)_2$	1.8×10^{-2}	4501	1194	0.2653	0.7347	19.6×10^{-4}
$Ni(Detu)_6(BF_4)_2$	1.5×10^{-2}	4232	1058	0.2500	0.7500	14.5×10^{-4}
$Ni(Etu)_6(ClO_4)_2$	1.9×10^{-3}	4232	1653	0.3906	0.6094	8.4×10^{-4}
$Ni(Tu)_4Cl_2$	-	5968	5063	-	-	-
$Ni(Tu)_6Br_2$	5.9×10^{-3}	5658	5356	0.9466	0.0534	5.6×10^{-2}
$Ni(Tu)_6I_2$	9.1×10^{-3}	4500	4085	0.9078	0.0922	10.2×10^{-2}
$Ni(Nptu)_2Br_2$	7.5×10^{-3}	4231	3972	0.9387	0.0613	6.5×10^{-2}
$Ni(Nptu)_2I_2$	9.9×10^{-3}	3972	3719	0.9363	0.0637	6.8×10^{-2}

Table (5-5d-1): Equilbrium constants for Ni(II) Complexes in acetone-d_6 at 27°C.

nature of the substituent group present and it increases in the order

$$\mathrm{Ni(Tu)_6(NO_3)_2} \sim \mathrm{Ni(Tu)_6(BF_4)_2} \sim \mathrm{Ni(Dmtu)_6(ClO_4)_2} \sim \mathrm{Ni(Etu)_6(ClO_4)_2}$$

$$< \mathrm{Ni(Detu)_6(BF_4)_2} < \mathrm{Ni(Detu)_6(ClO_4)_2}$$

The differences between corresponding compounds of thiourea and N,N'-dimethylthiourea are relatively small but indicate that N,N'-diethylthiourea perchlorate and tetrafluoroborate are most dissociated followed by ethylene thiourea and the remaining compounds in the given order.

All nitrate compounds are paramagnetic and octahedral in solution. Their ^1H NMR spectra show broad contacted shifted line indicating rapid ligand dissociation. The dissociation equilibria of these compounds in acetone may be shown as follows:

$$\mathrm{Ni(L)_6(NO_3)_2} \rightleftharpoons \mathrm{Ni(L)_4(NO_3)_2} + 2L$$

$$\mathrm{Ni(L)_4(NO_3)_2} + yS \rightleftharpoons \mathrm{Ni(L)_x(S)_y(NO_3)_2} + (4-x)L$$

where $x + y = 4$ and S is a solvent molecule. The ^1H NMR spectra at low temperature indicate that there is a possibility of existence of equilibrium involving species with two nitrate groups bonded in cis and trans positions to Ni. All nitrate compounds are less soluble in acetone. Therefore, quantitative measurements on solution equilibria are impractical.

(5-6) THE LIGAND EXCHANGE PROCESS

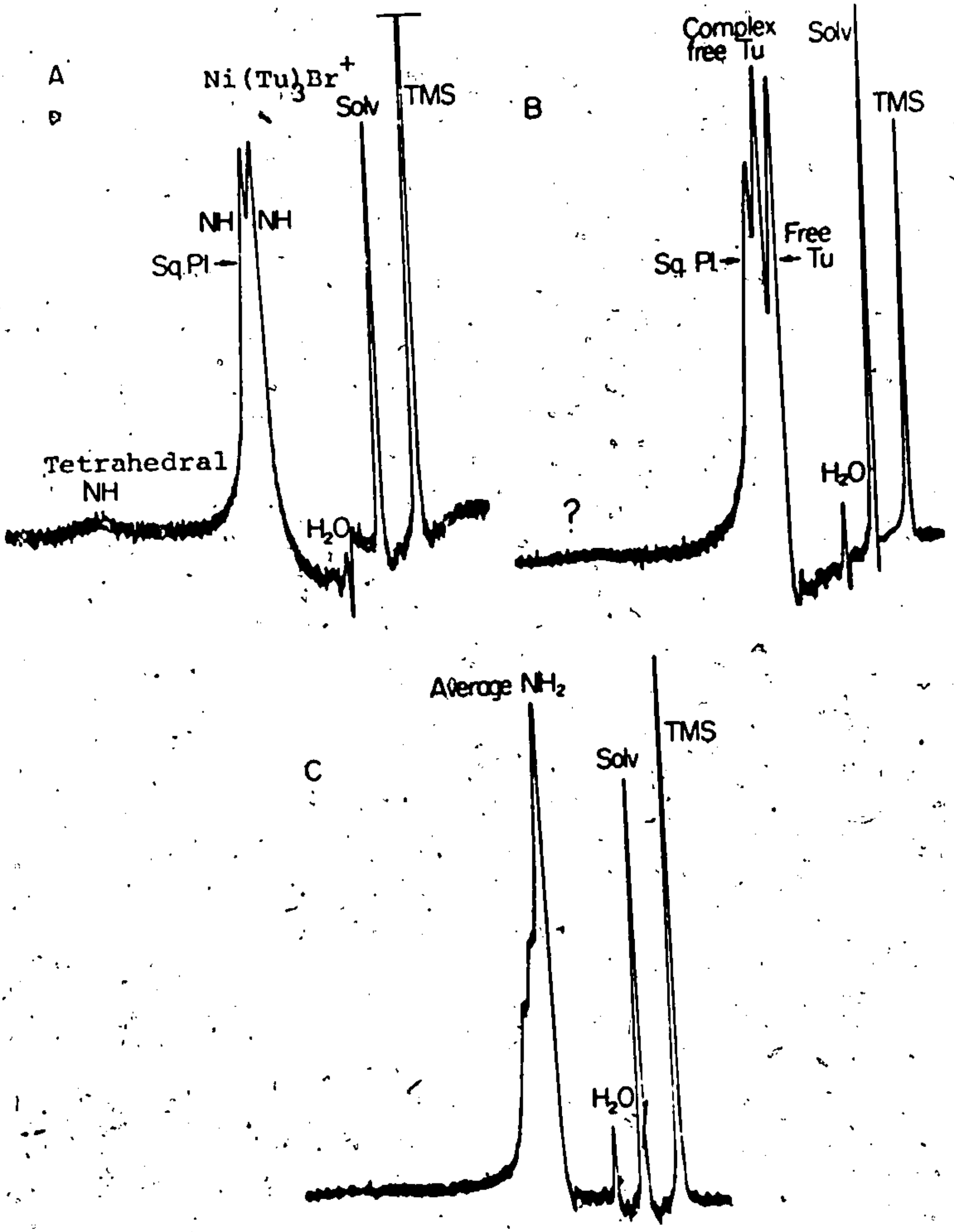
Tables (5-6-b) and (5-6-c) summarize the results of a semi-quantitative study of ligand exchange kinetics in these Ni(II) complexes. Coalescence temperatures and the dependence of line width on ligand and complex concentrations are reported. The latter experiments indicate whether associative or dissociative mechanism is involved as discussed in Chapter IV. For the tetrahedral complexes $Ni(L)_2X_2$, ligand exchange occurs through a bimolecular associative type of mechanism and the rates decrease in the series

$$Ni(Tu)_2Cl_2 > Ni(Tu)_2Br_2 > Ni(Tu)_2I_2.$$

A similar trend was noted in the analogous triphenylphosphine complexes reported in the literature.[89,90] We were unable to obtain data for the series $Ni(Nptu)_2X_2(X=Br,I)$ since they precipitate solid on adding ligand. For square-planar complexes, we have used equation (2-21) to obtain approximate rates from coalescence temperatures and find that both reactions proceed by an associative mechanism but that ligand exchange rates decrease in the order

$$Ni(Tu)_3I^+ > Ni(Tu)_3Br^+$$

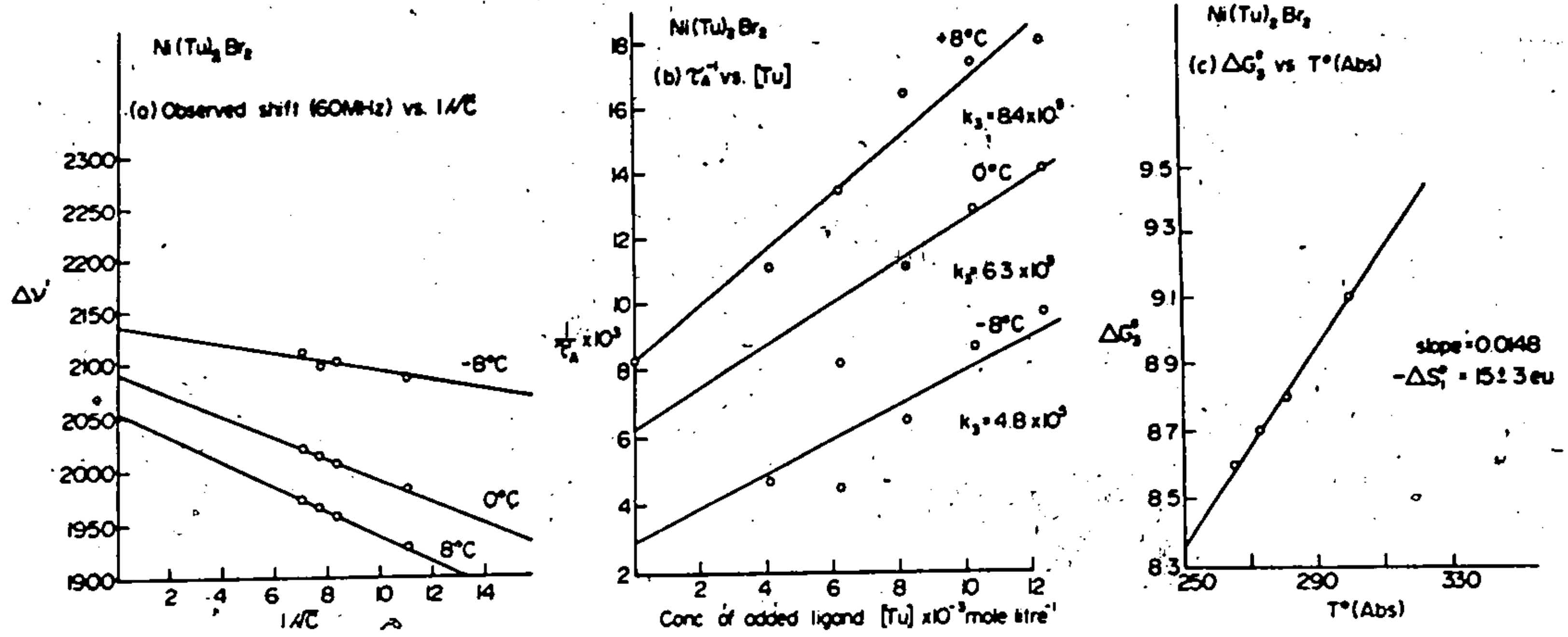
Thus the square-planar complexes apparently show the opposite halide dependence to the tetrahedral complexes. We suspect that this probably reflects the difference in charge rather than in geometry. Figure (5-6) shows some representative spectra of square-planar $Ni(Tu)_3Br^+$ with excess ligand.



Figure(5-6): ^{1}H NMR Spectra of Ni(Tu)$_3$Br$^+$ [A= Ni(Tu)$_3$Br$^+$, B=with excess of Tu(slow exchange), C=Intermediate Exchange (solution warmed)]

The line broadening technique in the limit of fast exchange has been applied to obtain semi-quantitative data of the kinetics of ligand exchange for tetrahedral $Ni(Tu)_2X_2$. The experiments are limited for $Ni(Tu)_2Cl_2$ and $Ni(Nptu)_2X_2$(X=Br,I) which are relatively less soluble in acetone-d_6. Measurements were made on the line-width variations of the "inside" proton resonance. Measurements were possible over the temperature range of + 27° to -20°C. Over this temperature range, a solution of the complex $Ni(Tu)_6X_2$ contains tetrahedral $Ni(Tu)_2X_2$ and excess of free ligand Tu under rapid exchange. It is therefore impractical to obtain limiting line widths from a plot of observed line width versus 1/ ₵ as was done in the ligand exchange study of analogous Co-complexes. However, there remains the problem of getting T_{2A}^{-1} to ~~fit in~~ the equation (2-25) though T_{2B}^{-1} would be directly obtained from the measurement of the line width of the free ligand resonance under the conditions of the experiment. A solution of tetrahedral $Ni(Tu)_2Cl_2$ at very low temperature (i.e. -90°) would show a limiting spectrum. At this temperature, the ligand exchange process is completely frozen out and a measurement of the line width of the complexed resonance is possible. It has been found that the line width of the complexed resonance (i.e. "inside" NH) of tetrahedral $Ni(Tu)_2Cl_2$ at this temperature is ~180 Hz (60 MHz). This value is used in the calculations of kinetic and activation parameters of ligand exchange in tetrahedral $Ni(Tu)_2X_2$. It may also be noted that the observed line width ($\frac{1}{T_2}$) varies from 200 Hz to 400 Hz, and therefore the T_{2A}^{-1} term contributes between 40% and 80% of the total width. The results are of course, not accurate but they are still meaningful enough to make a comparative study with those of analogous Co complexes. Table (5-6-a) shows a summary of kinetic

Figure (5-6-a)


Ni(Tu)₂Br₂
(a) Observed shift (60MHz) vs. 1/√C
Δν'
2300
2250
2200
2150
2100
2050
2000
1950
1900
2
4
6
8
10
12
14
1/√C
-8°C
0°C
8°C
Ni(Tu)₂Br₂
(b) τ_A⁻¹ vs. [Tu]
1/τ_A x10³
18
16
14
12
10
8
6
4
2
+8°C
k₃=8.4x10⁸
0°C
k₃=6.3x10⁸
-8°C
k₃=4.8x10⁸
Conc of added ligand [Tu] x10⁻³ mole litre⁻¹
Ni(Tu)₂Br₂
(c) ΔG₃° vs T°(Abs)
ΔG₃°
9.5
9.3
9.1
8.9
8.7
8.5
8.3
250
290
330
T°(Abs)
slope=0.0148
-ΔS₁° = 15±3eu

data for $Ni(Tu)_2Br_2$. Plots of $\Delta\nu$ vs $1/\sqrt{c}$, τ_A vs [Tu] and $\Delta G^{\ddagger}_3$ vs T(absolute) are shown in Fig. (5-6-a). The variation of life-times with added ligand concentration lead to the bimolecular rate constants (k_3) summarized in Table (5-6-a). A similar study was carried out for octahedral $Ni(Dmtu)_6(ClO_4)_2$ using the limiting line widths of complexed and free ligand lines (~100 Hz and ~20 Hz) respectively. All the measurements were based on the line width of the CH_3 signal. The bimolecular rate constants are found to be 1.5 x 10^6 $mole^{-1}$ sec^{-1} for $Ni(Tu)_2I_2$ respectively at + 27°C. The variation of rate constant with temperature allows $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to be evaluated. It is found that the entropy of activation ($\Delta S^{\ddagger}$) for the ligand-exchange reaction of $Ni(Tu)_2Br_2$ is more negative than that of $Ni(Tu)_2I_2$ and that this determines the difference in rates. The enthalpy of activation ($\Delta H^{\ddagger}$) is actually smaller for the bromide than the iodide. This behaviour parallels that for $Co(Tu)_2X_2$ reported in the previous chapter. The findings of second order kinetics are to be expected. In this case, there is no direct evidence for a second mechanism involving prior solvent coordination. However, this does not preclude the presence of small concentrations of solvated species which might act as intermediates in the exchange process. We would in fact, conclude that most probably, both processes occur for all tetrahedral complexes and only their relative contributions are changing.

