HYDROLYSIS AND INNER-SPHERE ELECTRON TRANSFER REACTIONS OF IRON AND COBALT COMPLEXES CONTAINING 2,2′-BIPYRIDINE AND 4-FLUORO-2,2′-BIPYRIDINE

by

© TUAN QUANG NGUYEN

A thesis
submitted to the Faculty of Graduate Studies
in partial fulfilment of the requirements for
the degree of Master of Science

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To my wife Thanh-Van

ABSTRACT

The synthesis of the new compound 4-fluoro-2,2′-bipyridine is described. The iron and cobalt complexes containing 2,2′-bipyridine and 4-fluoro-2,2′-bipyridine as ligands were well characterized by means of ^{1}H, ^{19}F and ^{15}N-NMR spectroscopy. The ^{1}H and ^{19}F-NMR spectra of octahedral complexes $Fe(fbpy)_3^{2+}$, $Fe(fbpy)_3^{3+}$, $Co(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$ confirmed the presence of fac- and mer- isomers in a ratio of 1:3 . All non-equivalent nitrogens in a 1:3 mixture of fac- and mer-$Fe(fbpy)_3^{2+}$ and in cis-$Co(bpy)_2(H_2O)_2^{3+}$ were observed by ^{15}N-NMR. Assignments for the ^{1}H and ^{19}F-NMR spectra of the mixed ligand complexes of Fe(II) and Co(II) were also made.

Evidence which strongly suggests that hydrolysis is the mechanism of ligand exchange in Fe and Co complexes, and consequently provides an inner-sphere pathway of electron transfer in these complexes, has been obtained.

A new mechanism in which electron transfer occurs via the formation of a hydroxo-bridged intermediate has been proposed.

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I. GENERAL INTRODUCTION

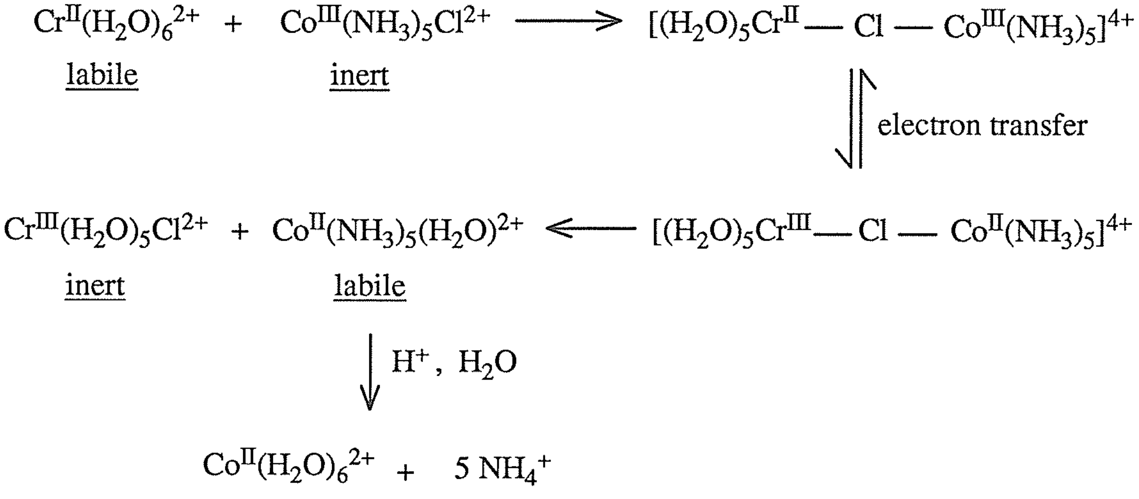
1. ELECTRON TRANSFER REACTIONS

There are two general mechanisms, namely inner-sphere and outer-sphere, that have been proposed for the electron transfer reactions. The establishment of inner-sphere and outer-sphere processes is the most important development in the understanding of the mechanism of redox reactions. In inner-sphere electron transfer reactions, there are marked changes in the coordination spheres of the reactants in the formation of the activated complex, whereas outer-sphere electron transfer involves intact coordination shells of the reactants, there is no bond breaking or making during the electron transfer (1).

(a) Inner-sphere electron transfer reactions

Early observations of an inner-sphere activated complex have been reported for the electron transfer reaction between $Co(NH_3)_5Cl^{2+}$ and $Cr(aq)^{2+}$ (2),(3), in which chlorine makes a bond simultaneously to cobalt and chromium. An intramolecular electron transfer from Cr(II) to Co(III) occurred within the chloro-bridged intermediate, producing Cr(III) and Co(II) (Scheme 1).

The experiment with radioactive chloride showed that transfer of chlorine from the oxidizing agent to the reducing agent was direct and thus led to the formulation of the activated complex. The significance and success of these experiments rest on the facts that the Co(III) complex is inert and the Cr(II) ion is labile to substitution, whereas in the products the $Cr(H_2O)_5Cl^{2+}$ ion is not labile but the Co(II) ion is labile.



Scheme 1

Williams and Garner (4) also reported that the electron transfer reactions between $Cr(aq)^{2+}$ and Cr(III) complexes of the type $[Cr(NH_3)_n(H_2O)_{5-n}Cl]^{2+}$ occur by an inner-sphere pathway in which the chloro ligand is transferred via a chloro-bridged activated complex to the oxidized product $Cr(H_2O)_5Cl^{2+}$.

The reactivity of OH^- as a bridging ligand is known to be comparable to that of Cl^-. Taube and his co-workers (5) suggested that the hydroxo-bridged complex $[(NH_3)_5Co^{III}–OH–Cr^{II}]^{4+}$ can provide a path for electron transfer between $Co(NH_3)_5(H_2O)^{3+}$ and $Cr(H_2O)_6^{2+}$.

$$Co(NH_3)_5H_2O^{3+} + Cr(H_2O)_6^{2+} \xrightarrow{H^+} Co(H_2O)_6^{2+} + 5\,NH_4^+ + Cr(H_2O)_6^{3+}$$

Tracer experiments with ^{18}O showed that oxygen transfer from Co to Cr is quantitative and that Cr^{2+} attacks the oxygen in the coordination sphere of Co(III).

The hydroxo-bridged complex $[Fe^{III}–OH–Cr^{II}]^{4+}$ was also suggested as an intermediate for the electron transfer reaction between Fe^{3+} and Cr^{2+} in perchlorate solution (6).

$$Fe(H_2O)_6^{3+} \quad + \quad Cr(H_2O)_6^{2+} \longrightarrow Fe(H_2O)_6^{2+} \quad + \quad Cr(H_2O)_6^{3+}$$

For complexes containing H_2O as a ligand, a marked increase in rate of electron transfer with increase in pH is indicative that an inner-sphere mechanism involving bridging OH is at least a contributing mechanism. The H_2O ligand has been found to be a poor bridging group, but deprotonation with increasing pH increases the concentration of M–OH groups that can react rapidly by an inner-sphere mechanism (7).

In these examples of the inner-sphere mechanism, it is the transfer of the bridging ligand from the oxidant to the reductant that provides the definitive evidence for an inner-sphere process. However, this is not an essential feature of an inner-sphere electron transfer reaction. The cyanide bridge is supplied by $Fe(CN)_6^{4-}$ in some reactions and remains with the iron after electron transfer and breakup (8).

(b) Outer-sphere electron transfer reactions

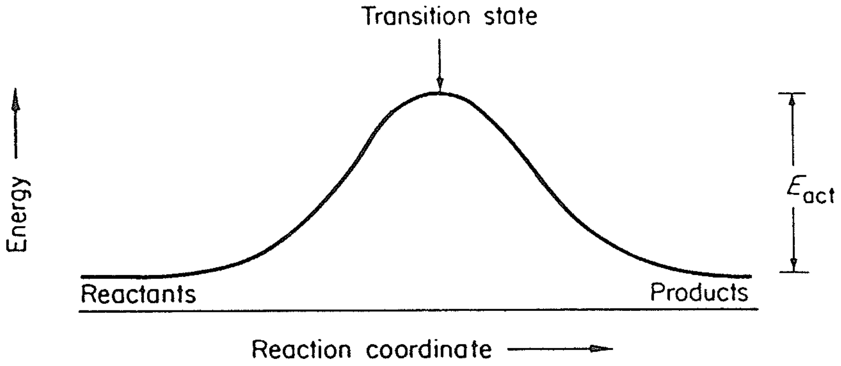
In an outer-sphere process, electron transfer takes place through the intact coordination spheres of the reactants. An example is the electron transfer reaction between Fe(II) and Ir(IV), where both reactants are classified as inert (7).

$$Fe^{II}(CN)_6^{4-} \quad + \quad Ir^{IV}Cl_6^{2-} \longrightarrow Fe^{III}(CN)_6^{3-} \quad + \quad Ir^{III}Cl_6^{3-}$$

Even when one of the reactants is substitution-labile, as pointed out by Taube (5), if the other reactant does not offer a suitable site to engage the metal ion of the labile partner, reaction by an outer-sphere mechanism will be favored. The reduction of $Co(NH_3)_6^{3+}$ (9) or of $Co(NH_3)_5py^{3+}$ (10),(11) by $Cr(aq)^{2+}$ is an example of this situation. It appears that containing an unshared electron pair after coordination is a minimum requirement for a ligand to be a potential bridging group, since it has to function as a Lewis base towards to metal cation. Thus $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5py^{3+}$ oxidize

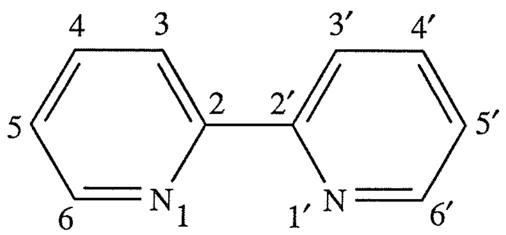
$Cr(aq)^{2+}$ by an outer-sphere mechanism without alteration of the ligand environment of either metal, giving Cr^{3+} as the product.

Important among fundamental questions about the mechanism of electron transfer for outer-sphere reactions is the question of the distance of approach which is optimum for electron transfer (5). For the outer-sphere electron transfer reactions, a plot of the energy vs. reaction coordinate takes the symmetrical form as shown below (7).

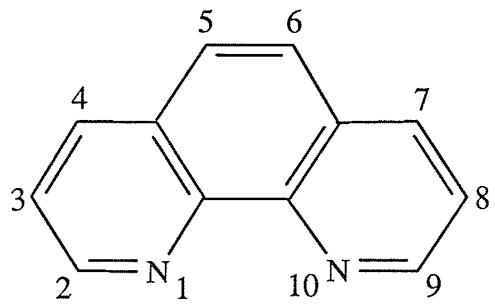


As suggested by Cotton and Wilkinson, the transition state for electron exchange is one in which each species has the same dimensions, i.e. the reacting ions first adjust their configurations so that each meets the other one only halfway and then exchanges the electron. A transition state for a process in which two reacting species differ initially in their sizes will have a much higher energy (7).