A noticeable feature of these results is that the nickel complexes are more labile than the corresponding cobalt ones. The difference appears to be primarily in the enthalpies of activation [see Table(5-6-c) and Table (4-7)]. It is note-worthy that both $Ni(Tu)_2Br_2$ and $Co(Tu)_2Br_2$ at 27°C exhibit different bimolecular rate constants of 1.5 x 10^6 $mole^{-1}$ sec^{-1} and 3.3 x 10^5

Table (5-6-a): Kinetic and Activation Parameters for Ligand Exchange in Tetrahedral $Ni(Tu)_2Br_2$

Contact Shift (Hz) 60 MHz	Line width (Hz) $\Delta\nu_{1/2}$	Conc. of Tu $\times 10^{-3}$M	P_A	τ_A sec	τ_A^{-1} sec^{-1}	Slope k_3 = $mole^{-1}$ sec^{-1}	t°c
1931	185	0.0	0.96	1.6×10^{-4}	6.3×10^{3}	8.4×10^{5}	+ 8
1862	195	4.1	0.93	1.1 -	9.1 -		
1764	218	6.2	0.88	8.7 -	11.5 -		
1709	223	8.2	0.85	6.9 -	14.5 -		
1681	229	10.3	0.84	6.5 -	15.4 -		
1653	236	12.4	0.83	6.3 -	16.0 -		
2019	257	0.0	0.97	1.3×10^{-4}	7.7×10^{2}	6.3×10^{5}	0
1943	264	4.1	0.93	3.7 -	2.7×10^{3}		
1848	271	6.2	0.88	1.6 -	6.3 -		
1764	278	8.2	0.84	1.1 -	9.1×10^{-3}		
1722	285	10.3	0.82	9.1×10^{-5}	10.9 -		
1695	292	12.4	0.81	8.6×10^{-5}	12.0 -		
2090	320	0.0	0.98	4.7×10^{-3}	2.1×10^{2}	4.8×10^{5}	- 8
2000	334	4.1	0.93	7.1×10^{-4}	1.4×10^{3}		
1940	348	6.2	0.91	4.0 -	2.5 -		
1850	362	8.2	0.86	2.2 -	4.5 -		
1778	369	10.3	0.83	1.5 -	6.7 -		
1723	375	12.4	0.80	1.3 -	7.7 -		

All shifts measured relative to free ligand resonance

Continued from Table (5-6-a)

t°c	k_3 mole^{-1}sec^{-1}	$\Delta H^{\ddagger}$ kcal . mole^{-1}	$\Delta S^{\ddagger}$ e.u.	limiting line width Hz(60 MHz)	limiting shift Hz (60 MHz)
+27°	1.5×10^6			-	-
+ 8°	8.4×10^5	4.6 ± 0.9	-15 ± 3	180	2000
0°	6.3×10^5			180	2090
- 8°	4.8×10^5			180	2140

e.u.= cal.K^{-1}.mol^{-1}.

$mole^{-1}$ sec^{-1} respectively indicating a faster ligand exchange in the former. This is directly reflected in the difference in both enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation. While a great number of factors affect the relative activation energies, one factor in particular, the ligand field stabilization energy is expected to be different for cobalt and nickel.[27] The ligand field stabilization for tetrahedral cobalt (d^7) and nickel are $(6/5)\Delta_t$ and $(4/5)\Delta_t$ respectively, where Δ_t is the splitting between the lower "e" and upper "t_2" levels. By taking Δ_t for the MCl_4^{-2} species,[156,162] a rough estimate for the difference in the ligand field stabilization energy contribution to the ground-state energies between the cobalt and nickel complexes is 3.0 k.cals. $mole^{-1}$. This rough estimate is probably somewhat low, since the sulphur atom of thiourea causes a larger ligand-field splitting than do halides. An estimate of the ligand field stabilization of the pentacoordinate transition state is even more tenuous since the geometry is uncertain. However, both trigonal-bipyramidal and square-pyramidal geometries cause approximately equal ligand field stabilization energies for cobalt and nickel cases.[27]

Thus it is not unreasonable that the increased lability of the present tetrahedral nickel complexes over the cobalt ones is at least in part due to ligand-field effects. The opposite trend, cobalt more labile than nickel, is generally observed in octahedral complexes of these ions and can be explained by similar arguments.

Solutions of $Ni(L)_6(X)_2$($X=ClO_4$, BF_4) exhibit a rapid equilibrium between paramagnetic octahedral NiL_6^{+2} and diamagnetic square-planar NiL_4^{+2} (L=Tu,Dmtu,Detu). Therefore, the shift observed for such a system is in average frequency and it is not possible to make measurements of reaction rates at high temperatures. Below -60°C, however, most of the square-planar complex NiL_4^{+2} is converted into octahedral complex NiL_6^{+2} by association as has been discussed previously. A line-width variation technique with excess of free ligand in a slow exchange region indicates that all NiL_6^{+2} exchanges via a dissociative mechanism. Application of formula (2-21) at their coalescence temperatures (Table 5-6-b) signifies that the unimolecular rate constants k_I is in the order 2×10^4 sec^{-1} at the coalescence temperature. The lability of these complexes is found to increase in the order

$$Ni(Detu)_6(BF_4) < Ni(Detu)_6(ClO_4)_2 < Ni(Dmtu)_6(ClO_4)_2 < Ni(Tu)_6(BF_4)_2 < Ni(Tu)_6(ClO_4)_2$$

Thus in these compounds, the unsubstituted nickel complexes are more labile than the corresponding substituted ones. This behaviour also parallels that for cobalt perchlorate complexes discussed in the previous chapter. However, it is noticeable that a nickel perchlorate complex exchanges at a higher rate relative to the corresponding cobalt analogue.

It is interesting that this series of labilities parallels the ligand field stabilization energies of the thiourea ligands (10 Dq for $Ni(Tu)_6^{+2}$ = 8300 cm^{-1}, $Ni(Dmtu)_6^{+2}$ = 8600 cm^{-1}, $Ni(Etu)_6^{+2}$ = 8800 cm^{-1}).

Direct evidence for a dissociative mechanism is provided by line broadening studies on $Ni(Dmtu)_6^{+2}$ with excess of added ligand. The line broadening effect is nicely shown within a fast exchange limit when the temperature range is between -70°C to -78°C. The results are summarized in the Table (5-6-b). The most interesting feature of the results is the positive value

Kinetic Parameters of Ni(II) Complexes [Coalescence Temperatures (56.4 MHz)]

Table(5-6-b)

Complexes	Mechanism	Coalescence Temp. °C	Rate Constants k	Exchanging Species
$Ni(Tu)_4Cl_2$	A	-	-	$Ni(Tu)_2Cl_2$ less soluble
$Ni(Tu)_6Br_2$	A	-90°	2×10^3	$Ni(Tu)_3Br^+$
$Ni(Tu)_6I_2$	A	-90°	3×10^3	$Ni(Tu)_3I^+$
$Ni(Nptu)_2X_2$ X-Br, I	A	-	-	$Ni(Nptu)_2X_2$ less soluble
$Ni(Tu)_6(NO_3)_2$	D	-	-	$Ni(Tu)_4(NO_3)_2$ less soluble
$Ni(Dmtu)_6(NO_3)_2$	D	-65°	2×10^4	$Ni(Dmtu)_4(NO_3)_2$
$Ni(Detu)_6(NO_3)_2$	D	-36°	2×10^4	$Ni(Detu)_4(NO_3)_2$
$Ni(Tu)_6(ClO_4)_2$	D	-	-	$Ni(Tu)_6^{+2}$ extremely broad line
$Ni(Dmtu)_6(ClO_4)_2$	D	-77°	2×10^4	$Ni(Dmtu)_6^{+2}$
$Ni(Detu)_6(ClO_4)_2$	D	-58°	2×10^4	$Ni(Detu)_6^{+2}$
$Ni(Tu)_6(BF_4)_2$	D	-	-	$Ni(Tu)_6^{+2}$ extremely broad line
$Ni(Detu)_6(BF_4)_2$	D	-55°	2×10^4	$Ni(Detu)_6^{+2}$

D = Dissociative mechanism

A = Associative mechanism

Kinetic and Activation Parameters of Some Ni(II) Complexes (60 MHz)

Table(5-6-c)

Complex	k_I sec^{-1}	k_3 $mole^{-1} sec^{-1}$	Temp.	Mechanism	ΔS^* e.u.	ΔH^* k. cals/mole
$Ni(Tu)_2Cl_2$	-	-	-	A	-	-
$Ni(Tu)_2Br_2$	-	1.5×10^6	+27°	A	-15±3	4.6 ± 0.6
$Ni(Tu)_2I_2$	-	7.5×10^5	+27°	A	- 9±3	6.8 ± 0.6
$Ni(Dmtu)_6^{+2}$	1.0×10^4	-	-78°	D	+32±5	14.0 ± 1.0

A = Associative mechanism

D = Dissociative mechaism

Solvent = Acetone-h_6

e.u. = $cal.K^{-1}.mole^{-1}$.

of entropy of activation ($\Delta S^{\ddagger}$) which is expected for a dissociative mechanism and contrasts with the negative $\Delta S^{\ddagger}$'s found for associative processes. Examples of such a process exhibiting a positive entropy of activation are well known[164,165] in the acid hydrolysis of some metal octahedral complexes such as $[Co(NH_3)_5N_3]^{+2}$, $[Cr(H_2O)_5N_3]^{+2}$, and $IrCl_6^{-3}$. Their entropies of activation vary from +14 e.u. to +19 e.u. which compares very reasonably with the present result.

All nitrate compounds also exhibit a dissociative type of mechanism. The first rate constants, k_I at the coalescence temperatures are in the order 2×10^4 sec^{-1} respectively. $Ni(Tu)_6(NO_3)_2$ forms solid with added thiourea in solution and is therefore not accessible to study. However, ligand-exchange rate decreases in the order

$$Ni(Tu)_6(NO_3)_2 >> Ni(Dmtu)_6(NO_3)_2 > Ni(Detu)_6(NO_3)_2$$

This parallels the perchlorate and tetrafluoroborate complexes.

CHAPTER VI

Π-ALLYLNICKEL COMPLEXES

(6-1) INTRODUCTION

Extensive studies on Π-allyl transition metal chemistry have been recently made by a number of investigators.[166,167] The results of these studies lead to the conclusion that allyl metal system of Ni(II) evidently plays an important role and essential part in many of the reactions of unsaturated hydrocarbons, and takes part in extremely stereoselective homogeneous catalytic processes.[166,167] A number of the compounds studied contain thiourea ligands and it is of interest to compare the structure and lability of these catalytically active compounds with those of the simpler compounds described previously.

(6-2) PREVIOUS WORK

Π-allylnickel bromide $[(\Pi\text{-}C_3H_5)NiBr]_2$ and Π-crotylnickel bromide $[(\Pi\text{-}CH_3.C_3H_4)NiBr]_2$ have been studied spectroscopically.[166,168] These studies indicate that they assume a dimeric form in solid. The ^{1}NMR spectra of the former complex in C_6D_6 at 27° reveal a symmetric pattern consisting of two doublets and a group of closely spaced lines (at least seven components) in the ratio of intensity 2:2:1 respectively.[166] This is consistent with the structure of Π-allyl group symmetrically bonded to a nickel atom. The ^{1}H NMR spectra of Π-crotyl complex lead to the same conclusion. All complexes exhibit a dynamic equilibrium involving Π- and σ-bonded species at high temperatures.[166] Later workers have synthesized a number of Π-allylnickel or Π-crotylnickel complexes with thioureas.[169] X-ray structural studies have been reported.[167] The ^{1}H NMR evidence suggests that both allyl and crotyl remain as a Π-bonded ligand in solution.

(6-3) EXPERIMENTAL SECTION

The following complexes have been synthesized.[170,171]

$(\Pi\text{-}C_3H_5)Ni(Tu)_2Br$	$(\Pi\text{-}C_3H_5)Ni(Nptu)_2Br$
$(\Pi\text{-}C_3H_5)Ni(Mtu)_2Br$	$(\Pi\text{-crotyl})Ni(Tu)_2Br$
$(\Pi\text{-}C_3H_5)Ni(Dmtu)_2Br$	$(\Pi\text{-crotyl})Ni(Dmtu)_2Br$

Except those of thiourea, all complexes have not been reported previously. The latter complexes were prepared by the methods closely analogous to those described in the literature.[170] A typical preparation was carried out as follows.[172,173]

A 250 ml double-necked flask with counter stream cooler and No-pressure safety valve was set up. The flask was fitted with a nitrogen line to remove the air inside the vessel. 150 ml of nitrogen saturated benzene, 8.3 g of allylbromide and 15 ml of $Ni(CO)_4$ were heated to 70-80°C. The solution first turns yellow and then finally red with carbon-monoxide formation and precipitation of nickel.

$$Ni(CO)_4 + CH_2BrCH{=}CH \longrightarrow (Ni(C_3H_5)Br)_2 + 8CO$$

$$Ni(CO)_4 \longrightarrow Ni + 4CO$$

After 15 minutes standing, the mixture was refluxed with continuous flow of nitrogen for an hour. The dark red solution obtained was cooled to room temperature and filtered over a piece of glass-wool under nitrogen. The dark red filtrate was taken and the solvent was pumped off on a vacuum line. The dried sample was in dark red colour. It was washed with 3 ml of n-pentane and dried under high vacuum. The dark red substance was kept in a sublimation tube and it was allowed to sublime at a constant temperature of 80-90°C. This gave 1.2 g . of dark red air-sensitive crystal of $[(C_3H_5)NiBr]_2$. The corresponding $[(\Pi\text{-crotyl})NiBr]_2$ was synthesized by a similar procedure.

Π-allylnickel complexes of thioureas were synthesized by reacting 1 mole of Π-allylnickel halide dimer and 4 moles of thiourea or alkylthiourea in a methanol solution at - 5° under nitrogen atmosphere. They separated as pure orange-red crystalline solids on cooling to -78° (dry ice and acetone). In a similar procedure, complexes containing crotyl group and thiourea or alkylthiourea were isolated.

(6-4) THE NUCLEAR MAGNETIC RESONANCE SPECTRA

This chapter discusses NMR studies of Π-allylnickel complexes of thioureas in some detail. It is necessary to present some preliminary NMR data before discussing the results. There are two aspects which require consideration. Firstly, we need to know the assignments and chemical shifts of various coordinated ligand protons. Secondly, we are interested in any rate processes associated with ligand exchange or molecular rotation which may occur.

The ^{1}H NMR studies of $CH_2{=}CHCH_2X$ and $CH_3CH{=}CHCH_2X$ have been previously reported.[174,175] Their NMR spectra in acetone-d_6 are quite similar to those reported in the literature. [Fig. (6-1a) and Fig. (6-1b)].

Π-allylnickel bromide and Π-crotylnickel bromide complexes have been investigated in C_6D_6 [Fig. (6-1c) and Fig. (6-1d)]. However, they have not been studied in acetone. The ^{1}H NMR spectra of these complexes in acetone-d_6 show similar patterns to those previously reported in the literature.[169] The only difference which is noticeable is that the observed lines (two doublets and a group of closely spaced lines) of Π-allyl group are extremely broad, possibly due to a chemical exchange involving a dimeric and solvated monomeric species[(Fig. (6-2a) and Fig. (6-2b)]. Because of this effect, the chemical shift data are different from those obtained in C_6D_6 (Table 6-1).

The ^{1}H NMR spectra of $RNi(L)_2Br$(R=Π-allyl, Π-crotyl) where L=Tu, Mtu, Dmtu, and Nptu in acetone, have not been previously studied in detail. (Π-allyl)$Ni(Tu)_2Br$ in acetone-d_6 exhibits a ^{1}H NMR spectrum at -10°C consisting of a broad line assignable to thiourea under a rapid exchange. On cooling to -30°C, it splits into a doublet of equally intense lines attributable to "inside" and "outside" protons of coordinated thiourea [Fig. (6-3-a,b,c)]. The corresponding Π-crotyl complex shows a similar spectrum [Fig. (6-3-g)]. It seems that rotational barrier of complexed thiourea is higher than that of free thiourea. The water resonance does not show a significant shift from its diamagnetic position. Cooling the complex solution does not affect the thiourea resonances but a noticeable change in intensity of the two doublets of the Π-allyl group is observed. It is possible

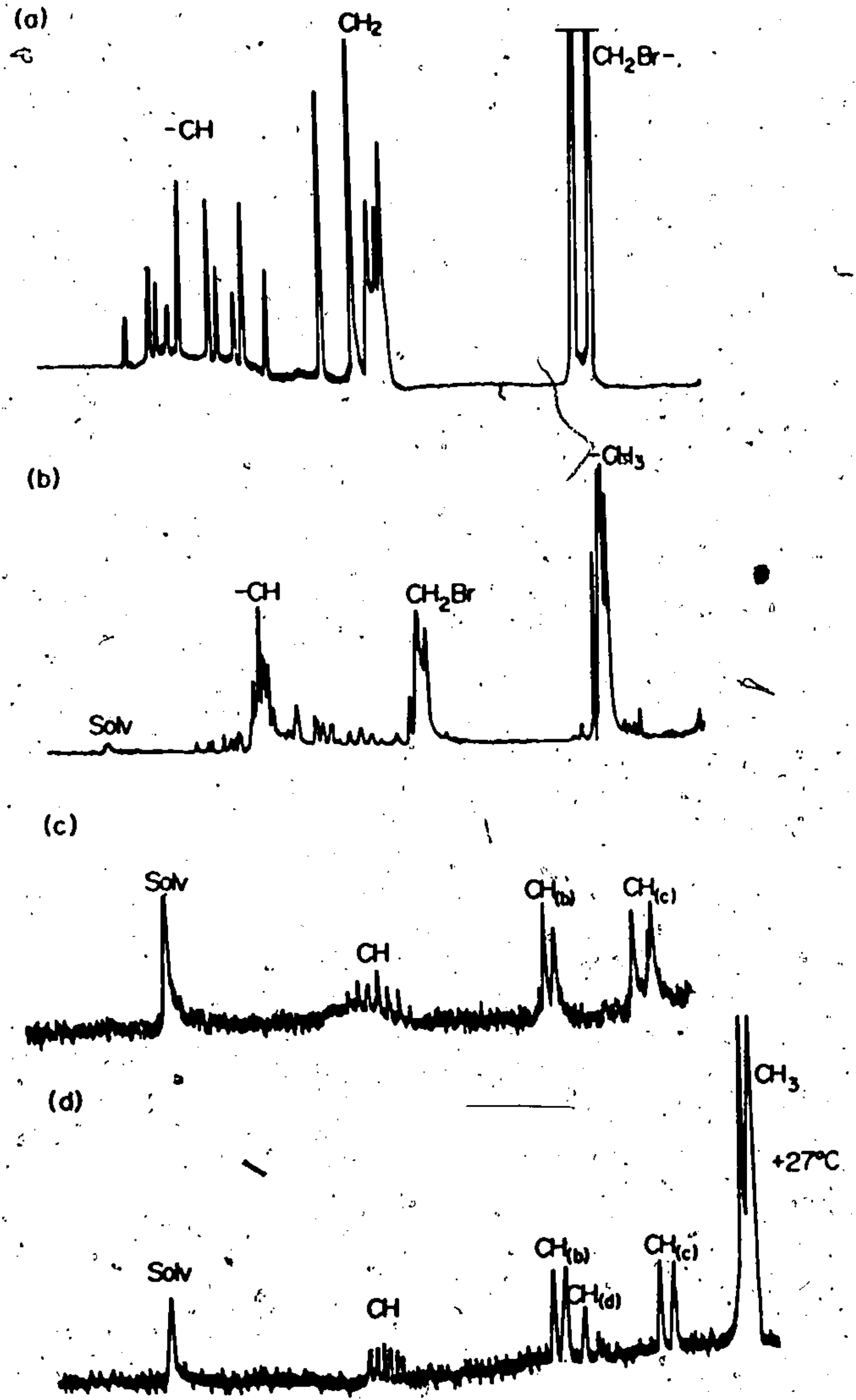
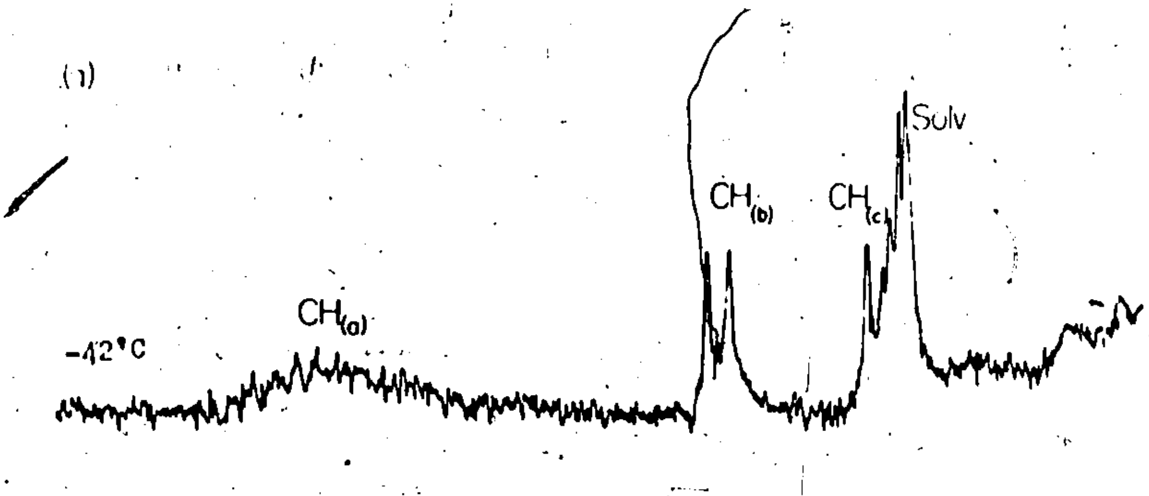


Figure (6-1) a & b: ^{1}H NMR spectra of CH_2=CHCH$_2$Br and CH$_3$CH=CH CH$_2$Br.
c & d: ^{1}H NMR spectra of [(Π-R ^{2})NiBr]$_2$ in benzene-d$_6$ at 27°C.



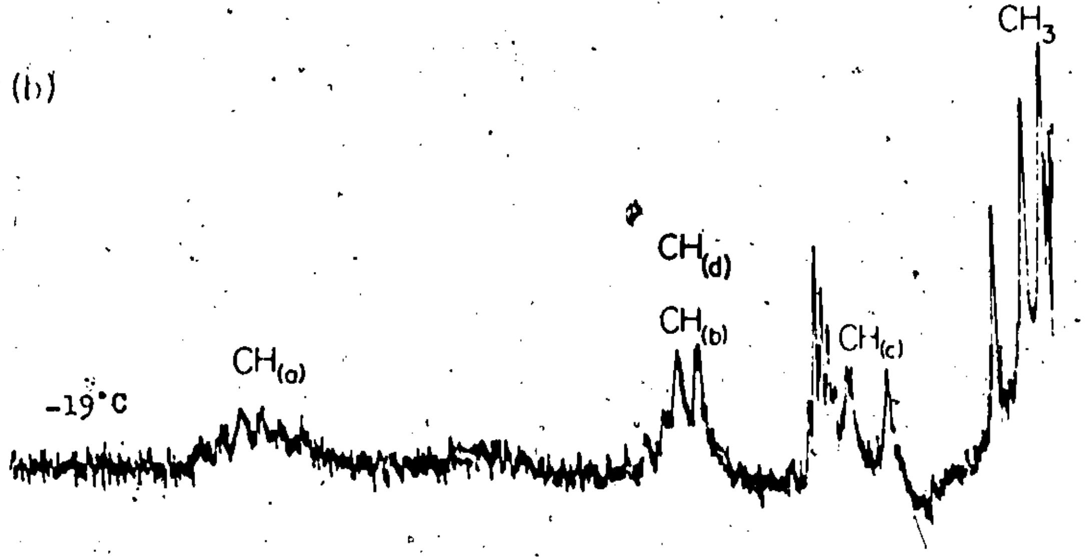


Figure (6-2a): ^1H NMR spectrum of $[(\Pi\text{-}C_3H_5)NiBr]_2$

Figure (6-2b): ^1H NMR spectrum of $[(\Pi\text{-}CH_3C_2H_4)NiBr]_2$

Solvent: acetone-d_6

Table (6-1)

^{1}H NMR Data for $[RNiBr]_2$ Complexes (56.4 MHz)

Complex	H_a	H_b	H_c	H_d	CH_3	t°c
$[(\Pi\text{-}C_3H_5)NiBr]_2^*$	-270	-154	-123			27°
$[(\Pi\text{-}C_3H_5)NiBr]_2^\dagger$	-308	-176	-121			-42°
$[(\Pi\text{-}CH_3C_3H_4)NiBr]_2^*$	-263	-148	- 84	-148	-35	27°
$((\Pi\text{-}CH_3C_3H_4)NiBr)_2^\dagger$	-306	-160	-101	-160	-46	-19°

*solvent C_6D_6

†solvent acetone-d_6

All shifts measured from TMS

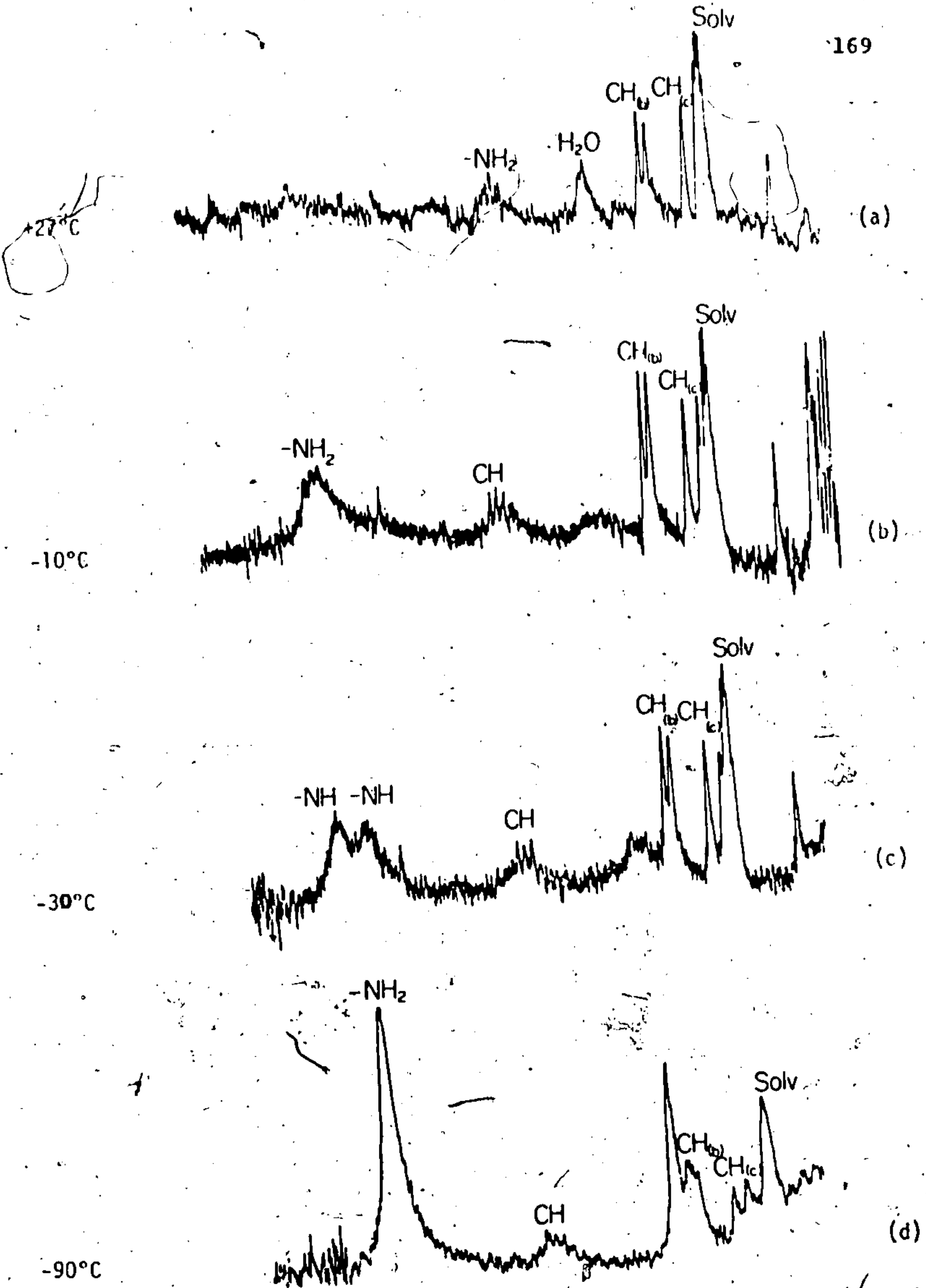


Figure (6-3-a,b,c): ^1H NMR spectra of $(\Pi\text{-}C_3H_5)Ni(Tu)_2Br$ at various temperatures.