A large number of electron transfer reactions are believed to proceed by the outer-sphere mechanism. Among these are electron transfer reactions of iron and cobalt complexes containing 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) as ligands.



bpy



phen

2. 2,2′-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES OF IRON (II) AND IRON (III)

The well-known red tris-bipyridine iron (II) complex, $Fe(bpy)_3^{2+}$, has been prepared (12)-(14) by heating a mixture of ferrous sulphate and 2,2′-bipyridine in water with the sodium salt of a corresponding anion ($X = Cl^-, ClO_4^-, PF_6^-$).

$$FeSO_4 + 3\ bpy \longrightarrow Fe(bpy)_3(SO_4) \xrightarrow{NaX} Fe(bpy)_3X_2$$

The kinetics of formation and dissociation of $Fe(bpy)_3^{2+}$ have been well studied (15)-(18) . The formation of $Fe(bpy)_3^{2+}$ involves the formation of intermediates $Fe(bpy)^{2+}$ and $Fe(bpy)_2^{2+}$ according to the equations :

$$Fe^{2+} + bpy \rightleftharpoons Fe(bpy)^{2+} \qquad [1]$$

$$Fe(bpy)^{2+} + bpy \rightleftharpoons Fe(bpy)_2^{2+} \qquad [2]$$

$$Fe(bpy)_2^{2+} + bpy \rightleftharpoons Fe(bpy)_3^{2+} \qquad [3]$$

Baxendale and George (15) considered step [3] to be rate-determining but some workers (16) later considered step [1] to be rate-determining. Deb, Hazra and Lahiri pointed out that Fe^{2+} is octahedrally coordinated with H_2O molecules, thus an attack by bpy and consequent replacement of two molecules of water from the coordination sphere should be the slow process, but after the formation of $Fe(bpy)_2^{2+}$, the addition of a third molecule of bpy and consequent removal of two molecules of water should be a fast process from symmetry and energy considerations (16).

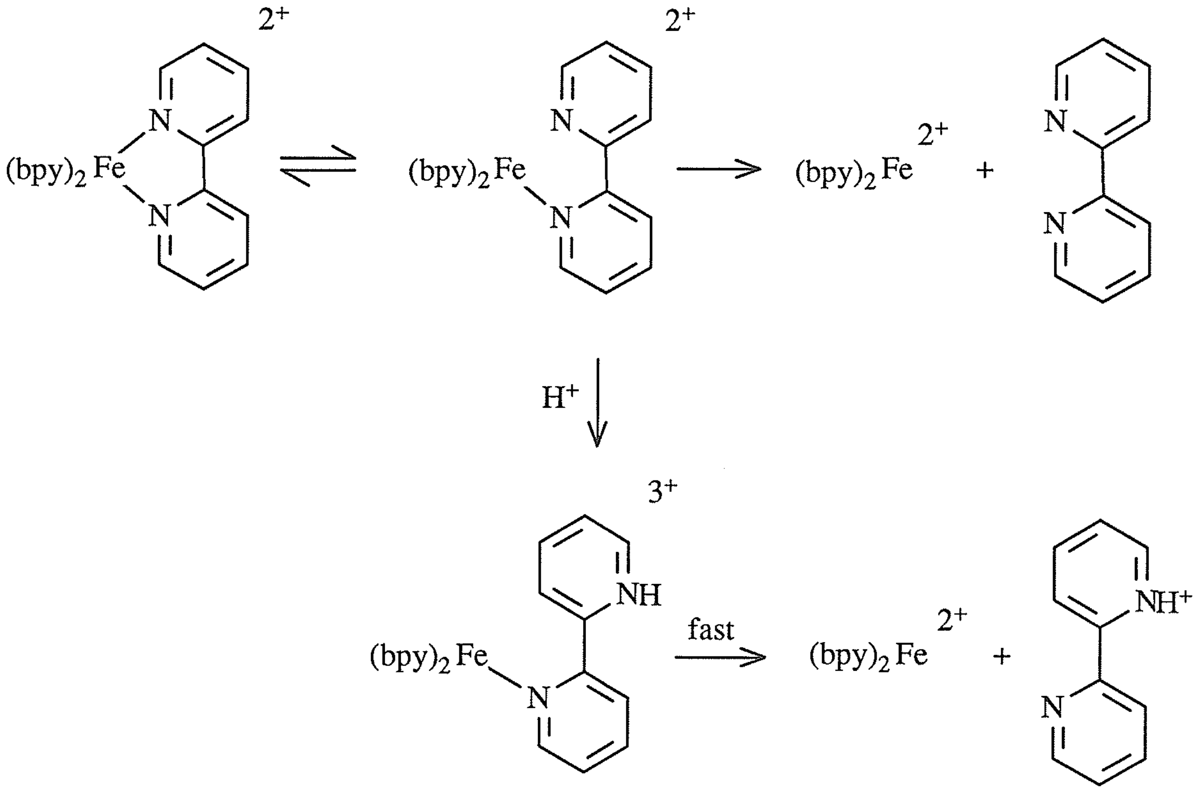
The dissociation of $Fe(bpy)_3^{2+}$ is first order in $[Fe(bpy)_3^{2+}]$ and is independent of $[H^+]$ at low acidities but increases to a limiting value at higher $[H^+]$ (15),(17). These observations indicate that $Fe(bpy)_3^{2+}$ can dissociate in two ways. At low concentration of H^+, the rate is independent of H^+ concentration and under these conditions presumably the rate of the following reaction was measured :

$$Fe(bpy)_3^{2+} \longrightarrow Fe(bpy)_2^{2+} + bpy$$

At higher $[H^+]$, obtained by using HCl and H_2SO_4, the rate constant for dissociation increases initially with acid concentration but ultimately becomes independent of it. The increase with $[H^+]$ can be accounted for by the existence of the ion $[Fe(bpy)_3H]^{3+}$ which dissociates more quickly than the simple $Fe(bpy)_3^{2+}$ ion (15). Such a complex was also suggested by Krumholtz (18) in 1949 for this system in which the proton could be combined with one of the nitrogen atoms which has been detached from the ferrous ion.

In 1954, Basolo, Hayes and Neumann (17) determined the rates of dissociation and racemization of tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridine)iron(II) ions and revealed that in each case the rate of racemization is faster than the rate of dissociation. The same observations were found in various solvents (19),(20). The data (17) for dissociation of $Fe(bpy)_3^{2+}$ showed the same dependence on acidity noted by Baxendale and George, i.e. an increasing rate of dissociation with increasing acidity until a constant rate is reached for acidities greater than 1M. The value for this limiting rate at 25°C is $7.8 \times 10^{-4}\ s^{-1}$ as compared to $7.3 \times 10^{-4}\ s^{-1}$ reported by Baxendale and George .

The fact that racemization is more rapid than dissociation implies that racemization takes place by some intramolecular, or non-dissociative, process. However, a mechanism involving rupture of a single Fe-N bond and formation of a "dangling" bipyridyl ligand was proposed (17) to account for the acid-dependent dissociation and racemization of $Fe(bpy)_3^{2+}$ (Scheme 2).



Scheme 2

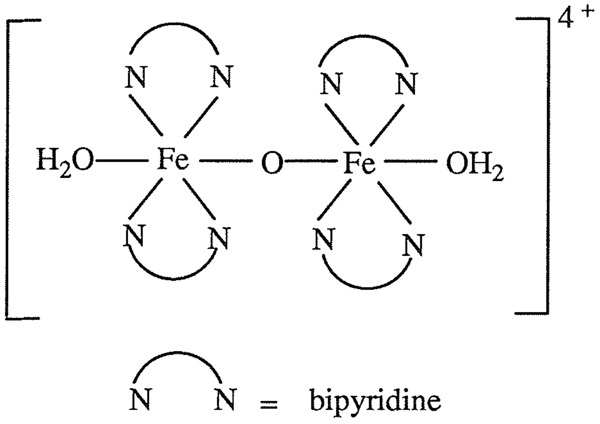
In the case of the intramolecular rearrangement of $Fe(phen)_3^{2+}$, there can be no opening of the chelate rings because of the geometry of the 1,10-phenanthroline molecule which has a fixed planar structure. The intramolecular process must involve the movement of the chelate rings about the central atom. This process is expected to be independent of acidity. Gillard, Kane-Maguire and Williams (21), however, reported that this is not the case, and that there is a decrease in the rate of racemization with increasing $[H^+]$, and the rate of racemization does not appear to decrease to zero with increasing acid concentration.

The blue Fe(III) complex, $Fe(bpy)_3^{3+}$, is produced by chemical (12),(22) or electrochemical oxidation (23)-(25) of the red Fe(II) complex, $Fe(bpy)_3^{2+}$. It is interesting to note that the $Fe(bpy)_3^{3+}$ complex can not be prepared by direct interaction of the metal ion and ligand. Gillard et al. (21) reported that the rates of racemization and dissociation of FeL_3^{3+} (L = bpy or phen) are zero in 100% H_2SO_4, i.e. no reaction takes place in the absence of water. However, the nature of the complexes FeL_3^{3+} in concentrated acids is yet to be properly understood. Lee, Kolthoff and Leussing (26) proposed that $Fe(phen)_3^{3+}$ is protonated in concentrated sulphuric acid through the following equilibrium reaction :

$$Fe(phen)_3^{3+} + H^+ \rightleftharpoons [Fe(phen)_3H]^{4+}$$

The existence of $[Fe(phen)_3H]^{4+}$ could not, however, be established. Dickens et al. (27) ruled out the possibility of a protonated species being responsible for the decreased reaction rate and noticed some ion-pairing effects with $Fe(phen)_3^{3+}$. Gillard et al. (21) observed no change in the visible region of the electronic spectrum of $Fe(phen)_3^{3+}$ in concentrated H_2SO_4 and suggested that it seems most likely that the species in H_2SO_4 is unprotonated.

Although the 2,2′-bipyridine complex of Fe(III) has been studied by several groups (21),(25),(28)-(32), the nature of the hydrolysis of the blue Fe(III)-bpy complex has not been established. Ehman and Sawyer (25) reported a detailed electrochemical study of the iron-bpy complexes and proposed a mechanism for the hydrolysis of the $Fe(bpy)_3^{3+}$ complex to the brown, oxo-bridged complex $[Fe_2(bpy)_4O(H_2O)_2]^{4+}$ (33),(34).



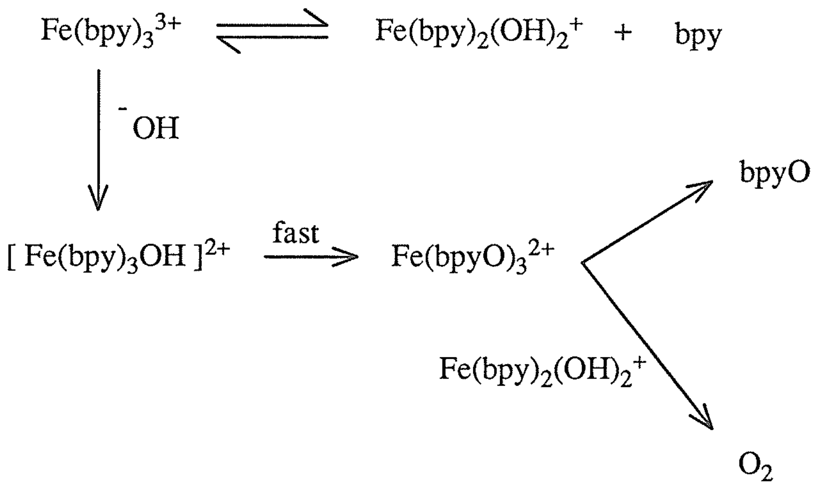
$$2\,Fe(bpy)_3^{3+} \;+\; 3\,H_2O \rightleftharpoons Fe_2(bpy)_4O(H_2O)_2^{4+} \;+\; 2\,bpy \;+\; 2\,H^+$$

Their data established that the hydrolysis of blue $Fe(bpy)_3^{3+}$ to brown $[Fe_2(bpy)_4O(H_2O)_2]^{4+}$ between pH 2 and 6 is first order in $[Fe(bpy)_3^{3+}]$ and first order in any base which is present, e.g. H_2O, OH^- and bpy. For details of this mechanism, the reader is referred to reference (25).