Figure (6-3d): with excess Tu.

that a change in geometry in allyl group might take place at low temperatures (below -80°C). The chemical shift data are summarized in Table (6-2).

Turning to Π-allyl- or Π-crotylnickel complexes of substituted thioureas [Fig.(6-3e) and Fig. (6-3h)]. the interpretation and assignment come out naturally. There are two lines ascribable to -NH or $-CH_3$ groups of coordinated ligands arising from the restricted rotation of C-N bond at low temperatures. Π-allyl and Π-crotyl group show a similar pattern as reported previously. $(\Pi\text{-}C_3H_5)Ni(Nptu)_2Br$ yields three resonances attributable to two "inside" and one "outside" protons. The naphthyl group does not appear to be shifted from the corresponding free ligand line [Fig. (6-3f)].

All complexes form reddish brown solutions with added acetylenes such as $CH_3C{\equiv}CH$, Ph.C≡C.Ph, and $ClCH_2C{\equiv}CCH_2Cl$. It is possible that coordination of these acetylenes might occur in solution. The ^1H NMR spectra of these solutions show only the complex resonances and that of added acetylene. Cooling the solution gives no additional evidence for complexed acetylene.

(6-5) DISCUSSION

(a) Ligand Dissociation

$[(\Pi\text{-allyl})NiBr]_2$ and $[(\Pi\text{-crotyl})NiBr]_2$ complexes form a more reactive species in acetone-d_6. Presumably it could be due to the formation of a solvated monomeric complex.

$$[(R)NiBr]_2 + 2S \rightleftharpoons 2(R)Ni(S)(Br)$$

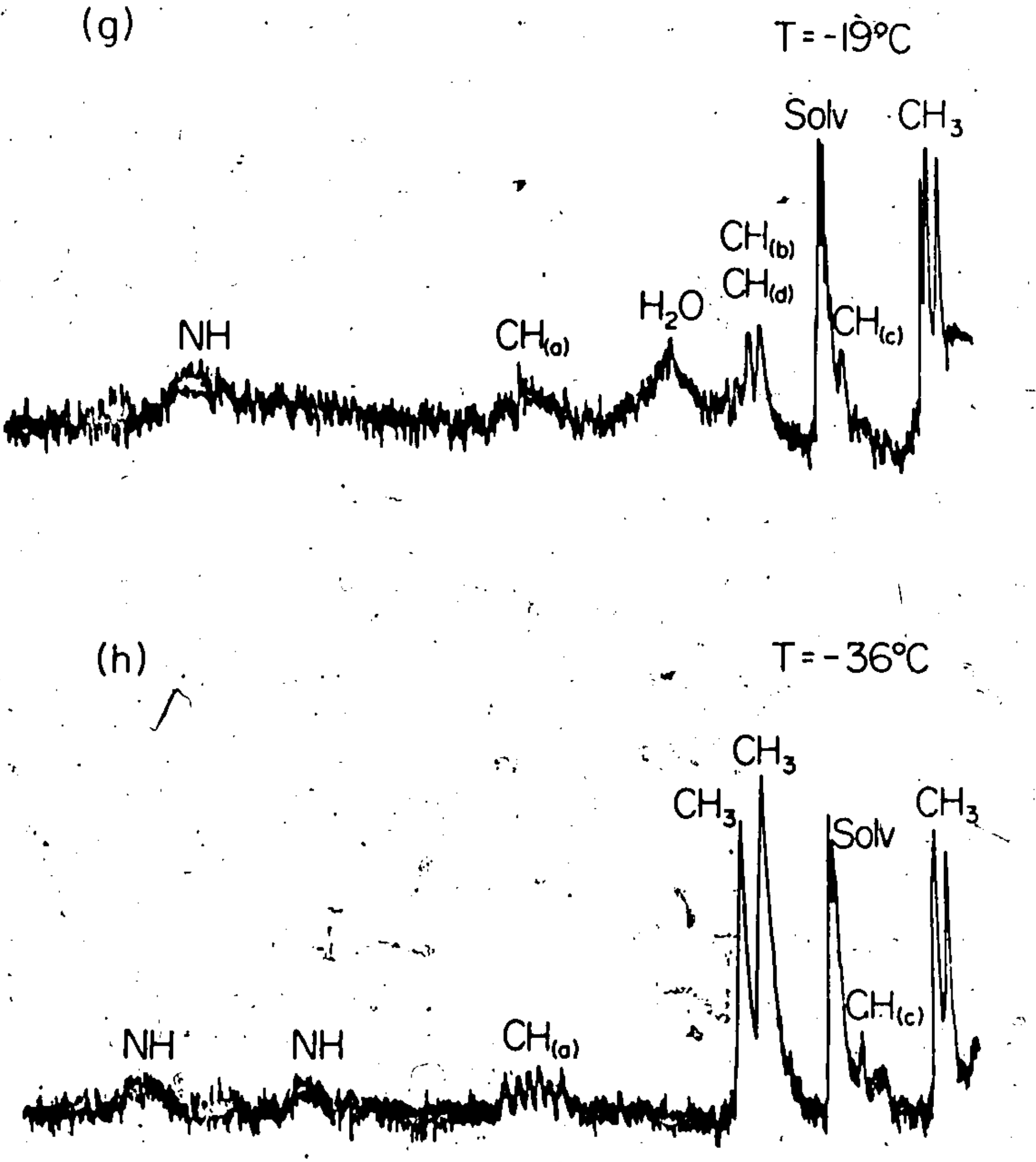


Figure (6-3g, h): ^{1}H NMR spectra of (Π-crotyl) Ni(Tu)$_2$Br and (Π-crotyl) Ni(Dmtu)$_2$Br in acetone-d$_6$

Table (6-2)

^1H NMR Data for Complexes $RNi(L)_2Br$

Π-allyl or Π-crotyl						Thiourea or Substituted Thiourea				
Complex	H_a	H_b	H_c	H_d	CH_3	"Inside" NH	"Outside" NH	"Inside" CH_3	"Outside" CH_3	t°c
$(\Pi\text{-}C_3H_5)Ni(Tu)_2Br$	-305	-172	-131	-	-	-473	-448	-	-	-35°
$(\Pi\text{-}C_3H_5)Ni(Mtu)_2Br$	-	-	-	-	-	-	-	-	-	-
$(\Pi\text{-}C_3H_5)Ni(Dmtu)_2Br$	-309	-174	-144	-	-	-509	-439	-170	-158	-17°
$(\Pi\text{-}C_3H_5)Ni(Nptu)_2Br$	-303	-178	-146	-	-	-593 -477.	-362	-	-	-10°
$(\Pi\text{-}CH_3C_3H_4)Ni(Tu)_2Br$	-289	-159	-101	-159	-54	-474	-446	-	-	-30°
$(\Pi\text{-}CH_3C_3H_4)Ni(Dmtu)_2Br$	-295	-160	- 97	-160	-54	-511	-419	-172	-156	-22°

All shifts measured from TMS (56.4 MHZ)

Solvent = acetone

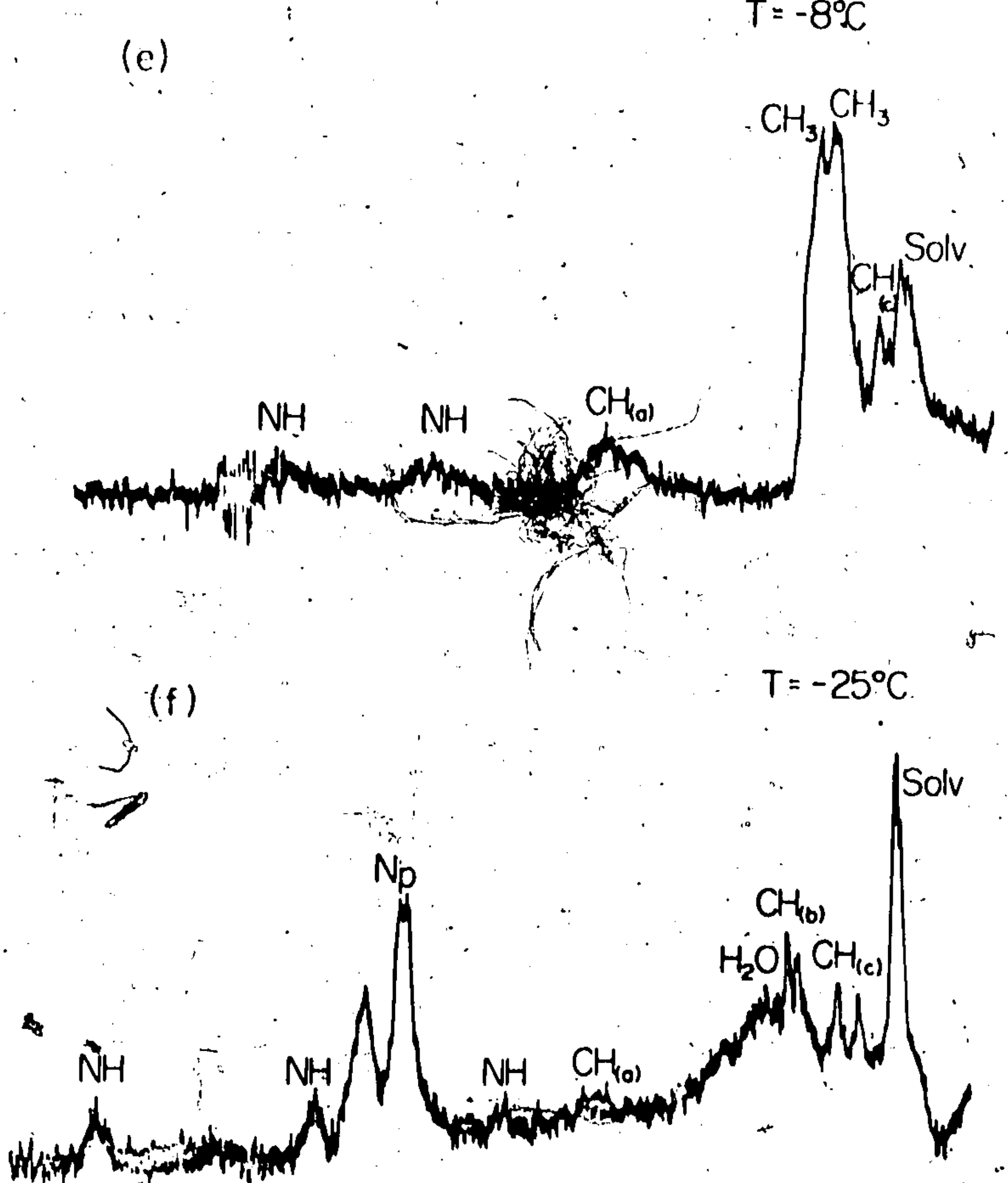


Figure (6-3e,f): ^{1}H NMR spectra of (Π-allyl) Ni(Dmtu)$_2$Br and (Π-allyl) Ni(Nptu)$_2$Br in acetone-d$_6$.

Conductivity data[171] indicate that orange-red (Π-C_3H_5)NiL_2Br exists as (Π-C_3H_5)$Ni(L)_2^+$ in methanol or acetone. All crotyl complexes behave similar. Ligand dissociation of these complexes can be expressed as

$$(R)NiL_2^+ + S \rightleftharpoons (R)NiL_2(S)^+$$

$$(R)NiL_2S^+ \rightleftharpoons (R)NiL(S)^+ + L$$

All these complexes are diamagnetic, and the shifts exhibited by the ligand protons are extremely small relative to their corresponding free ligand position. Therefore we do not feel that we can make quantitative measurements on the solution equilibria.

(b) Ligand Exchange Process

A qualitative study on ligand lability of these complexes have been made. The ^1H NMR spectrum of (Π-C_3H_5)$Ni(Tu)_2Br$ with excess free thiourea reveals a single -NH line attributable to a rapid exchange. The average line remains sharp up to -90° and no free ligand resonance is observed (i.e. ligand exchange remains fast). All other complexes show similar behaviour. The corresponding naphthyl complex is less soluble and we do not report its data. Previous exchange study with diamagnetic square-planar $Ni(Tu)_3X^+$ could possibly predict that all these complexes would exchange through a bi-molecular process. However, unlike $Ni(Tu)_3X^+$, these complexes undergo extremely fast chemical exchange down to -90°C, and neither a complexed nor a free ligand line has been observed. At higher temperatures the collapse of the "inside" and "outside" ligand protons can be observed. The temperature at which this occurs is different for the various complexes as is indicated below

$$RNi(Tu)_2Br \simeq RNi(Mtu)_2Br > RNi(Dmtu)_2Br \gg RNi(Nptu)_2Br$$

$$t°C \simeq \quad -35° \qquad -23° \qquad -17° \qquad -10°$$

This implies decreasing ligand dissociation along this series.

It is interesting to note that all lines attributable to the π-allyl group do not show any significant change during rapid exchange. A similar behaviour is shown by the crotyl complexes.

CHAPTER VII

STRUCTURE AND LIGAND EXCHANGE OF Zn(II) COMPLEXES OF THIOUREA

(7-1) INTRODUCTION

Relatively little information is available on the kinetics of ligand exchange reactions of tetrahedral complexes of non-transition metals such as zinc. These reactions are usually quite rapid and the NMR techniques can be applied. It would be of interest to compare rates with those of corresponding Co and Ni complexes.

(7-2) EXPERIMENTAL SECTION

The following complexes have been synthesized by literature methods.[176]

$Zn(Tu)_2Cl_2$

$Zn(Mtu)_2Cl_2$

$Zn(Tu)_4(NO_3)_2$

$Zn(Tu)_4(ClO_4)_2$

Stoichiometric quantities of zinc chloride and thiourea were dissolved in a mixture (water and ethanol 3:1 by volume) and the solution heated for 10 minutes until a clear solution was obtained. The hot solution was filtered and allowed to evaporate at room temperature for several days. The white colourless crystalline substance obtained was washed several times with ether and the remaining ether pumped off. The resulting crystals were dried in vacuo over P_4O_{10} to give a crystalline solid. Products were characterized by their melting points which agree well with data in the literature.[176]

(7-3) STRUCTURE

All thiourea complexes of Zn(II) have been investigated by infrared spectra. They are all bonded through the sulphur atom. They are also thought to have pseudo-tetrahedral geometry.[123] Spectroscopic studies have also shown that in solvents such as acetone, these complexes are partly dissociated.[178] Conductivity data indicate that it is the thiourea which dissociates. The perchlorate complex is a 1:2 electrolyte.

The ^1H NMR spectrum of $Zn(Tu)_2Cl_2$ (Fig. 7-1a) shows that the NH_2 resonance has been shifted downfield relative to free thiourea. Addition of free ligand shifts the resonance to high field indicating fast exchange. On cooling a solution of $Zn(Tu)_2Cl_2$ to around 0°C, the thiourea resonance is split into a doublet, which is attributed to restricted rotation about the C-N bond (Fig. 7-1b). Cooling a solution containing excess ligand to -80°C gives both free and complexed ligand peaks, i.e. the ligand exchange becomes completely slow (Fig. 7-1c). The spectra of $Zn(Tu)_4(NO_3)_2$ and $Zn(Tu)_4(ClO_4)_2$ are similar except that a temperature of -25°C is necessary to freeze out the C-N bond rotation in the nitrate and the line remains a singlet to -80°C in the perchlorate.

^1H NMR spectra of $Zn(Mtu)_2Cl_2$ in acetone-d_6 exhibit similar behaviour. The NH_2 resonance has been shifted downfield but the CH_3 resonance remains

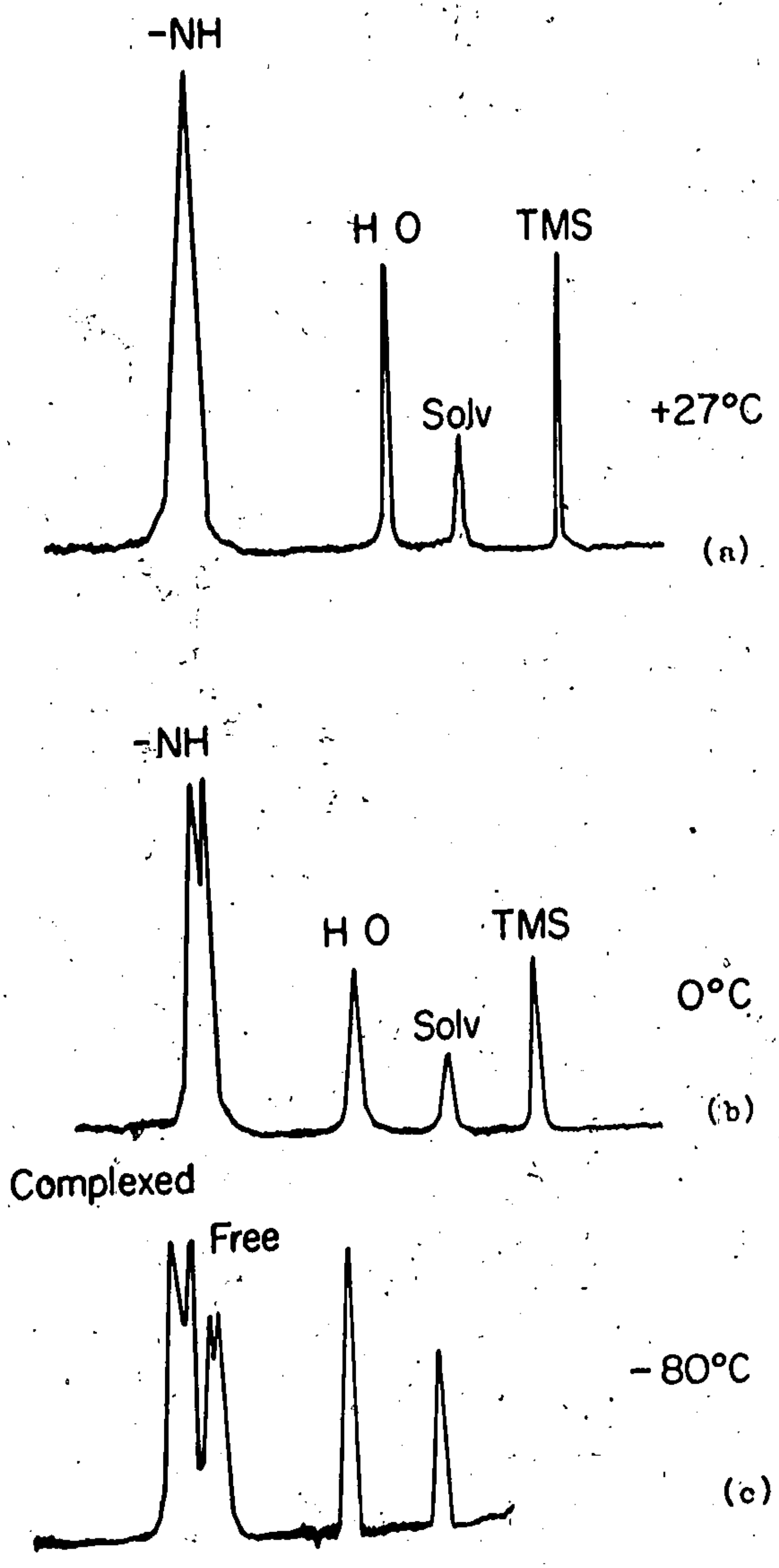


Figure (7-1) ^{1}H NMR Spectra of $Zn(Tu)_2Cl_2$ at 56.4 MHz. Solvent: acetone-d_6

unshifted relative to free ligand. At +8°C, both resonances are split into each doublet, which is again ascribed to restricted rotation about the C-N bond. This indicates that barrier of rotation is higher in $Zn(Mtu)_2Cl_2$ than in $Zn(Tu)_2Cl_2$ (Fig.7-2). Chemical shift data for all complexes are reported in Table(7-1).

(7-4) DISCUSSION

(7-4a) NUCLEAR MAGNETIC RESONANCE SPECTRA

All the NMR data can be readily interpreted on the assumption that thiourea is bonded to the metal through sulphur and that rotation about the C-N bond is completely restricted at low temperatures. All complexes show two resonances, one shifted to low field and one to high field. Since they all are diamagnetic, the effect of the metal on the chemical shifts of ligand protons is comparatively small. The behaviour of coordinated thiourea should be similar to that exhibited by a free ligand. Therefore, the "out-side" proton which is closer to thio-carbonyl group of the complexed ligand is assigned to high field line whereas the "inside" proton which is less close to the thio-carbonyl group of the complexed ligand to low field line. Similar assignment has been made for $Zn(Mtu)_2Cl_2$ for which the isomers with "outside" methyl group is preferred as might be anticipated on steric grounds.

Table(7-1) Chemical Shifts of Zinc Complexes

Compounds	NH		CH_3		Temp. °C
	Room Temp. (27°C)	Low Temp.	Room Temp. (27°C)	Low Temp.	
$Zn(Tu)_2Cl_2$	-441	-474 -457			-50
$Zn(Mtu)_2Cl_2$	-434	-457 -427	166	166 163	+ 8
$Zn(Tu)_4(NO_3)_2$	-430	-455 -438			-30
$Zn(Tu)_4(ClO_4)_2$	-456	-464			-60

All shifts measured from TMS at 56.4 MHz; solvent acetone-d_6

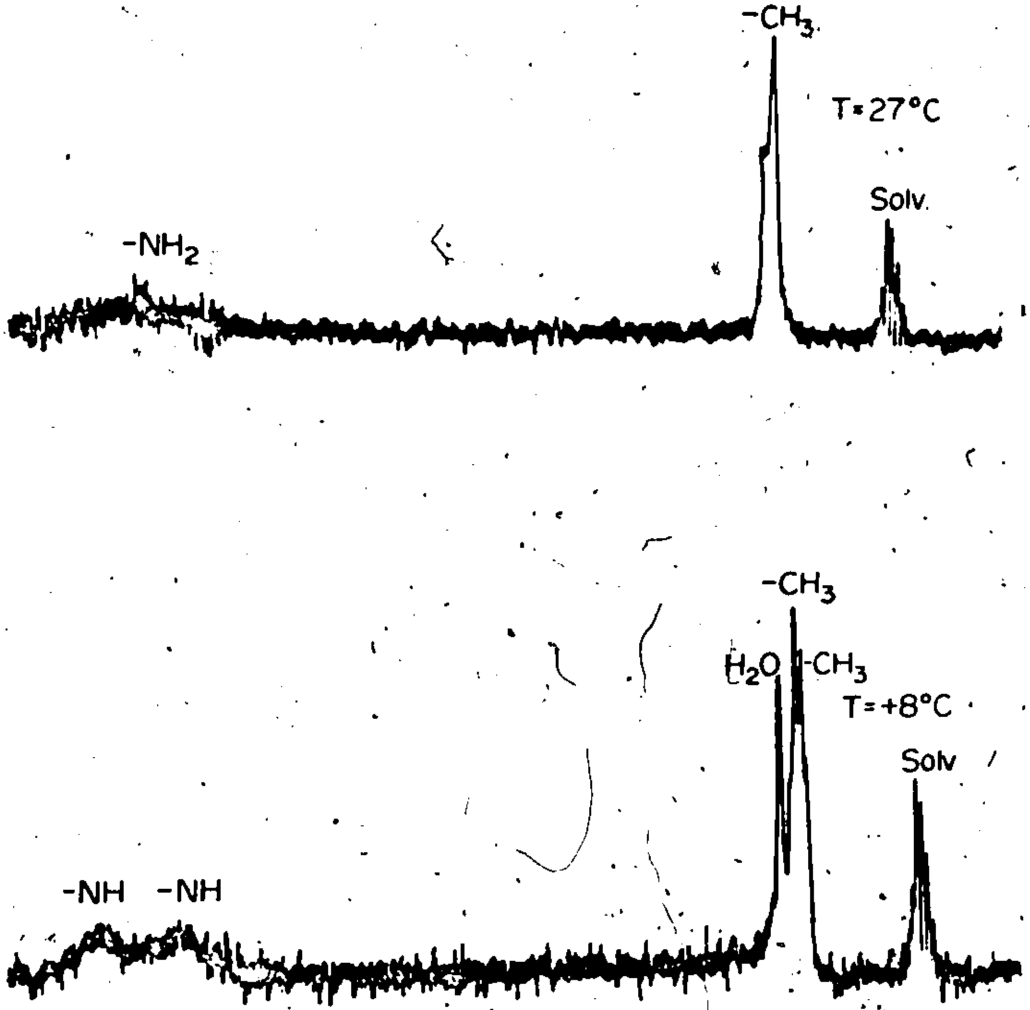


Figure (7-2) ^{1}H NMR Spectra of Zn(Mtu)$_2$Cl$_2$(56.4 MHz). Solvent: acetone-d_6

(7-4b) LIGAND DISSOCIATION

All complexes are diamagnetic both in solid and solutions and quantitative measurements on solution equilibria are difficult. However, the measured shifts from the free ligand position clearly decrease in the order:

$$Zn(Mtu)_2Cl_2 \approx Zn(Tu)_2Cl_2 > Zn(Tu)_4(NO_3)_2 > Zn(Tu)_4(ClO_4)_2$$

This implies that ligand dissociation is also increasing in this order. This behaviour closely parallels that of the analogous Co complexes.

(7-4c) THE LIGAND EXCHANGE PROCESS

Some deductions regarding mechanism from the variation of the line widths with concentration of added ligand have been made. It has been found that the line width of the complexed ligand increases with increase in concentration of added ligand, but the line width of free ligand remains constant. This indicates that an associative mechanism predominates.

The temperature at which coalescence of free and complexed ligand signals occurs is a qualitative measure of relative exchange rates. It has been found that the variation of this temperature is surprisingly small (-58° to -62°C) for $Zn(Mtu)_2Cl_2$ and $Zn(Tu)_2Cl_2$ (Fig. 7-3). The perchlorate complex does not show coalescence down to -90° indicating the ligand exchange remains fast. Estimation of τ has been made for both halide complexes at their coalescence temperatures and the bimolecular rate constant ($k_3 = 1/\tau[Tu]$) is found to be in the order of 10^3 mole^{-1} sec^{-1}.

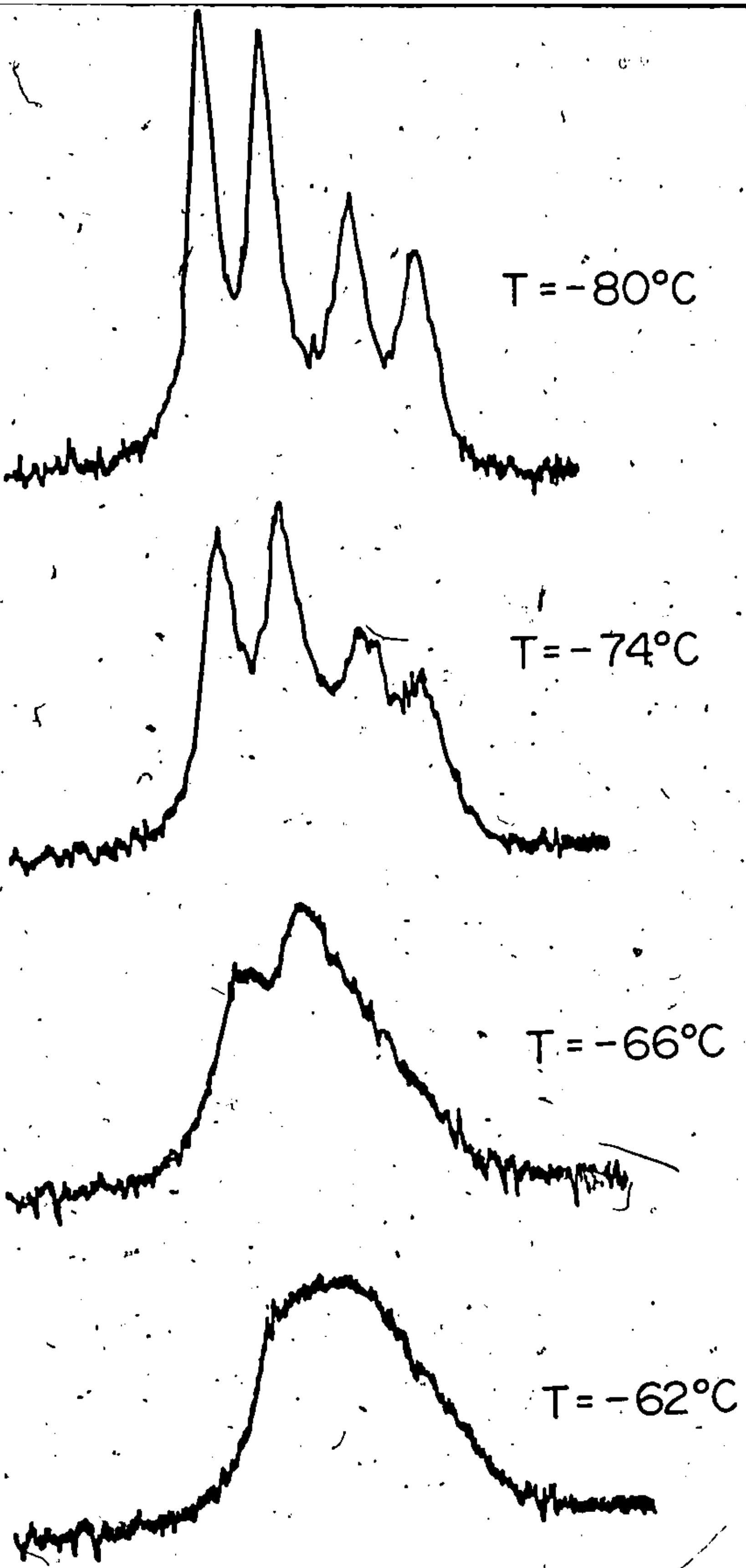


Figure (7-3) ^{1}H NMR spectra of $Zn(Tu)_2Cl_2$ with excess of free ligand at low temperatures.