The reduction of tris-bpy and tris-phen complexes of iron (III) by hydroxide ion, which was reported by Nord and Wernberg (30), occurs according to the following reaction with dioxygen as one of the products.

$$4\,FeL_3^{3+} \;+\; 4\,OH^- \longrightarrow 4\,FeL_3^{2+} \;+\; O_2 \;+\; 2\,H_2O$$

In a further study in 1983, Nord et al. (31) reported that $Fe(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ are always significantly dissociated in solution and that it is the hydroxo complexes which form dioxygen. In both cases, the O_2 yield is less than the yield of the tris Fe(II) complexes. It was also pointed out that the fast redox reactions of the Fe(III) complexes in basic solutions give the Fe(II) complexes and coordinated ligand N-oxide, $Fe(bpyO)_3^{2+}$, as primary products. Further reactions by parallel paths include dissociation to give the free ligand N-oxide (bpyO) and catalysis by hydroxy Fe(III) complexes, $Fe(bpy)_2(OH)_2^{+}$, leading to dioxygen (Scheme 3) .



Scheme 3

In 1985, a new mechanism was proposed for the reduction of $M(bpy)_3^{3+}$ (M = Fe, Ru, Os) by water. Lay and Sasse (32) suggested a mechanism in which the initial reaction is nucleophilic attack of water at the metal ion to form a seven-coordinate intermediate, followed by ligand dissociation and formation of dioxygen. Rather than discussing all details of this mechanism, the reader is referred to reference (32).

The rates of the electron-transfer reactions between $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ were investigated in 1958 (35) both by optical-active and by isotopic-tracer methods and the rates were found to be immeasurably large. The rates of a number of electron-transfer reactions between ML_3^{2+} and ML_3^{3+} complex ions have also been measured by the NMR line broadening method (M = Fe, Ru or Os and L = bpy, phen or their derivatives) (36),(37). Nuclear magnetic resonance methods have been used successfully for rate measurements of rapid exchange reactions (38). Any given proton on the ligand will effectively spend part of its time between two different environments, corresponding to the line positions in the diamagnetic and paramagnetic species. If the electron exchange is fast enough, the two resonance lines should average out to one at an intermediate position and one can calculate the rate of exchange since the positions of the separate lines are known .

Dietrich and Wahl (36) studied electron transfer between $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ ions by nuclear magnetic resonance method in 1963. They reported that spectra of mixtures of the two oxidation states contain only one set of peaks intermediate in position between the peak positions for the pure states. Changes in linewidths and positions of the proton NMR peaks for the diamagnetic species on addition of the corresponding paramagnetic species were interpreted as being due to very rapid electron transfer between the two species .

Wahl et al. (37) re-investigated these exchange reactions in 1978. On the assumption of electron transfer via the outer-sphere mechanism, they reported that the exchange reactions followed a second-order rate law, first-order in each reactant concentration, the rate constants determined were of the large magnitude ($\sim 10^6\ M^{-1}s^{-1}$) and their temperature dependences were small .

3. <u>2,2′-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES OF COBALT (II) AND COBALT (III)</u>

It has been reported that the tris(2,2′-bipyridine)cobalt(III) and tris(1,10-phenanthroline)cobalt(III) ions are inert to exchange with the corresponding free ligands in acid solution (39). These complexes do not undergo exchange after 15 hrs refluxing in 2M hydrochloric acid, however, they undergo exchange in neutral solution due to the presence of a small amount of cobalt (II) impurity. The results of Wilkins et al. (39) indicated that the dissociation of the Co(III) complexes in neutral solution is extremely slow.

Later in 1972, Sykes et al. (40) also reported that the complex $Co(bpy)_3^{3+}$ is inert to substitution and visible spectra of aqueous solutions, $[H^+] = 0.05 - 2.00$ M, remain unchanged over two days. In general, the rates of substitution of Co(III) complexes are slow, and exchanges that have been observed with such complexes in neutral solution are also slow. The only exception to this generalization is the rapid $H_2{}^{18}O$ exchange with the $Co(aq)^{3+}$ ion. The $Co(aq)^{3+}$ ion is known to oxidize water so that solutions are never completely free from labile $Co(aq)^{2+}$. As a result of this, a complete substitution of Co^{3+} ion can proceed by electron transfer between the Co^{2+} and Co^{3+} ions (41).

The rates of dissociation of complexes of Co(II), unlike those of Co(III), are rapid at ordinary temperatures (42). The lability of Co(II)-phen complexes has been demonstrated in three different ways :

(a) The ability of $Co(phen)_3^{2+}$ to catalyze the exchange of $Co(phen)_3^{3+}$ with ^{14}C-phenanthroline (39).

(b) The rapid development of a red colour (due to tris-phen iron (II)) when mono-, bis- or tris-phen cobalt (II) ions are added to ferrous ions in aqueous solution (43).

(c) The rapid exchange of $Co(phen)_3^{2+}$ with $^{60}Co^{2+}$ at 15°C in aqueous solution (44).

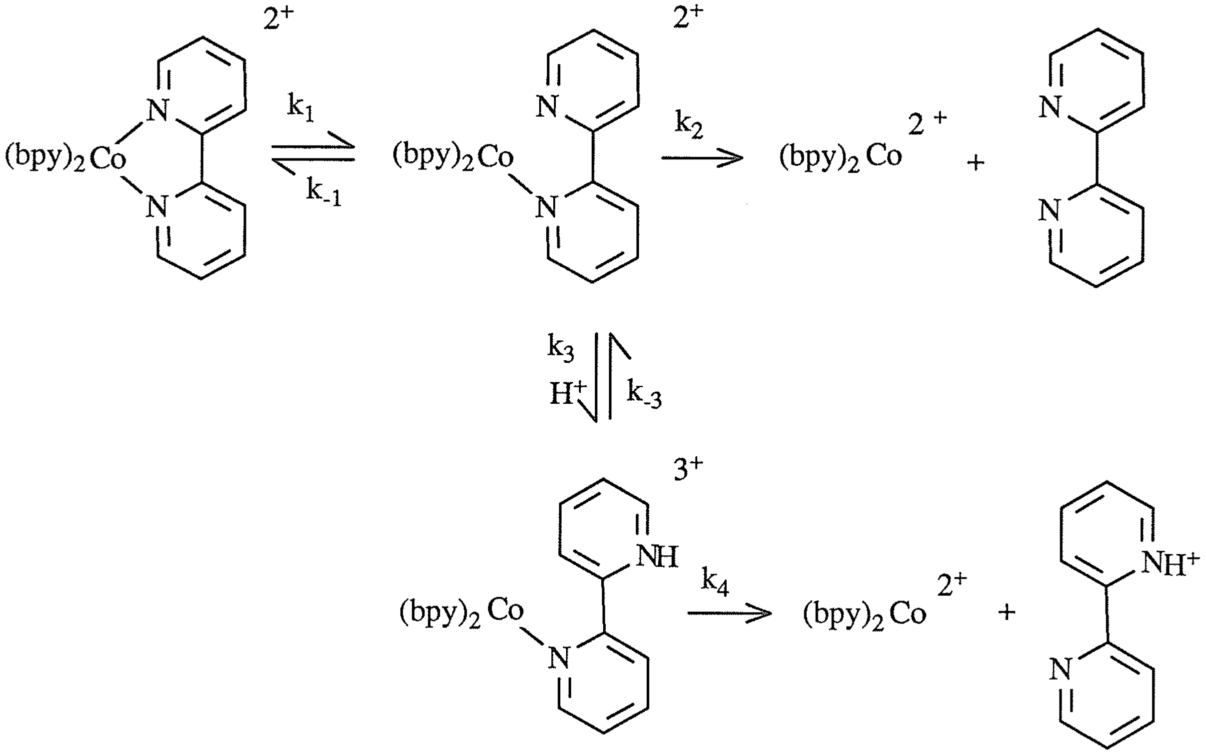
The dependence on H^+ concentration of the rates of acid dissociation of metal complexes with a variety of bidentate ligands has been well studied (45). It is believed that the proton acts as a scavenger for one released end of the bidentate ligand, giving a moderate accelerating effect on the rate with increasing $[H^+]$. Eventually a limiting rate is reached at sufficiently high acid concentration and the first-order rate constant in these conditions is equated to that of the metal-ligand bond rupture (46). From the studies of dissociation of iron (II) and cobalt (II)-bipyridine complexes, Wilkins et al. (46) reported that the order of kinetic stability of the metal-nitrogen bond is Co(II) < Fe(II) .

Davies, Green and Sykes (40) studied the dissociation (by aquation) of the product $Co(bpy)_3^{2+}$ in the vanadium (II) reduction of $Co(bpy)_3^{3+}$ by the stopped-flow method. At

25°C the rate constant for cleavage of the first chelate ring is 36.0 s^{-1}. They assigned the absorbance changes which were observed to the dissociation :

$$Co(bpy)_3^{2+} + 2\,H_2O \longrightarrow Co(bpy)_2(H_2O)_2^{2+} + bpy$$

A mechanism was also proposed to explain the dependence on $[H^+]$ of the dissociation of $Co(bpy)_3^{2+}$, which is slightly modified to that for the dissociation of $Fe(bpy)_3^{2+}$ (Scheme 4) .



Scheme 4

The ratio of rate constants $k_2/(k_{-1}+k_2)$ is a measure of the number of times complete dissociation occurs once the first metal-nitrogen bond has dissociated. For

$Co(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$, the values of this ratio are < 0.0045 and 0.16, respectively. From these results, Sykes et al. (40) concluded that with the partly dissocated form of $Co(bpy)_3^{2+}$, there is a much greater tendency for the chelate ring to reform than with $Fe(bpy)_3^{2+}$.

The rates of electron transfer in the system $Co(phen)_3^{2+} - Co(phen)_3^{3+}$ and analogous 2,2′-bipyridine and 2,2′,2″-tripyridine were studied by a tracer method using ^{60}Co , the activity being introduced either as Co(II) or Co(III) (47). Baker, Basolo and Neumann reported a value of 11.2 $M^{-1}s^{-1}$ for the rate constant of the $Co(phen)_3^{2+} - Co(phen)_3^{3+}$ system at 20°C , whereas the exchange rate constant for $Co(bpy)_3^{2+} - Co(bpy)_3^{3+}$ in water is 18 $M^{-1}s^{-1}$ at 25°C (48) .

The rates of electron transfer in the phenanthroline and bipyridine systems were also reported by Ellis, Wilkins and Williams (39) , but this was an indirect measurement, being obtained from the rate of exchange of ^{14}C-phenanthroline and ^{14}C-bipyridine with the cobalt (III) ions via the electron transfer with the labile cobalt (II) ions .