Diamagnetic Zn complexes do not show significant temperature depencence of their chemical shifts. Equation (7-1) can therefore be employed to obtain approximate activation parameters. Under the conditions such that both complexed and free ligand lines (A and B) are observed and that the ligand exchange process is barely frozen out, the life-time of the exchanging ligand can be related to the peak separation $(\nu_A - \nu_B)$ of the two resonances by

$$\tau_A = \frac{1}{\sqrt{2}\,\pi[(\overset{\circ}{\nu}_A - \overset{\circ}{\nu}_B)^2 - (\nu_A - \nu_B)^2]^{\frac{1}{2}}} \qquad (7\text{-}1)$$

where $(\overset{\circ}{\nu}_A - \overset{\circ}{\nu}_B)$ is the difference in frequencies of the two resonances under a complete exchange (i.e. -80°C). All these parameters were measured for $Zn(Tu)_2Cl_2$ in the temperature range of -60° to -80°C respectively [Fig.(7-3)]. The variation of life-time with temperature has been recorded in Table (7-2). The activation parameters were obtained by using equation (2-34) in Chapter II, and by plotting $\Delta G^{\ddagger}$'s versus the absolute temperatures as shown in Fig. (7-4).

It is interesting to note that the entropy ($\Delta S^{\ddagger} = -32 \pm 3$ cal. $°K^{-1}$ mole^{-1}) and enthalpy ($\Delta H^{\ddagger} = 2.2 \pm 0.6$ kcal/mole) of activation are quite similar to those obtained for the corresponding tetrahedral Co and Ni complexes discussed in Chapter IV and Chapter V. It is also important to know that the lability of a Zn complex is comparable with those of the corresponding paramagnetic compounds.

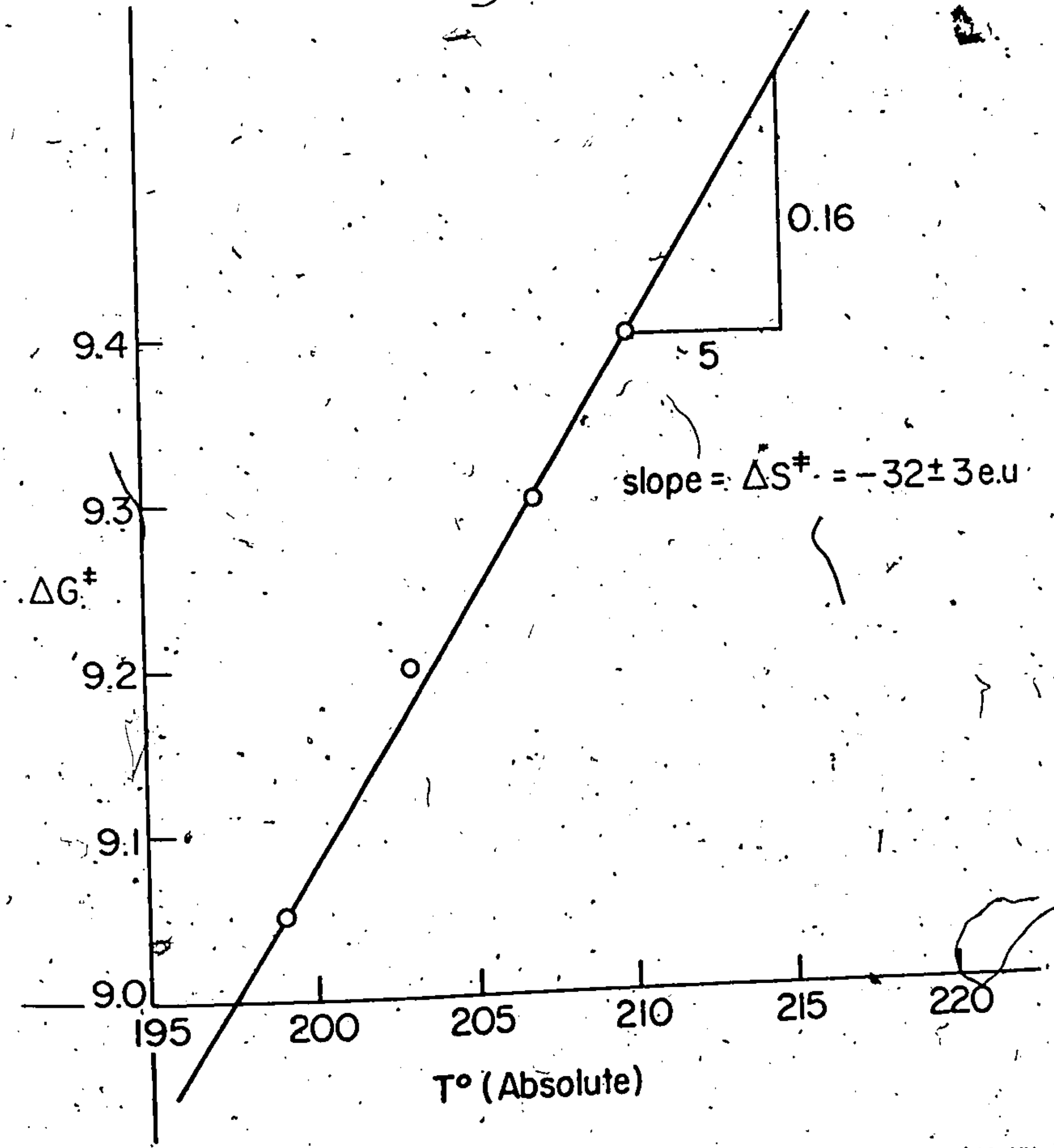


Figure (7-4): $\Delta G_3^{\ddagger}$'s versus T° (Absolute) for $Zn(Tu)_2Cl_2$ in acetone-d_6 (60 MHz).

Table (7-2): Kinetic and Activation Parameters for Ligand Exchange in $Zu(Tu)_2Cl_2$

t°C	cps $(\nu_A^\circ - \nu_B^\circ)$ (60 MHz)	cps $(\nu_A - \nu_B)$ (60 MHz)	τ_A^* sec.	$\tau_A[Tu]^*$	$k_3 = \frac{1}{\tau_A[Tu]^*}$ $mol^{-1} sec^{-1}$	ΔG^* K.cal.,mole^{-1}	T° Abs. Temp	ΔH^* K cal mole^{-1}	ΔS^* e.u.
coalescence									
-63°	-	28	5.0×10^{-3}	1.17×10^{-3}	8.5×10^2	9.4	210	+2.7±0.6	-32±3
-66°	-	38	6.2×10^{-3}	1.24×10^{-3}	6.9×10^2	9.3	207		
-70°	-	42	8.8×10^{-3}	2.06×10^{-3}	4.9×10^2	9.2	203		
-74°	-	46	12.0×10^{-3}	2.80×10^{-3}	3.6×10^2	9.1	199		
limiting									
-80°	46	-	-	-	-	-	-	-	-

$\tau_A^* = \frac{1}{\sqrt{2}\,\pi(\nu_A^\circ - \nu_B^\circ)}$ (coalescence temp.); $\tau_A^* = \frac{1}{\sqrt{2}\,\pi[(\nu_A^\circ - \nu_B^\circ)^2 - (\nu_A - \nu_B)^2]^{1/2}}$ (slow exchange)

[Complex] = 12.9×10^{-2}M; [Tu] = 10.5×10^{-2} M; [Tu]* = 23.4×10^{-2} M (total conc.) e.u.=Cal.K^{-1}.mole^{-1}.

The high-temperature data of $Ni(Tu)_2X_2$ and $Co(Tu)_2X_2$ have been extrapolated to lower temperature for comparison purposes with zinc complexes. It is found that at -62°C, the bimolecular rate constants of nickel and cobalt complexes are at least 10 times greater than those of zinc complexes. This is presimably due to a lower possibility of formation of an intermediate with higher coordination number in zinc than in nickel and cobalt complexes, despite the fact that crystal field stabilization effect would favour the reverse.

SUMMARY OF RESULTS ON THIOUREA COMPLEXES

STRUCTURAL STUDIES

a) The Co(II) complexes were previously known to have tetrahedral geometry in acetone solution with some replacement of thiourea by solvent. Equilibrium constants and thermodynamic parameters for this process have been measured. The extent of thiourea dissociation is found to increase in the order

$$Cl < Br < I < NO_3 < ClO_4$$

b) The Zn(II) complexes were also known to be tetrahedral. The small chemical shifts restrict quantitative measurements but it has been shown that the extent of the dissociation varies with anion in the same order as for Co(II).

c) The Ni(II) halides have been shown to exist in solution as equilibrium mixtures of tetrahedral NiL_2X_2 and square-planar NiL_3X^+. The proportion of square-planar complex increases at low temperature. At a given temperature, the proportion of square-planar complex increases in the order $Cl < Br < I$. At very low temperatures, some octahedral $Ni(Tu)_6^{2+}$ is present in solutions of the iodide.

Complexes of N-naphthyl thiourea are present in solution only as tetrahedral NiL_2X_2.

The perchlorate and borofluoride complexes show an equilibrium between square-planar NiL_4^+ and octahedral NiL_6^{2+}. Thermodynamic parameters for the tetrahedral$\rightleftharpoons$square-planar and octahedral$\rightleftharpoons$square-planar equilibrium are presented and the dependence of geometry on metal charge is discussed.

Ni(II) complexes with thiourea and π-allyl ligands are diamagnetic and square-planar in solution. There is some displacement of thiourea by solvent acetone in all of these complexes.

KINETICS AND MECHANISM OF LIGAND EXCHANGE

(a) Two mechanisms are available for ligand exchange of the Co(II) complexes. The first is a direct associative exchange with free ligand. The second involves prior replacement of thiourea by solvent acetone. Activation parameters for both mechanisms are presented. In each case, the rate-determining step is formation of a five-coordinated intermediate. Analysis of the data yields $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the three processes

$$CoL_2X_2 + L \longrightarrow CoL_3X_2$$

$$CoL_2X_2 + S \longrightarrow CoL_2SX_2$$

$$CoLSX_2 + L \longrightarrow CoL_2SX_2$$

The rates for these three processes are very different.

(b) The [redacted] of complex mixtures of isomers restricts quantitative rate studies of the Ni(II) complexes. The tetrahedral complexes undergo ligand exchange by a associative mechanism with the rates increasing in the order

I < Br < Cl as was found for the cobalt complexes. The rates are somewhat greater for Ni than Co. The square-planar complexes also show an associative mechanism with the rate for the Br being less than that for the I. The rate of exchange of thiourea in the Π-allyl complexes is very high. The octahedral compounds exchange by a dissociative mechanism. This process shows a positive $\Delta S^{\ddagger}$ in contrast to the large negative $\Delta S^{\ddagger}$ found for the associative reactions.

(c) The tetrahedral Zn complexes exchange ligands by an associative process. The rates are lower than for Co(II) or Ni(II).

APPENDIX

A NUCLEAR MAGNETIC RESONANCE STUDY OF DIACETAMIDE COMPLEXES OF SOME TRANSITION METAL IONS

(8-1) INTRODUCTION

The bulk of this thesis has been concerned with NMR studies of labile complexes of monodentate thiourea complexes. This appendix reports some preliminary work on diacetamide (DA=$CH_3CONHCOCH_3$) complexes. This work was undertaken with two objectives in mind. First of all, it appeared probable that the complexes would provide examples of labile compounds involving bidentate ligands and it is of interest to compare the exchange mechanisms with those found for monodentate ligands. Secondly, the diacetamide ligand is isoelectronic with acetylacetone. Complexes involving the anion of acetylacetone have been extensively studied and the spin delocalization mechanisms of the paramagnetic complexes discussed at length.[179]

By comparison very few complexes of neutral acetylacetone are known[1] and in general, such compounds are not formed with paramagnetic metal ions. A comparison between spin delocalization in a neutral acetylacetonate, e.g. $Fe(acac)_3$ and in the isoelectronic charged diacetamide, e.g. $Fe(DA)_3^{+3}$, would therefore be of interest. The obvious prediction is that metal to ligand charge transfer processes would be inhibited and ligand to metal charge transfer processes enhanced.[179] A number of factors have prevented the complete achievement of either of these objectives but some initial results concerned mostly with the solution structure of diacetamide complexes are presented here.

(8-2) EXPERIMENTAL SECTION

The following compounds were synthesized following methods reported in the literature.[180,181]

$Zn(DA)_3(ClO_4)_2$

$Co(DA)_3(ClO_4)_2$

$Co(DA)_3Br_2$

$Co(DA)_3(CoBr_4)$

$Ni(DA)_3(ClO_4)_2$

$Fe(DA)_3(ClO_4)_2$

$Fe(DA)_3(BF_4)_2$

$Mn(DA)_3(ClO_4)_2$

Separate solutions of metal perchlorate hydrate (0.010 mole) in 25 ml of ethylacetate and diacetamide (0.040 mole) in 25 ml of ethylacetate were filtered into a common receiver. Precipitation of the solid complexes usually began immediately. The solid complex was collected by filtration and washed with ether for several times. Residual solvent and water were removed under vacuum. The corresponding bromide complexes were prepared by grinding together stoichiometric amounts of the $CoBr_2$ and diacetamide, washing with ether and drying the product.