The possible participation of low-spin $^*Co(bpy)_3^{2+}$ in the electron exchange between $Co(bpy)_3^{2+}$ and $Co(bpy)_3^{3+}$ has been invoked (47) as a partial explanation for the abnormally low rate constant of this system. Such a low-spin species was also suggested later by some workers (49),(50). However, Berkoff, Krist and Gafney (51) found it difficult to attribute the slowness of the observed rate to a spin change in the Co(II) complex, i.e. the high-spin Co(II) complex, which has a $t_{2g}^5\,e_g^2$ configuration rearranged to a low-spin $t_{2g}^6\,e_g^1$ configuration prior to electron transfer. In spite of the fact that a potentially serious difficulty is the possibility of aquation of the Co(II) complexes prior to the electron-transfer reactions between $Ru(bpy)_3^{3+}$ and $Co(bpy)_3^{2+}$ or $Co(phen)_3^{2+}$, Gafney et al. reported that aquation of the Co(II) complexes is negligible and would not be competitive with the electron-transfer reactions .

4. GENERAL SCOPE OF THIS WORK

All current views of electron transfer in 2,2′-bipyridine complexes of iron (II) and iron (III), as well as cobalt (II) and cobalt (III), assume an outer-sphere process, in which the complexes remain intact and rigid during the electron transfer step .

$$\mathrm{Fe(bpy)_3}^{2+} + {}^{*}\mathrm{Fe(bpy)_3}^{3+} \rightleftharpoons \mathrm{Fe(bpy)_3}^{3+} + {}^{*}\mathrm{Fe(bpy)_3}^{2+}$$

$$\mathrm{Co(bpy)_3}^{2+} + {}^{*}\mathrm{Co(bpy)_3}^{3+} \rightleftharpoons \mathrm{Co(bpy)_3}^{3+} + {}^{*}\mathrm{Co(bpy)_3}^{2+}$$

The early observation of Werner that racemization of $\mathrm{Cr(C_2O_4)_3}^{3-}$ in water is faster than in aqueous acetone (52), or the findings that electron exchange reactions are considerably faster in water than in isopropyl alcohol (53) or slower in rigorously dried nitromethane (54), illustrate the fact that water is intimately involved in reactions of octahedral complexes .

Mechanistic interpretations of the role of water have usually emphasized the hydrogen bonding, hydrogen atom transfer, Lewis base, or solvating properties of water. However, the unravelling of mechanistic details is a difficult task because of the high rates generally observed for any steps involving water-complex interactions (55) .

Another molecular interpretation of the role of water assumes that water can take part in rapid four-center reactions. Early descriptions of the hydrolysis of B, Si and P chlorides belong to this category (56) as do more recent studies of hydrolysis and ligand exchange reactions of Si, S and P compounds (57)-(59) . One of the interesting consequences of such an interpretation is that rapid hydrolysis may provide an inner-sphere pathway of electron transfer for systems that are generally assumed to undergo electron transfer by the outer-sphere mechanism .

The purpose of this work then was to re-investigate the mechanism of electron transfer of iron and cobalt complexes containing 2,2′-bipyridine and

4-fluoro-2,2′-bipyridine as ligands via ^{1}H and ^{19}F-NMR in order to gain some evidence for an alternative "inner-sphere" mechanism to the accepted "outer-sphere" mechanism of electron transfer.

II. GENERAL PROCEDURE, APPARATUS AND REAGENTS

1. GENERAL

Due to the air and moisture sensitivity of some of the starting materials or the products, the handling of these compounds was carried out as much as possible under a dry nitrogen atmosphere. All apparatus used to manipulate these compounds were pre-dried and flushed with dry nitrogen. The NMR samples of these compounds were prepared under nitrogen atmosphere and the NMR tubes were sealed under vacuum .

2. INSTRUMENTAL

All nuclear magnetic resonance spectra were recorded on Bruker AM-300 and WH-90 NMR spectrometers. Fluorine NMR spectra were run in deuterated acetonitrile or acetone with hexafluorobenzene C_6F_6 as the internal reference standard (-162.9 ppm with respect to $CFCl_3$). ^{19}F-NMR spectra were recorded at 84.7 MHz on WH-90 and at 282.4 MHz on AM-300 spectrometers. Proton NMR spectra were run in deuterated acetonitrile or acetone. The protonated acetonitrile (1.93 ppm with respect to TMS) or protonated acetone (2.04 ppm with respect to TMS) present as an impurity in the deuterated solvent was used as the internal reference standard .

3. CHEMICALS

2,2′-Bipyridine (Sigma Chemical Company) was checked by ^1H-NMR and used without further purification.

1,10-Phenanthroline hydrate (BDH Chemicals Ltd.) was used without further purification.

Acetonitrile d-3 99% D (Aldrich Chemical Company) was dried and purified according to Coetzee (60) .

Acetone d-6 (Aldrich Chemical Company) was distilled from phosphorous pentoxide P_2O_5 in a dry box to remove traces of water.

Dichloromethane (Fisher Scientific Company) was dried and purified according to Vogel (61) .

Sodium hexafluorophosphate was prepared by the procedure of Mohamed, Padma, Kalbandkeri and Murthy (62).

$FeSO_4.7H_2O$ and $CoCl_2.6H_2O$ (Fisher Scientific Company) were used without further purification.

Other chemicals used in the experiments were reagent grade.

III. EXPERIMENTAL

1. 4-FLUORO-2,2′-BIPYRIDINE

4-Fluoro-2,2′-bipyridine (fbpy) was synthesized via the following scheme designed by Huang et al. (63).

Preparation of 4-nitro-2,2′-bipyridine-N-oxide

Following the method of Sont and Alper (64), 2,2′-bipyridine-N-oxide was obtained as an oil (2.6 g, 15.0 mmole) from the oxidation of 2,2′-bipyridine (5.0 g, 32.0 mmole) with m-chloroperbenzoic acid (7.5 g, 43.5 mmole) in chloroform. The oil was dissolved in concentrated sulphuric acid (15 mL). Fuming nitric acid (24 mL) in concentrated sulphuric acid (13 mL) was added during 10 min and the mixture was refluxed for 2.5 hrs. The solution was poured onto ice (100 g) and neutralized, with cooling, to pH 8 by 38% NaOH. The light yellow precipitate was filtered and washed with water. Recrystallization from hot ethanol gave 4-nitro-2,2′-bipyridine-N-oxide (1.45 g, 6.7 mmole, 21%), mp. 180-181°C, lit. 183-185°C (65).

A molecular ion peak of mass number 217 was visible in the mass spectrum. Other peaks corresponding to expected molecular fragments were present. Some of the major fragments are assigned as follows:

		m/z
$C_{10}H_7N_2O^+$	$[M-NO_2]^+$	171
$C_{10}H_7N_2^+$	$[M-(NO_2+O)]^+$	155
$C_9H_7NO^+$	$[M-(NO_2+CN)]^+$	145

Preparation of 4-amino-2,2′-bipyridine

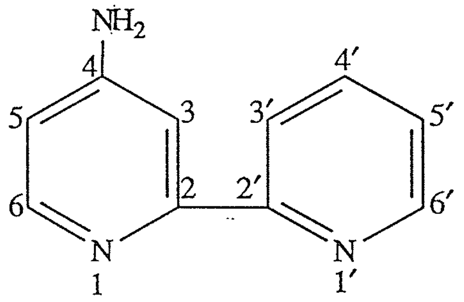
4-Nitro-2,2′-bipyridine-N-oxide (0.42 g, 1.90 mmole) and palladium-carbon (Pd content 5%, 150 mg) were suspended in methanol (20 mL). Sodium borohydride (0.85 g, 22.50 mmole) was added, with cooling, to the mixture in several portions (to control liberation of hydrogen gently). The reaction mixture was stirred for 30 min, filtered to remove catalyst and washed with methanol. After evaporating methanol, the solution was extracted with diethyl ether three times and dried over NaOH pellets. Ether was removed to give 4-amino-2,2′-bipyridine (0.28 g, 1.60 mmole, 85%), mp. 115-116°C, lit. 128-129°C (65).

The mass spectrum of 4-amino-2,2′-bipyridine shows a peak of mass number 171 corresponding to the molecular ion. Other major peaks are assigned as follows:

		m/z
$C_{10}H_8N_3^+$	$[M-H]^+$	170
$C_9H_9N_2^+$	$[M-CN]^+$	145
$C_9H_8N_2^+$	$[M-HCN]^+$	144
$C_9H_7N_2^+$	$[M-(H+HCN)]^+$	143

The ^{1}H-NMR chemical shifts and coupling constants of 4-amino-2,2′-bipyridine are listed in Table 1 and its spectrum is shown in Figure 1 .

Table 1. The proton chemical shifts of 4-amino-2,2′-bipyridine in $CDCl_3$



Chemical shifts (ppm)		Coupling constants (Hz)		
H-3	7.66	$J_{3,5} = 2.4$	$J_{3,6} = 0.5$	
H-3′	8.34	$J_{3',4'} = 8.0$	$J_{3',5'} = 1.2$	$J_{3',6'} = 0.9$
H-4′	7.78	$J_{4',5'} = 7.5$	$J_{4',6'} = 1.8$	
H-5	6.54	$J_{5,6} = 5.5$		
H-5′	7.27	$J_{5',6'} = 4.8$		
H-6	8.29			
H-6′	8.63			
4-NH_2	4.27			

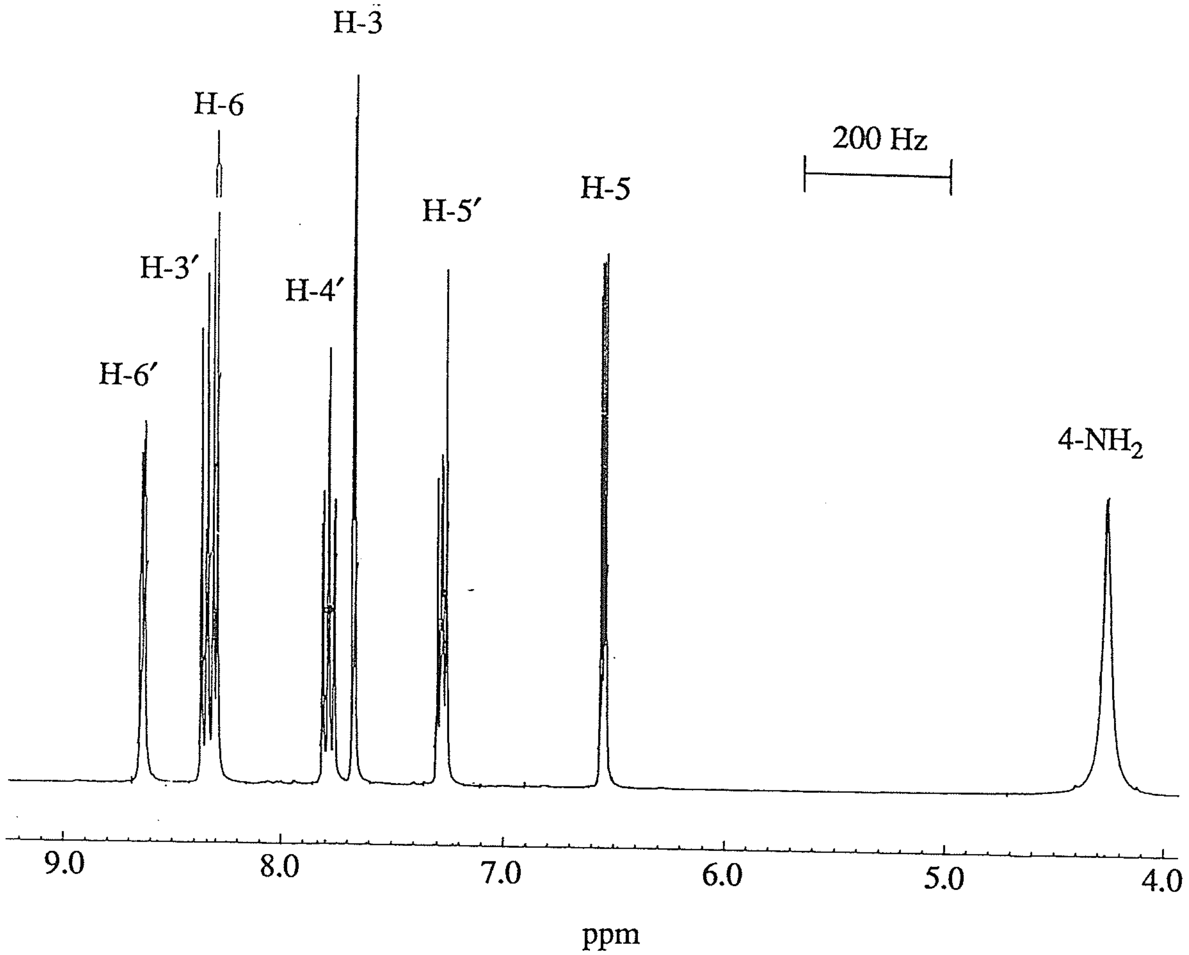


Figure 1. ^{1}H-NMR spectrum of 4-amino-2,2′-bipyridine in $CDCl_3$

Preparation of 4-fluoro-2,2′-bipyridine

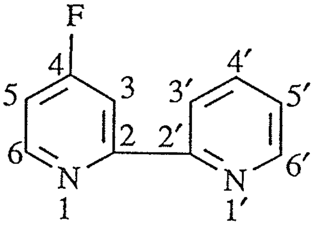
Fluoroboric acid (12.0 g, 137.0 mmole) was added gradually to 4-amino-2,2′-bipyridine (1.0 g, 5.8 mmole), with cooling, and a solution of sodium nitrite (1.1 g, 16.0 mmole) in 10 mL of cold water was added. The solution was then cooled in liquid nitrogen and the precipitate was filtered to give the diazonium salt. After drying, the diazonium salt was decomposed by heating and 20% aqueous sodium hydroxide was added until no more solid was formed. The brown solid was then filtered, washed with cold water and extracted with petroleum ether. Removal of ether gave 4-fluoro-2,2′-bipyridine (0.53 g, 3.0 mmole, 52%), light yellow solid, mp.83-85°C .

In the mass spectrum, a molecular ion peak of mass number 174 was visible. Some of the major fragments are assigned as follows:

		m/z
$C_{10}H_6N_2F^+$	$[M-H]^+$	173
$C_9H_7NF^+$	$[M-CN]^+$	148
$C_9H_6NF^+$	$[M-HCN]^+$	147
$C_9H_5NF^+$	$[M-(H+HCN)]^+$	146

The ^1H, ^{13}C, ^{19}F and ^{15}N-NMR spectra of 4-fluoro-2,2′-bipyridine are shown in Figures 2, 3 and 4. The ^1H, ^{13}C and ^{19}F-NMR chemical shifts are summarized in Table 2. The ^{15}N-NMR chemical shifts are listed in Table 3.

Table 2. ^{1}H, ^{13}C and ^{19}F-NMR data for 4-fluorobipyridine in $CDCl_3$



Chemical shifts (ppm)

	H-3	H-3′	H-4′	H-5	H-5′	H-6	H-6′
^{1}H-NMR(a)	8.17 (10.4)	8.40	7.83	7.04 (8.1)	7.34	8.64 (8.5)	8.68

	C-2	C-3	C-4	C-5	C-6
^{13}C-NMR(b)	159.7 (7)	108.8 (19)	169.7 (261)	111.5 (17)	151.5 (7)
	C-2′	C-3′	C-4′	C-5′	C-6′
	154.9 (4)	121.3	137.0	124.3	149.3

^{19}F-NMR(c)	-103.2

(a) TMS as internal reference ; proton-fluorine coupling constants in Hz are given in parentheses.

(b) TMS as internal reference ; carbon-fluorine coupling constants in Hz are given in parentheses

(c) Proton-decoupled ; C_6F_6 as internal reference (-162.9 ppm).