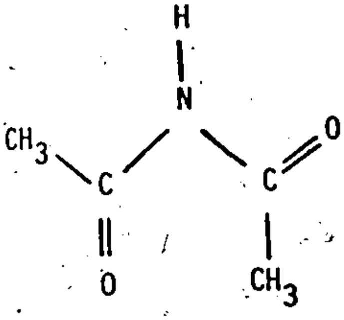
(8-3) PREVIOUS WORK

Diacetamide complexes with many of the first row transition metal elements have been known for over a decade. They have been extensively investigated using spectroscopic and magnetic measurements.[180,181] They have not previously been studied by NMR. Conductivity data indicate that all perchlorate complexes are 1:2 electrolytes in acetone.[181] Complexes of type $Co(DA)_3Br_2$ and $Co(DA)_3(CoBr_4)_2$ have a lower conductivity, indicating the dissociation of diacetamide and retention of bromide ion. Infrared study suggests that diacetamide retains a trans-trans configuration upon complexation although there are reports of some possible other structures.[182]

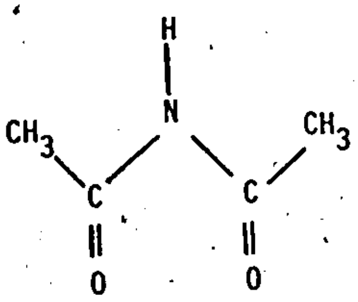
Therefore, the most reasonable method of attachment of a trans-trans diacetamide molecule to a transition metal ion is by chelation through the two amide oxygen atoms. The structural similarity of the ligand in this position to that found for the isolectronic acetylacetonato ion is of course readily apparent. However, electron delocalization is reported to be considerably smaller in the diacetamide complexes than in the acetylacetonato complexes on the basis of optical data.[181] The complex cations probably have D_3 symmetry.[181] The observed electronic spectra are extremely similar to those obtained for species with O_h symmetry.

(8-4) RESULTS

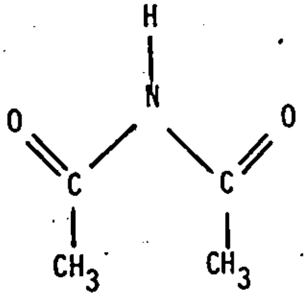
The ^1H NMR spectrum of diacetamide does not appear to have been previously examined in solution. There are some reports of solid state infrared studies[181,183] which indicate that diacetamide exists in two possible configurations (cis-trans and trans-trans) of which it prefers the cis-trans form (A). The trans-trans (B) form is relatively less stable and readily reverts to (A) upon dissolution in organic solvents.



(A)



(B)



(C)

The ^{1}H NMR spectrum of diacetamide (+27°C) in acetone-d_6 reveals a single methyl resonance and a NH line at -120 Hz and -535 Hz respectively from [Fig.(8-1a)]. This is consistent with either structure (B) or (C) but not with a static structure (A). However, rapid rotation about the C-N bond would also lead to the observed spectra for structure (A) and this is a reasonable possibility. Previous reports[183] excluded the existence of structure (C). On cooling a solution of diacetamide down to -80°C, the methyl resonance broadens (partially overlapped with a solvent line) [Fig.(8-1b)], suggesting a slow exchange between (A) and (B). Further cooling to -90°C results in the separation of the methyl resonance into a doublet of unequal intensity [(Fig.8-1c)]. The low field line is assigned to "inside" CH_3 and the high field line, to "outside" CH_3. It seems that the barrier of rotation of C-N bond is lower than that of thiourea. The internal rotation is fast above -80°C but slow below -90°C. The NH line does not show splitting at any temperature. The lifetime for the rotation is estimated to be $\sim 1.8 \times 10^{-2}$ sec. at the coalescence temperature (-80°C). Previous studies assume that diacetamide retains the trans-trans configuration upon complexation. This would allow stabilization by resonance involving

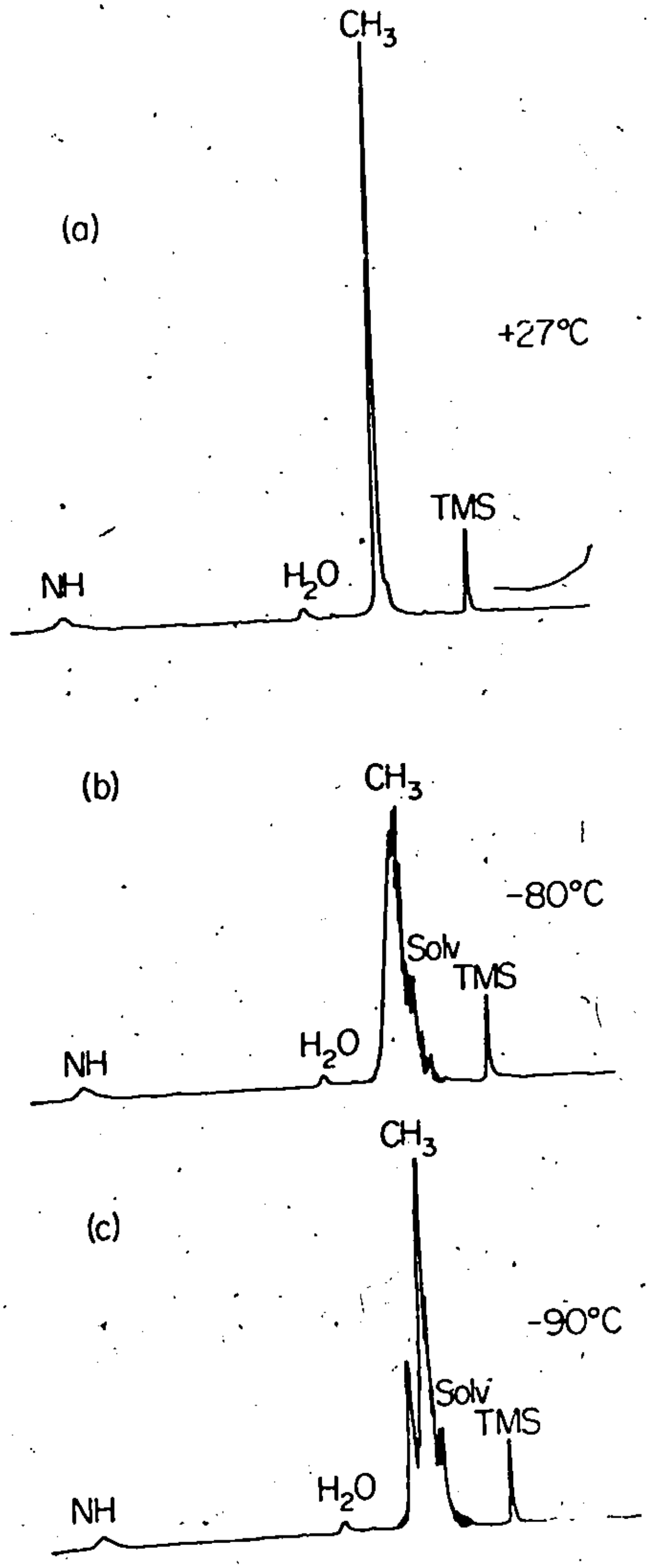
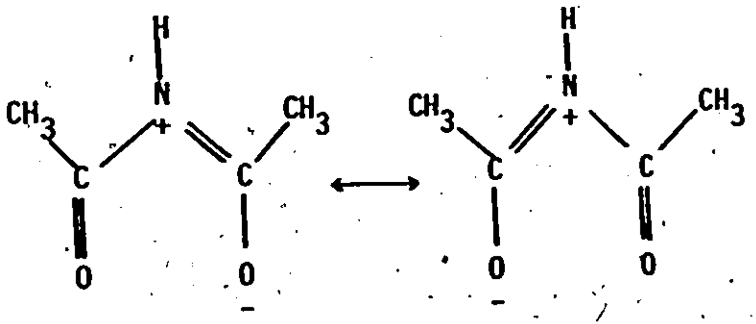


Figure (8-1): ^{1}H NMR spectra of diacetamide at various temperatures.

Solvent: acetone-d_6

structure (D). Such a structure would be planar with two "outside" methyl groups. Restricted rotation is scarely surprising since it occurs in many other amides and the phenomenon has been discussed in the case of thiourea (i.e. chapter III).



(D)

Turning to the diacetamide complexes, only one structural conclusion has been drawn. From the infrared study,[180,182] it has been concluded that they are all bonded through the oxygen atoms rather than the nitrogen. They are also thought to have octahedral geometry about the metal atom.

Figure (8-2a) exhibits the NMR spectra of $Zn(DA)_3(ClO_4)_2$ in acetone-d_6. The NH resonance (-607 Hz) has been shifted down field relative to free diacetamide but the CH_3 resonance remains unshifted. Addition of free ligand shifts the resonance to high field indicating fast exchange. The water resonance is also shifted to low field, which suggests that water is also involved in fast exchange. On cooling the solution down to -110°C, both free and complexed resonances of diacetamide and water are observed. This indicates slow exchange, and the most likely, an equilibrium involving $Zn(DA)_2(H_2O)_2^{+2}$. The NH and water resonances of the complex appear at (-693 Hz) and (-380 Hz) respectively from TMS [Fig.(8-2b)].

Figure (8-3) shows some representative spectra of Co complexes.

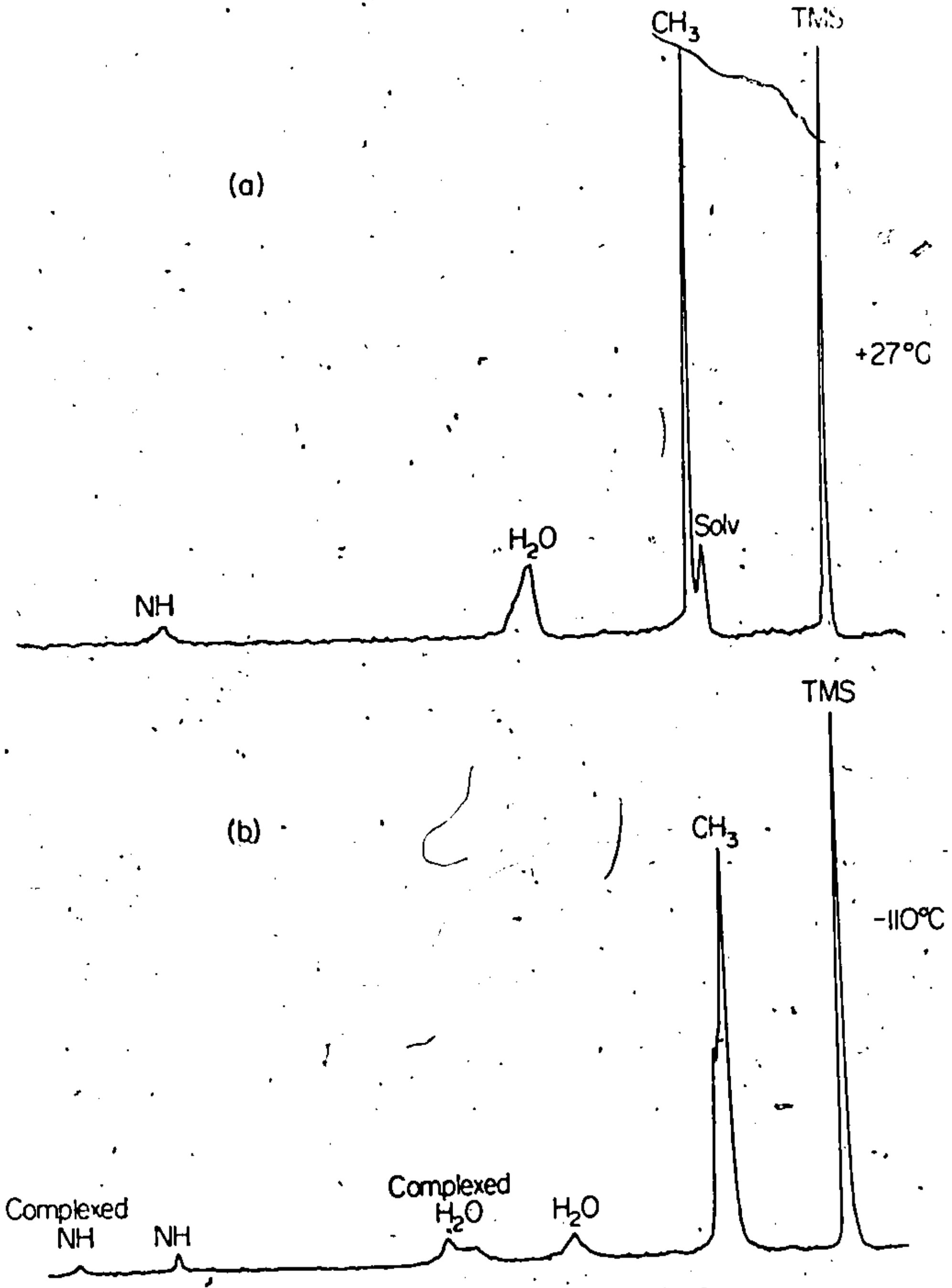


Figure (8-2): ^{1}H NMR spectra of $Zn(DA)_3(ClO_4)_2$ in acetone-d_6 at various temperatures.

As anticipated for paramagnetic compounds, the shifts are much larger than those of the diamagnetic zinc complex [Fig. (8-3a)]. Three broad lines are observed for all Co complexes. The third line may be due to complexed water. Addition of excess ligand shifts these lines to high field suggesting fast exchange [Fig. (8-3b)]. At -110°C, perchlorate complex shows two resonances at -2962 Hz and -2333 Hz from TMS, attributable to NH and CH_3 groups of coordinated ligand. In addition, there are three broad lines with still larger shifts (~ -4000 Hz), and their interpretation and assignment are dubious. Also, two resonances attributable to free diacetamide are observed. It is possible that the free diacetamide can occupy a second coordination sphere site through hydrogen bondong. Addition of free ligand increased their intensities indicating slow exchange [Fig. (8-3d)]. Turning to $Co(DA)_3Br_2$, there are two sets of methyl resonances at -2962 Hz and -769 Hz respectively from TMS [Fig. (8-4a)]. There is no observable NH resonance at low field. A similar spectrum is given by the corresponding $Co(DA)_3(CoBr_4)$. It is possible that $Co(DA)_2Br_2$ might be present in solution.

The assignment and interpretation of the NMR spectra exhibited by Co complexes are highly uncertain and a more detailed study is in need. However, in the perchlorate complex, there is a strong possibility of a hydrogen-bonded diacetamide occupying an outer-sphere coordination site. As the water resonance is shifted from its diamagnetic position, there is a possibility of water competing with diacetamide.