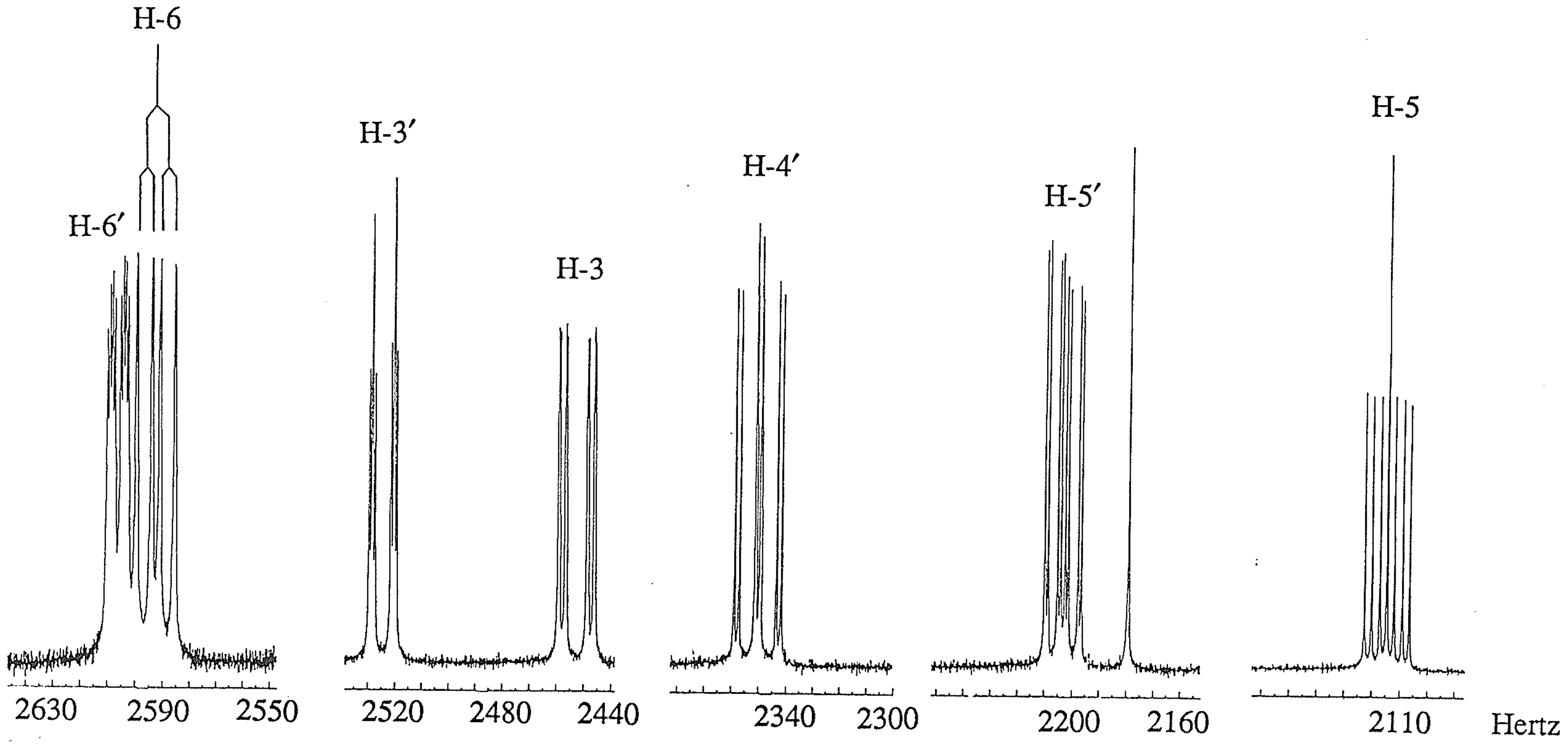


Figure 2. ^{1}H-NMR spectrum of fbpy in $CDCl_3$

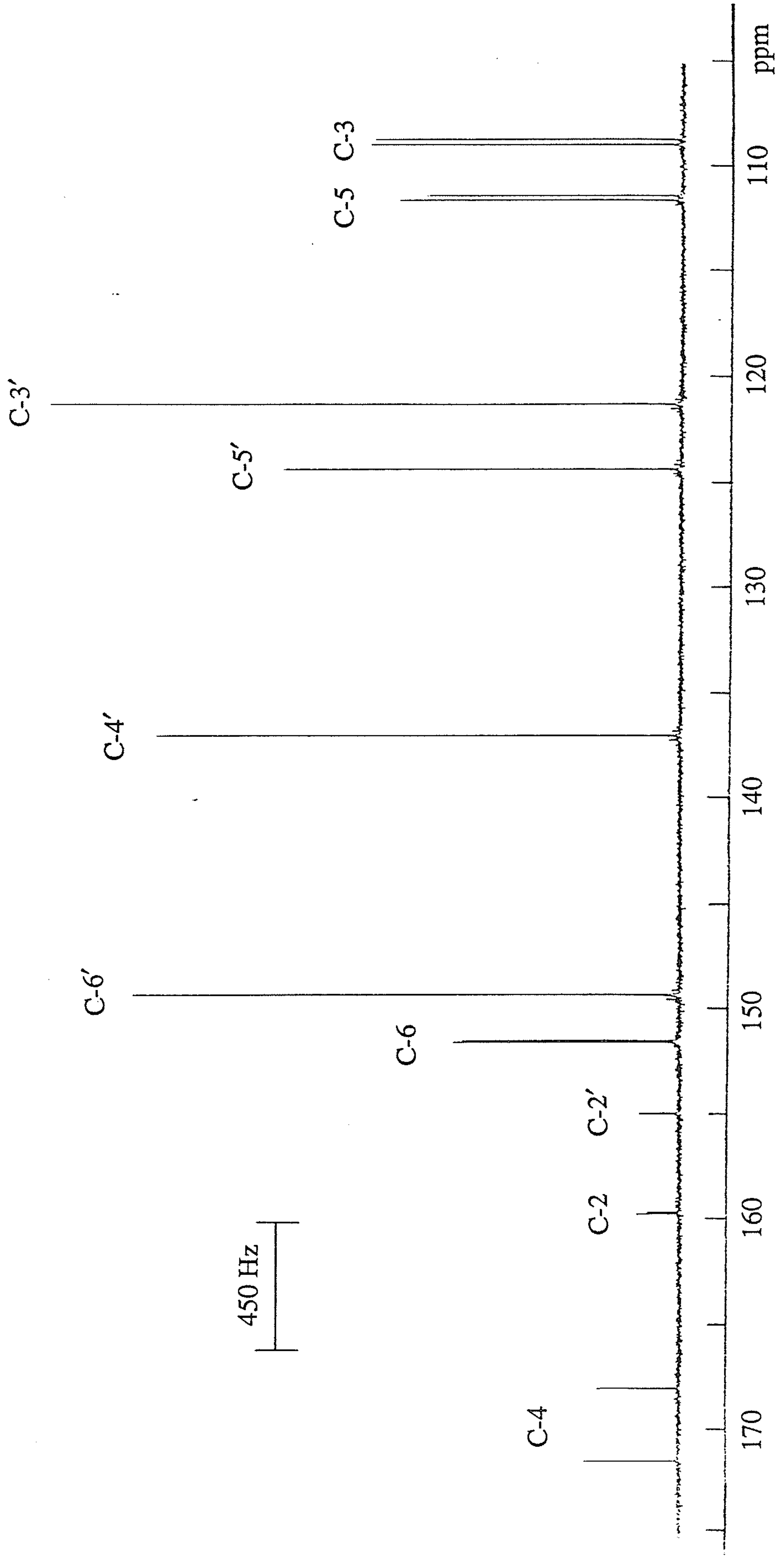


Figure 3. ^{13}C-NMR spectrum of fbpy in $CDCl_3$

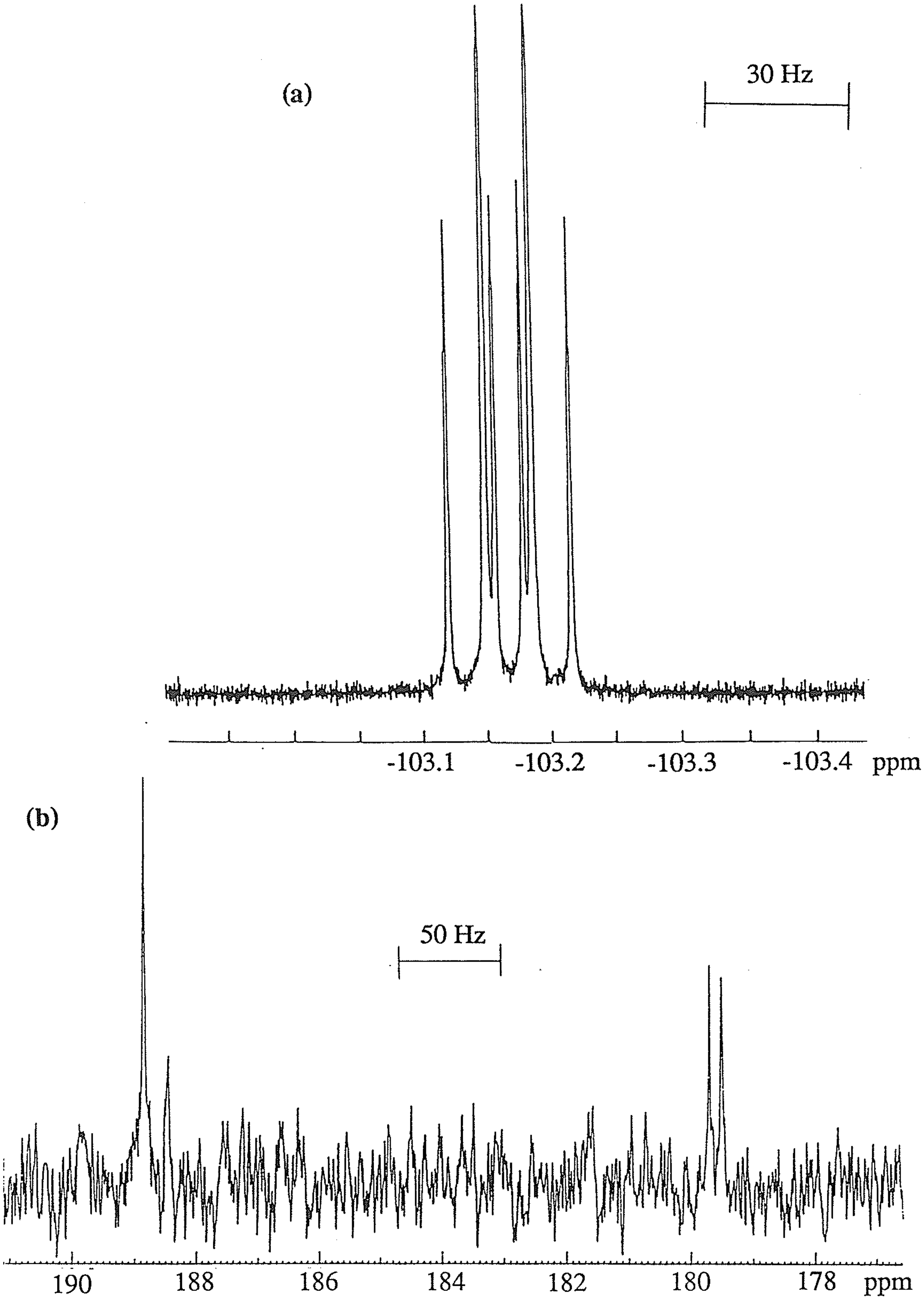


Figure 4. (a) ^{19}F-NMR spectrum of fbpy in $CDCl_3$ (proton-coupled)

(b) ^{15}N-NMR spectrum of fbpy in $CDCl_3$

Table 3. ^{15}N-NMR data for fbpy, Fe(II) and Co(III) complexes

	$Fe(bpy)_3^{2+}$ in D_2O	$Co(bpy)_2(H_2O)_2^{3+}$ in D_2O	fbpy in $CDCl_3$	$Fe(fbpy)_3^{2+}$ in acetone d-6
(a)	138.7	66.4	179.6 (d)	128.17 (d)
		91.3	188.9 (s)	128.24 (d)
				128.66 (d)
				128.90 (d)
				141.38 (s)
				141.52 (s)
				142.00 (s)
				142.20 (s)
(b)	-5.4	-77.7	35.5 (d)	-15.94 (d)
		-52.8	44.7 (s)	-15.87 (d)
				-15.45 (d)
				-15.21 (d)
				-2.73 (s)
				-2.59 (s)
				-2.11 (s)
				-1.91 (s)
(c)	-2.8	-75.1	40.7 (d)	
		-50.2	49.9 (s)	

(a) Chemical shifts were measured relative to an external sample of pyridine in acetone d-6 (205.9 ppm).

(b) Chemical shifts were converted to the nitromethane scale by addition of 61.79 ppm (66).

(c) Corrections were made to acetone d-6 solvent (2.04 ppm)

s = singlet d = doublet

2. BIPYRIDINE AND 4-FLUOROBIPYRIDINE COMPLEXES OF IRON (II), IRON (III), COBALT (II) AND COBALT (III)

Preparation of tris(2,2′-bipyridine)iron(II) hexafluorophosphate

Following the methods reported in the literature (12)-(14), a saturated solution of sodium hexafluorophosphate was added to an aqueous solution containing a 1:3 mixture (mole ratio) of ferrous sulphate heptahydrate and 2,2′-bipyridine. The red precipitate was filtered, washed with distilled water and dried in vacuum over P_2O_5.

The ^{15}N and ^1H-NMR chemical shifts are listed in Tables 3 and 4, respectively. The ^1H and ^{15}N-NMR spectra are shown in Figures 5a and 6a, respectively.

Preparation of tris(4-fluoro-2,2′-bipyridine)iron(II) hexafluorophosphate

$Fe(fbpy)_3(PF_6)_2$ was prepared by a method similar to that described for the preparation of $Fe(bpy)_3(PF_6)_2$.

The ^{15}N, ^1H and ^{19}F-NMR data for $Fe(fbpy)_3(PF_6)_2$ are listed in Tables 3, 4 and 5, respectively. The ^1H, ^{15}N and ^{19}F-NMR spectra are shown in Figures 5b, 6d and 7a, respectively.

Anal. calcd. for $FeC_{30}H_{21}F_3N_6.2PF_6$: C 41.50, N 9.68; found : C 41.23, N 9.50.

Elemental analyses of all complexes, as reported in this thesis, were performed by Mr. B. Hauser from Freshwater Institute (Fisheries and Oceans).

Preparation of mixed ligand complexes of iron (II) containing bipyridine and 4-fluorobipyridine

(i) $FeSO_4.7H_2O$ (25.0 mg, 0.1 mmole) was added to an aqueous solution containing a mixture of bipyridine (28.1 mg, 0.2 mmole) and 4-fluorobipyridine (15.7 mg, 0.1 mmole). The red solution was heated on the water-bath for 10 min. The red complex was precipitated by addition of a saturated solution of $NaPF_6$. The precipitate was filtered, washed with distilled water and dried over P_2O_5 under vacuum.

The ^{19}F-NMR spectrum shows the presence of a mixture of mono- and bis-fbpy iron(II) complexes, $Fe(fbpy)(bpy)_2^{2+}$ and $Fe(fbpy)_2(bpy)^{2+}$, in a relative ratio of 4:1, respectively.

(ii) Using the above procedure, $FeSO_4.7H_2O$ (25.0 mg, 0.1 mmole) was added to an aqueous solution containing a mixture of bipyridine (14.0 mg, 0.1 mmole) and 4-fluorobipyridine (31.4 mg, 0.2 mmole). The red complex was precipitated by addition of $NaPF_6$. The precipitate was filtered, washed with distilled water and dried over P_2O_5 under vacuum.

A mixture of mono-, bis- and tris-fbpy iron(II) complexes, $Fe(fbpy)(bpy)_2^{2+}$, $Fe(fbpy)_2(bpy)^{2+}$ and $Fe(fbpy)_3^{2+}$, was observed in the ^{19}F-NMR spectrum. From integration available, a relative value of 2:3:1 for the mono : bis : tris ratio was found. The fluorine chemical shifts for these mixed ligand complexes are summarized in Table 5. The ^{19}F-NMR spectra are shown in Figure 8.

Preparation of tris(2,2′-bipyridine)iron(III) hexafluorophosphate

An aqueous solution containing a 1:3 mixture (mole ratio) of ferrous sulphate heptahydrate and 2,2′-bipyridine was treated with concentrated sulphuric acid and cooled to 0°C in a ice bath. An excess of PbO_2 was added to the red solution at 0°C and a deep blue colour was developed. The blue solution was then filtered and $Fe(bpy)_3(PF_6)_3$ was precipitated by addition of $NaPF_6$. The blue precipitate was filtered, washed with cold water, dried in vacuum over P_2O_5 and stored in a dark place. In sunlight the compound gradually became red.

Preparation of tris(4-fluorobipyridine)iron(III) hexafluorophosphate

$Fe(fbpy)_3(PF_6)_3$ was prepared by a method similar to that described for the preparation of $Fe(bpy)_3(PF_6)_3$.

The proton chemical shifts for $Fe(bpy)_3^{3+}$ and $Fe(fbpy)_3^{3+}$ are tabulated in Table 4 and their spectra are shown in Figure 9. The ^{19}F-NMR data for $Fe(fbpy)_3^{3+}$ are shown in Table 5 and its spectrum is shown in Figure 7b.

Table 4. The proton chemical shifts of Fe(II)(a) and Fe(III)(b) complexes containing bpy and fbpy as ligands.

	$Fe(bpy)_3^{2+}$	$Fe(fbpy)_3^{2+}$	$Fe(bpy)_3^{3+}$	$Fe(fbpy)_3^{3+}$
H-3	8.8	8.73	7.2	9.6 [2](c) 8.9 [2]
H-3′		8.86		7.3 [2] 6.7 [2]
H-4	8.3	----	1.5	----
H-4′		8.28		(d)
H-5	7.6	7.44	0.2	(d)
H-5′		7.6		(d)
H-6	7.7	7.87 7.84 [2] 7.79 [2] 7.75 [2] 7.70	-44.9	-44.4 [8]
H-6′				

(a) In acetone d-6 ; the anion was PF_6^- ; referenced against protonated acetone (2.04 ppm).

(b) In acetonitrile d-3 ; the anion was PF_6^- ; referenced against protonated acetonitrile (1.93 ppm).