The remaining compounds of Ni and Mn are less soluble in acetone-d_6 and their NMR spectra could not be obtained. However, $Fe(DA)_3X_2$ ($X=ClO_4$, BF_4)

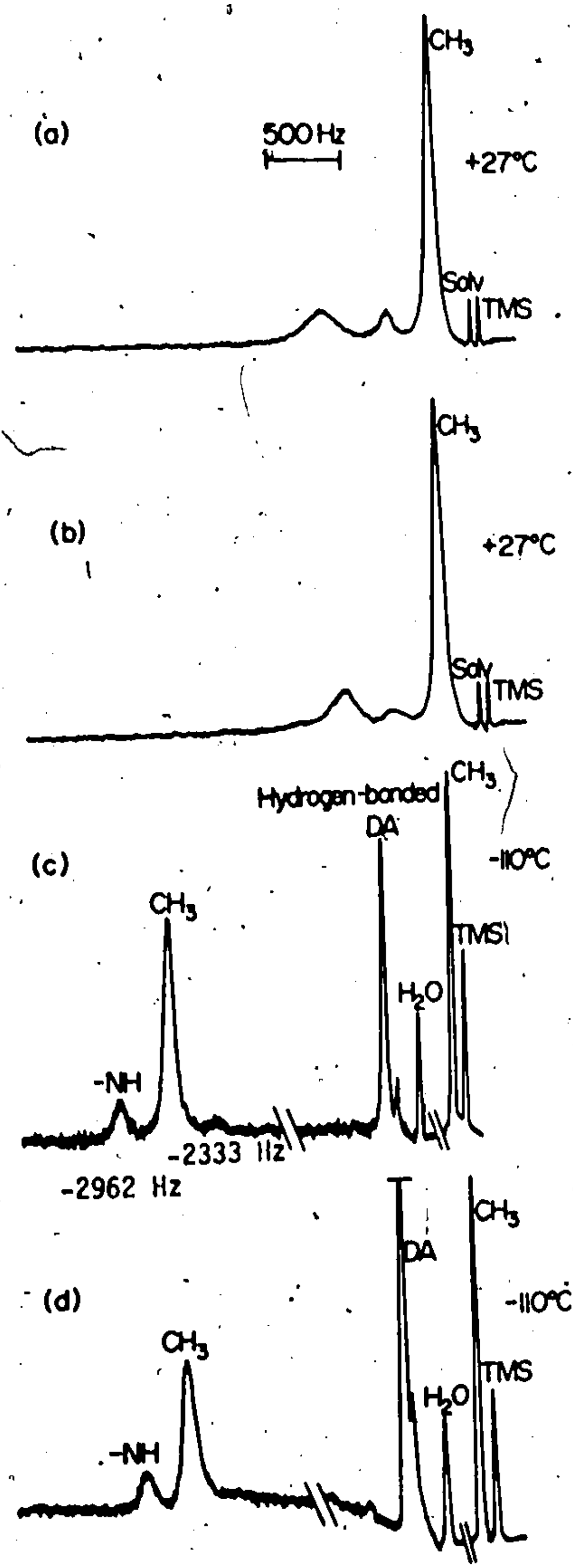


Figure (8-3): ^{1}H NMR spectra of Co(DA)$_3$(ClO$_4$)$_2$ in acetone-d$_6$ at various temperatures. (a) and (c) = spectra at +27°C and -110°C (b) and (d) = spectra with excess ligand.

are fairly soluble in acetone and their ^1H NMR spectra at room temperature are found to be quite similar to those of the corresponding cobalt Co Complexes [Fig. (8-4b)]. On cooling the solution, all the resonance lines disappear and no informative results are obtained. Spectra of the complexed ligands are not observed at -90°C. The chemical shift data for all complexes are reported in Table (8-1).

(8-5) DISCUSSION

(8-5a) THE NUCLEAR MAGNETIC RESONANCE SPECTRA

All the NMR data can be readily interpreted on the assumption that diacetamide is bonded to metal through two amide oxygen atoms and rotation about the C-N bond is completely restricted. Thus, $Co(DA)_3^{+2}$ shows two complexed lines (NH and CH_3), both shifted to low field. In addition, there is a line close to the diamagnetic free ligand position attributed to hydrogen-bonded diacetamide. The analogous complexes $Co(DA)_3Br_2$ and $Co(DA)_3(CoBr_4)$ exhibit similar spectra. It has been well known that octahedral Co(II) complexes have a triply orbitally degenerate ground term producing magnetic anistropy, and a significant dipolar contribution to the shifts is expected. Similar considerations apply to $Fe(DA)_3^{+2}$.

The NMR studies of the paramagnetic acetylacetonates of first-row transition metals have been well established.[179] The isotropic shifts exhibited by these complexes predominantly arise form contact mechanism which requires partial delocalization of the electron spin from metal to

Table (8-1)

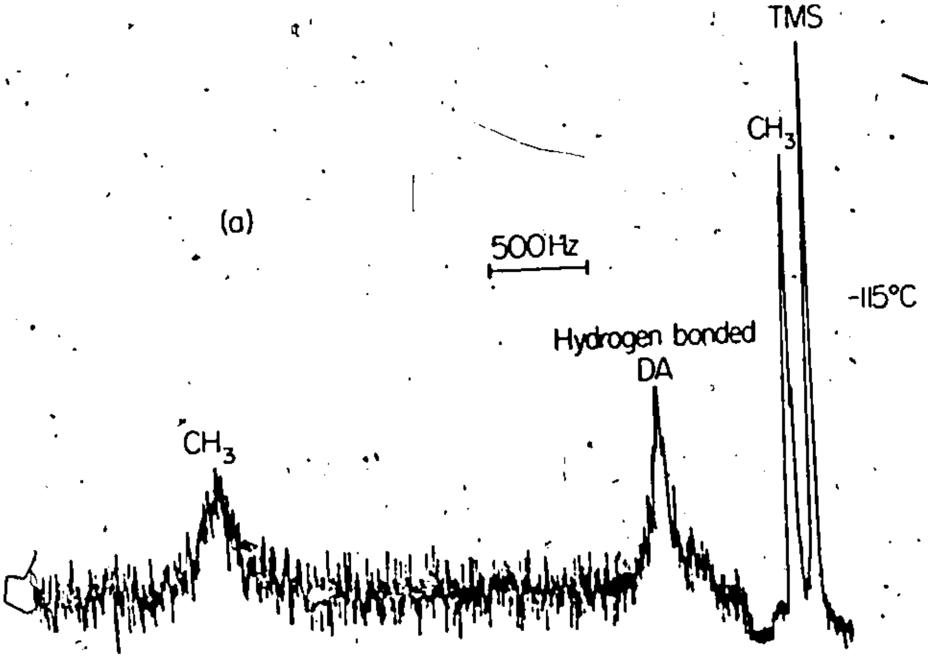
^1H NMR Data for Paramagnetic Complexes of Co(II) and Fe(II) with diacetamide

(shifts measured from TMS at 56.4 MHz)

Compound	t°C	+27°	+10°	+20°	-40°	-60°	-80°	-90°	-100°	-110°
$Co(DA)_3(ClO_4)_2$	CH_3	-658 and -1882 (average)	-750	-650	-1828	-1893	-2093	-2110	-2165	-2333
	NH				?	-2133	-2600	-2680	-2782	-2973
	t°C	+27°	0°	-10°	-90°	-106°	-115°	-117°		
$Co(DA)_3Br_2$	CH_3	Average -339	-343	?	-2395	-2697	-2962	-2970		
	CH_3	and -1064	?	?	-507	-592	-769	-770		
	t°C	+27°	0°	-10°	-20°	-40°	-60°	-80°	-95°	-110°
$Co(DA)_3(CoBr_4)$	CH_3	Average -364	-390	-396	-308	-?	-1950	-2380	-2782	-3200
	NH	and -1085	-1076	-978	-837	-?	-503	-520	-765	-800
	CH_3									
	t°C	27°	-80°							
$Fe(DA)_3(ClO_4)_2$	CH_3	-345	?							
	NH	-1715								
$Fe(DA)_3(BF_4)_2$	CH_3	-350	?							
	NH	-1800								
*$Fe(acac)_3$	CH_3	-1248								
	CH	+1644								
*$Fe(acac)_2$	CH_3	-1053								
	CH	-50								
*$Co(acac)_2(F_9)_2$	CH_3	-1577								
	CH	-1404								

*From reference (179). Shifts measured from TMS (60 MHz) $CDCl_3$, C_6D_6, C_5D_5N were used for $Fe(acac)_3$, $Fe(acac)_3^-$ and $Co(acac)_3^-$.

Solvent = acetone-d_6



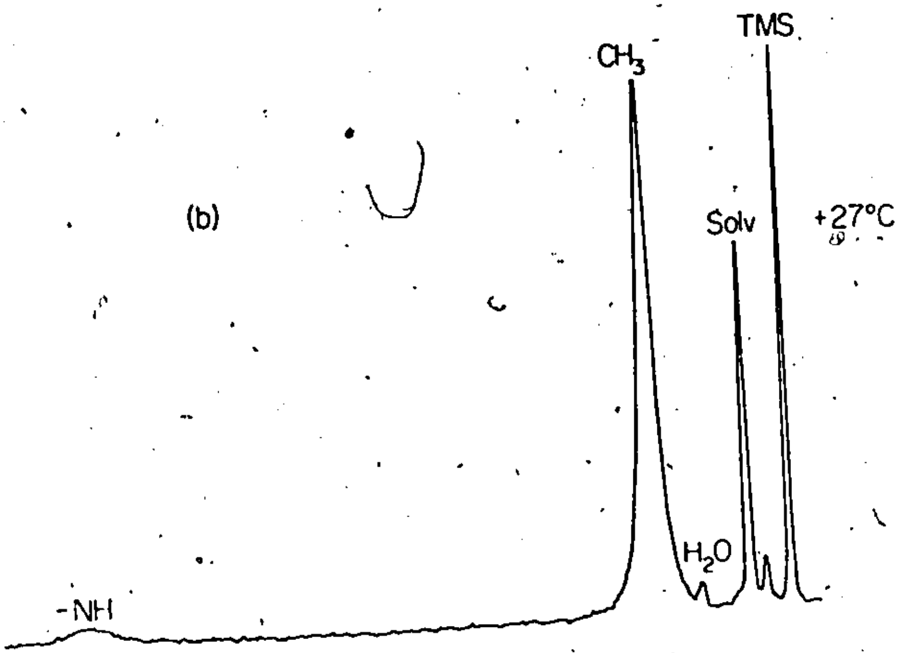


Figure (8-4a): ^{1}H NMR spectrum of $Co(DA)_3Br_2$.

Figure (8-4b): ^{1}H NMR spectrum of $Fe(DA)_3(ClO_4)_2$.

Solvent: Acetone-d_6 (56.4 MHz)

ligand through the Π-orbitals of acetylacetonate ion. The interaction of metal d-orbitals and anti-bonding ligand Π-orbitals or metal d-orbitals and top bonding ligand Π-orbitals would occur either through charge transfer from the metal to the ligand or charge transfer from the ligand to metal. It is possible that for those isoelectronic complexes such as M(acac)$_3$ and M(DA)$_3^{+2}$ having D$_3$ symmetry, both types of interaction are allowed by symmetry.[179] If metal-to-ligand charge transfer occurs, a large low-field CH$_3$ shift and a relatively small low-field CH shift would be observed in the NMR spectrum. If a ligand-to-metal charge transfer occurs, the NMR spectrum would reveal a small low-field CH$_3$ shift and relatively large low-field CH shift of the complexed ligand. It has been found that complexes of type M(acac)$_3$(M=Ti,V,Cr) exhibit a very large CH$_3$ shift and relatively small CH shifts (e.g. Ti(acac)$_3$, CH$_3$ = -3500 Hz; V(acac)$_3$, CH$_3$ = -2744 Hz, CH = -2404 Hz; Cr(acac)$_3$, CH$_3$ = -2320 Hz). It is interesting to compare the present shifts found for Co(DA)$_3^{++}$ with those reported for Co(acac)$_2$py$_2$. In the former case, the NH shift is larger the the CH$_3$ and in latter case it is smaller. On the arguments presented above, this would indicate a greater contribution of ligand to metal charge transfer as might have been anticipated for a positively charged complex. This trend is still more pronounced in the Fe(DA)$_3^{++}$ which shows an NH resonance shifted considerably further downfield than the CH$_3$. A direct comparison with the acac complex is not possible since Fe(acac)$_2$ is tetrahedral. The experimental data are summarized in Table (8-1).

(8-5b) LIGAND DISSOCIATION AND EXCHANGE

^1H NMR spectra of all diacetamide complexes at 27°C show broad lines of ligand protons indicating fast dissociation. However, quantitative measurements on solution equilibria have not been included in the present section.

The similarity of the temperature of coalescence of free and complexed ligand resonances shows that the rates of ligand exchange for all complexes are comparable although quantitative measurements to this conclusion are still doubtful. However, we can make some deductions regarding mechanism from the variation of line widths with concentration.

Under conditions such that separate complexed and free ligand lines are observed, $Zn(DA)_3^{+2}$ and $Co(DA)_3^{+2}$ shows that the line width of the complexed diacetamide is independent of free diacetamide concentration whereas that of the free diacetamide decreases with added ligand. A similar behaviour is exhibited by the bromide complexes. This is a suggestive of dissociative mechanism consistent with the octahedral structure postulated previously. The coalescence temperature for $Zn(DA)_3^{+2}$ is found to be -95° ± 5°C, and the first-order rate constant for ligand substitution at this temperature is found to be 10^3 sec^{-1}. Previous expeiments with $Zn(Tu)_2Cl_2$ indicate that coalescence temperature for ligand exchange in zinc complexes varies from -59° to -62°C. The difference in these temperatures of diacetamide and thiourea complexes reflects that $Zn(DA)_3^{+2}$ is much more labile than $Zn(Tu)_2Cl_2$. However, it has been found that experiments failed to find the similar temperature for the corresponding $Zn(Tu)_4^{+2}$. This indicates that

$Zn(Tu)_4^{+2}$ is relatively more labile than $Zn(DA)_3^{+2}$. Direct measurements of first-order rate constants for ligand exchange in paramagnetic diacetamide complexes at their coalescence temperatures are still doubtful as the frequencies of their shifts are temperature-dependent. This dependency would contribute errors in the measurements and we do not feel that we can report their data. However, unlike the corresponding six-coordinated metal complexes of symmetrical or unsymmetrical β-diketones,[184] these diacetamide complexes are extremely labile.

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