(c) The number of overlapping peaks is given in brackets.

(d) Not observed ; under solvent peak.

Table 5. ^{19}F-NMR data for Fe and Co complexes containing bpy and fbpy as ligands [(a)]

	Chemical shifts (ppm)			
$Fe(fbpy)_3^{2+}$	-97.55	-97.61	-97.63	-97.69
$Fe(fbpy)_2(bpy)^{2+}$	-97.65	-97.67	-97.71	-97.74
$Fe(fbpy)(bpy)_2^{2+}$	-97.76			
$Fe(fbpy)_3^{3+}$	-57.9	-58.4	-61.2	-61.7
$Co(fbpy)_3^{2+}$	-93.95	-95.54 [2][(b)]		-95.15
$Co(fbpy)_2(bpy)^{2+}$	-93.95	-94.54	-96.00	-96.60
$Co(fbpy)(bpy)_2^{2+}$	-96.00			
$Co(fbpy)_3^{3+}$	-88.02	-88.04	-88.09	-88.11

(a) In CD_3CN solution ; the anion was PF_6^- ; referenced against C_6F_6 (-162.9 ppm).

(b) Number in bracket is overlapping peaks.

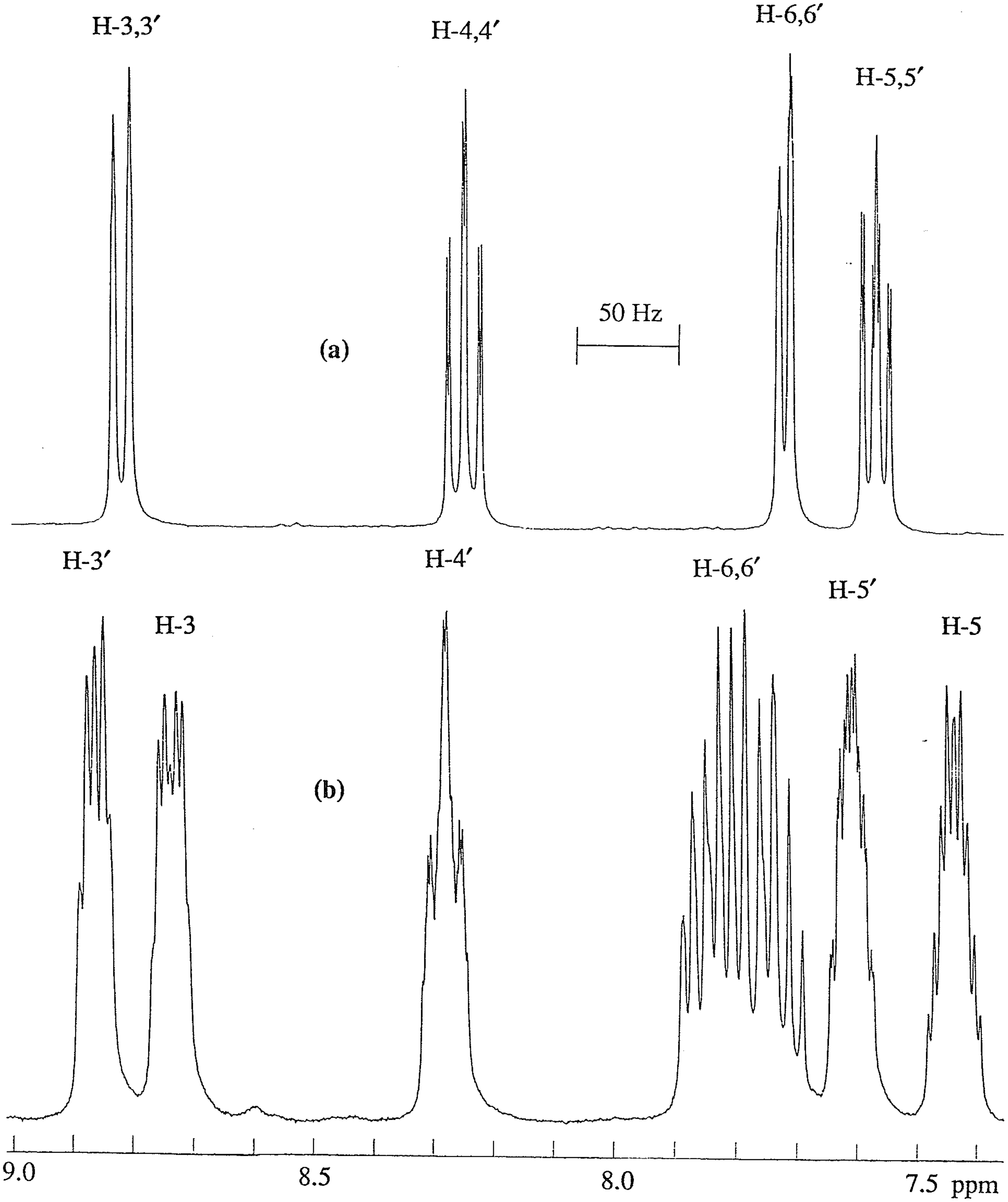


Figure 5. ^{1}H-NMR spectra of Fe(II) complexes in acetone d-6

(a) Fe(bpy)$_3$(PF$_6$)$_2$

(b) Fe(fbpy)$_3$(PF$_6$)$_2$

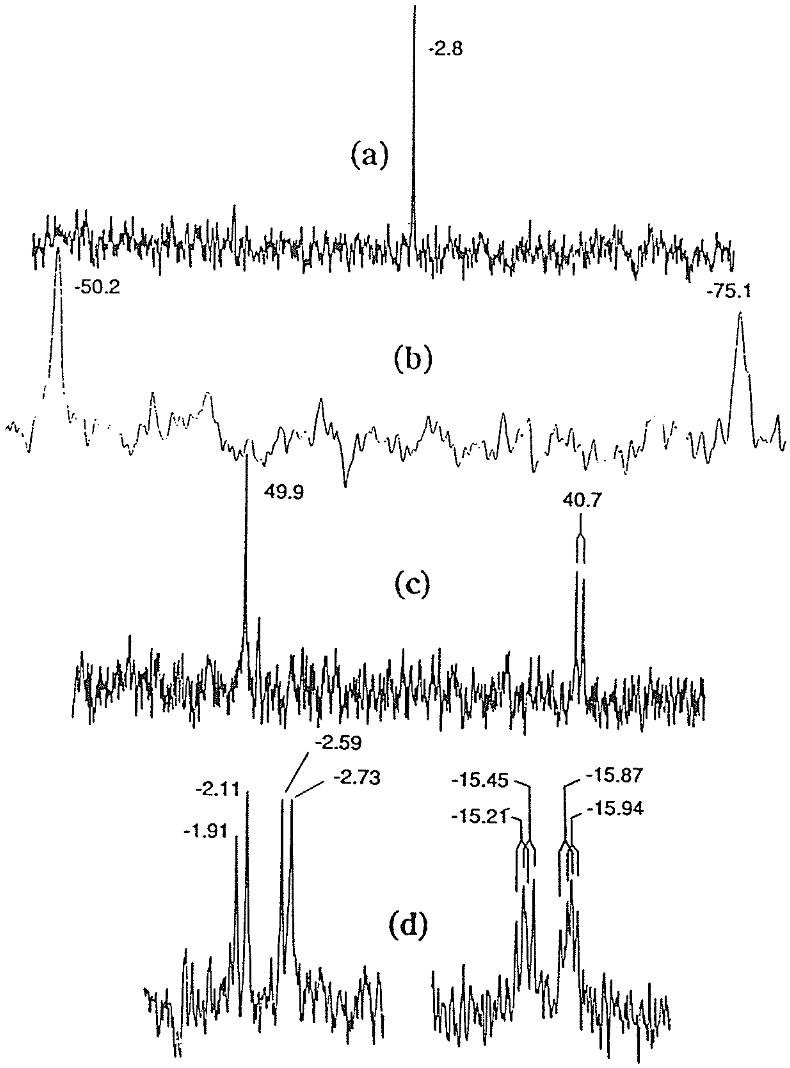


Figure 6. ^{15}N-NMR spectra of Fe(II) and Co(III) complexes (natural abundance , proton-decoupled)

(a) Fe(bpy)$_3$Cl$_2$ in D$_2$O

(b) cis-Co(bpy)$_2$(H$_2$O)$_2$(PF$_6$)$_3$ in D$_2$O

(c) fbpy in CDCl$_3$

(d) 3:1 mixture of mer- and fac-Fe(fbpy)$_3$(PF$_6$)$_2$ in acetone d-6

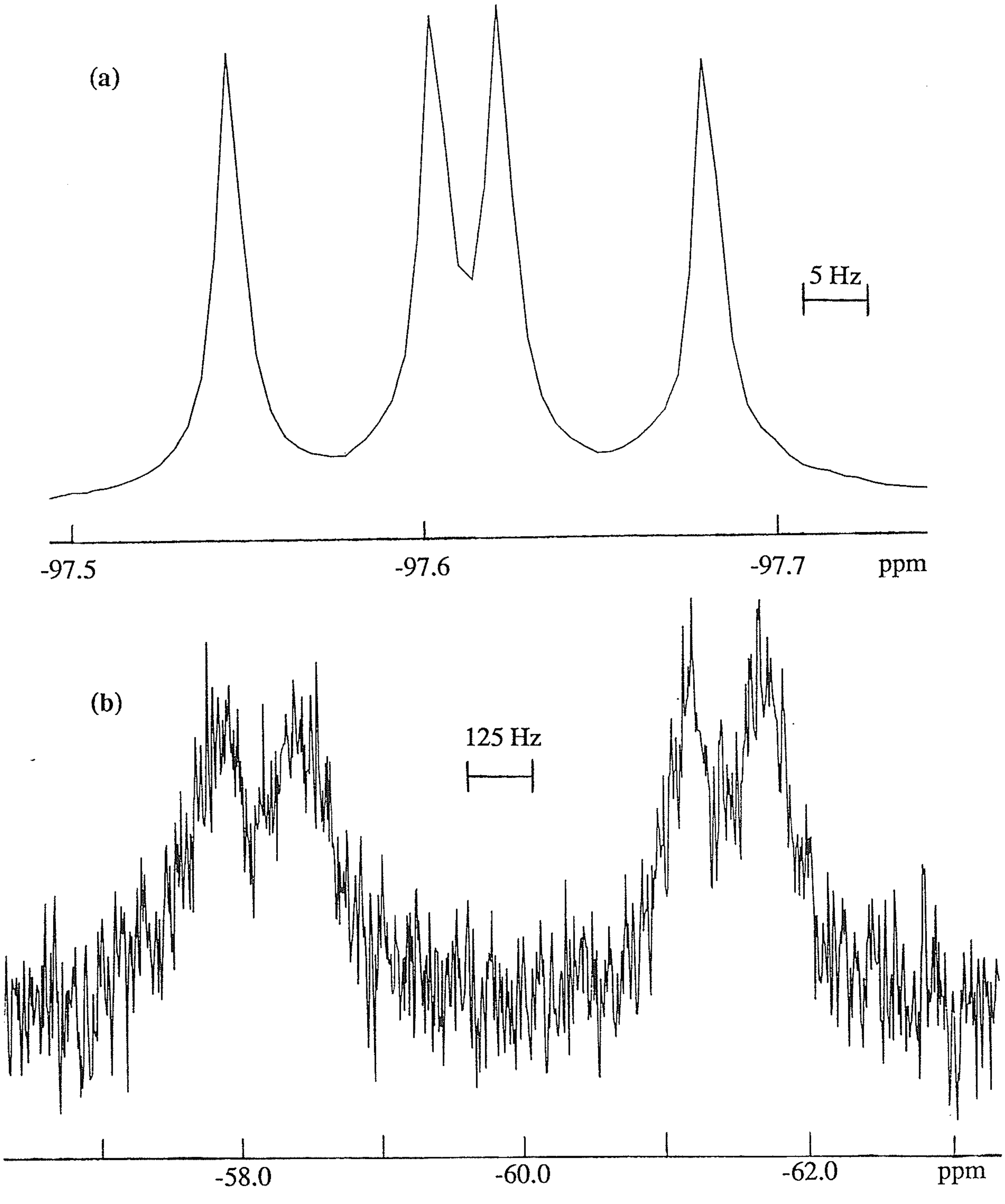


Figure 7. ^{19}F-NMR spectra of tris-fbpy complexes of Fe(II) and Fe(III) in CD_3CN .

(a) $Fe(fbpy)_3(PF_6)_2$

(b) $Fe(fbpy)_3(PF_6)_3$

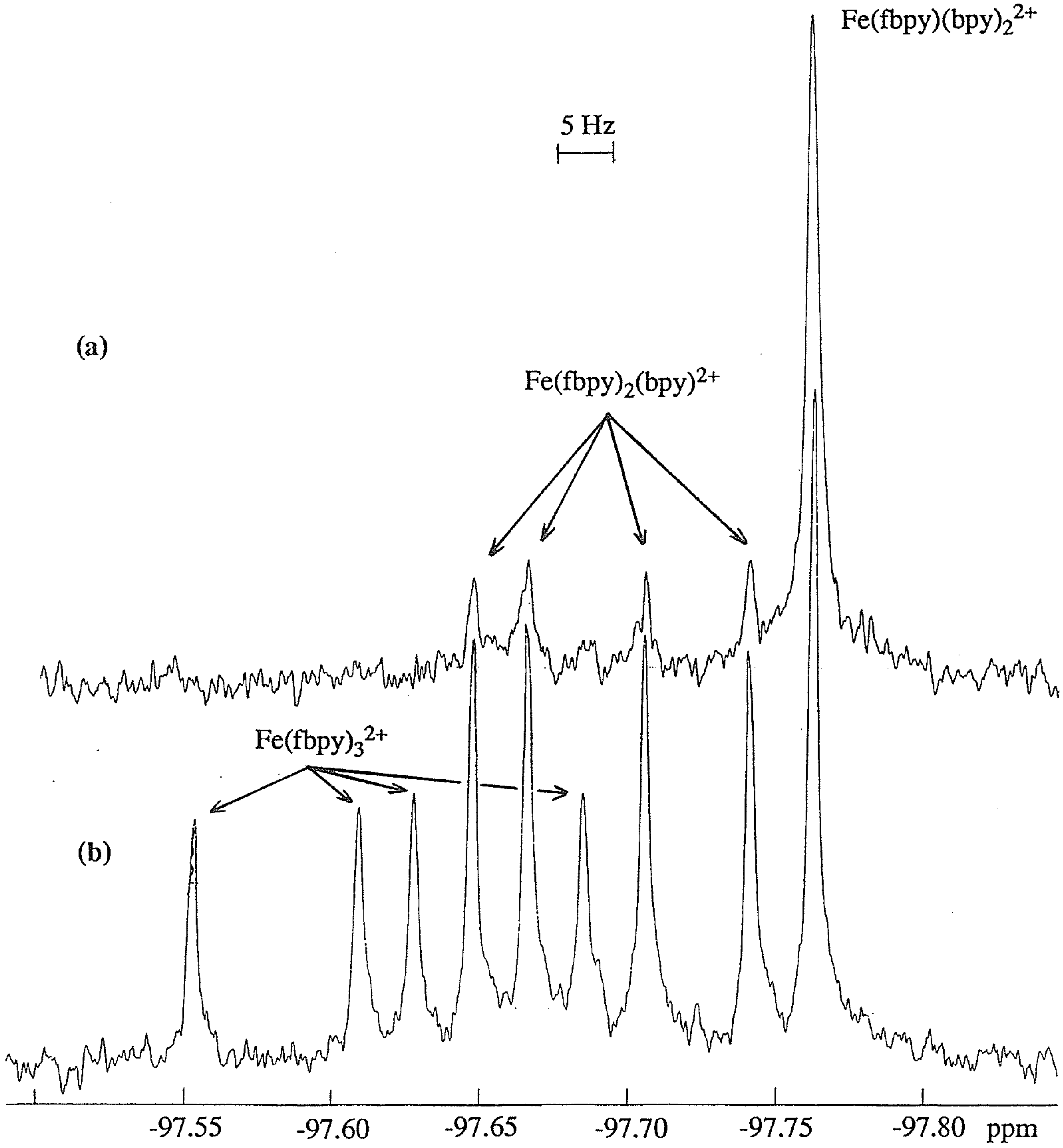


Figure 8. ^{19}F-NMR spectra of mixed ligand complexes of Fe(II) containing bpy and fbpy in CD_3CN.

(a) 1:2:1 mole ratio of $FeSO_4$: bpy : fbpy

(b) 1:1:2 mole ratio of $FeSO_4$: bpy : fbpy

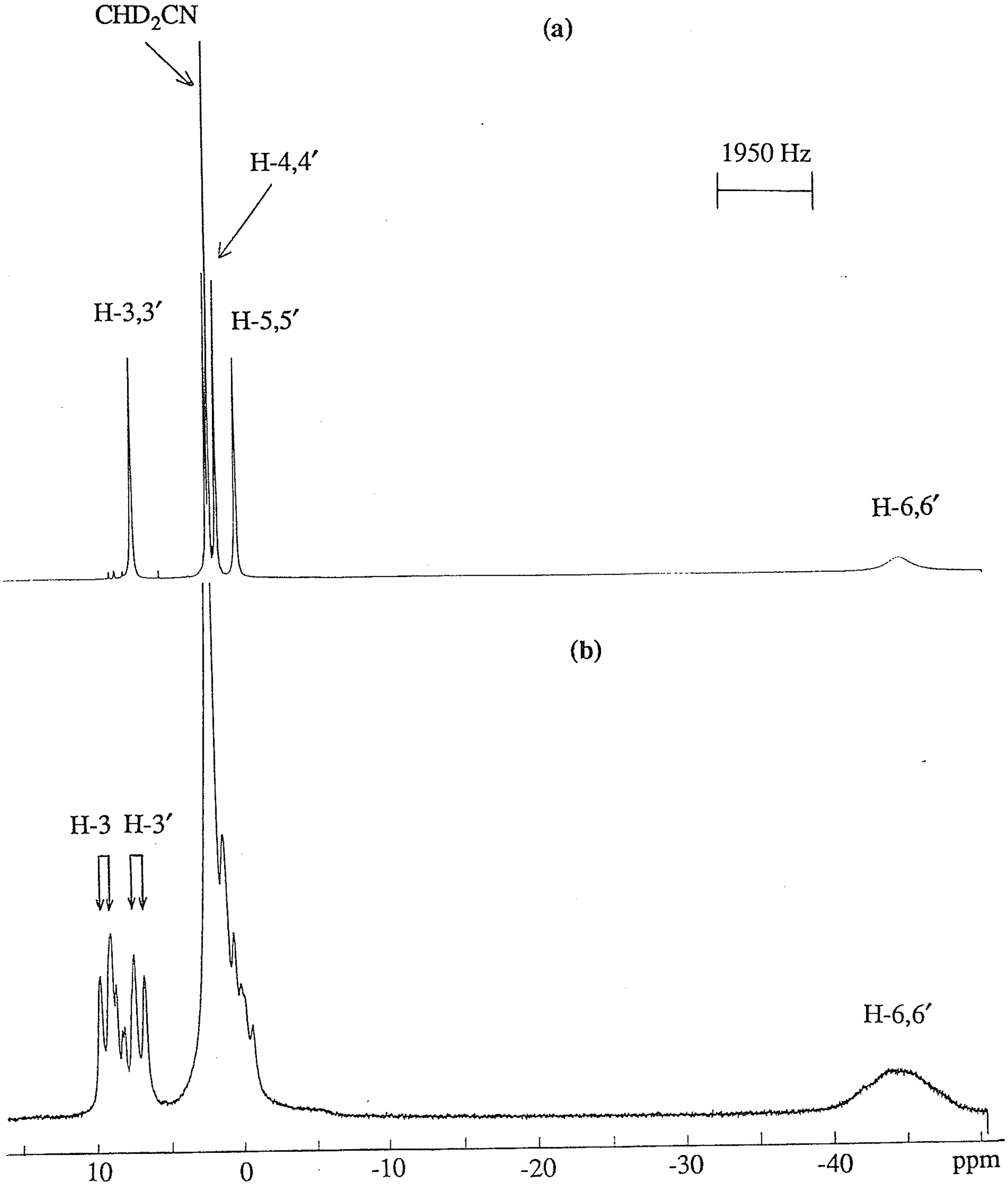


Figure 9. ^{1}H-NMR spectra of Fe(III) complexes in CD_3CN .

(a) $Fe(bpy)_3(PF_6)_3$

(b) $Fe(fbpy)_3(PF_6)_3$

The following cobalt complexes were kindly provided by F. Qu (67).

Preparation of tris(2,2′-bipyridine)cobalt(II) hexafluorophosphate

Following the methods reported in the literature (68), a solution of cobaltous chloride hexahydrate (0.12 g, 0.50 mmole) in absolute ethanol (10 mL) was treated with a solution of 2,2′-bipyridine (0.26 g, 1.7 mmole) in ethanol. The mixture was stirred and refluxed for 15 min. Diethyl ether (40 mL) was added to the solution and the precipitate was formed immediately. After filtering and washing with ether, the pink precipitate was re-dissolved in water (10 mL) and a saturated solution of $NaPF_6$ was added. The yellow precipitate was filtered, washed with water, ethanol, then with diethyl ether and dried under vacuum. The whole procedure was performed under nitrogen atmosphere.

Preparation of tris(4-fluorobipyridine)cobalt(II) hexafluorophosphate

$Co(fbpy)_3(PF_6)_2$ was prepared by the method similar to that described for the preparation of $Co(bpy)_3(PF_6)_2$.

The ^{19}F-NMR data for $Co(fbpy)_3^{2+}$ are listed in Table 5 and its spectrum is shown in Figure 10a. The proton chemical shifts for $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{2+}$ complexes are tabulated in Table 6 and their spectra are shown in Figure 11.

Anal. calcd. for $CoC_{30}H_{21}F_3N_6.2PF_6.2H_2O$: C 39.71 , N 9.26 ; found : C 40.24 , N 9.30 .

Preparation of mixed ligand complexes of cobalt (II) containing bipyridine and 4-fluorobipyridine

(i) A stoichiometric amount of $CoCl_2.6H_2O$ in absolute ethanol was added to a mixture of bipyridine and 4-fluorobipyridine (2:1 mole ratio), which were previously dissolved in ethanol. The yellow precipitate was obtained by the same procedure described as above.

The ^{19}F and ^{1}H-NMR spectra of the product show the presence of a mixture of $Co(bpy)_3^{2+}$, $Co(fbpy)(bpy)_2^{2+}$ and $Co(fbpy)_2(bpy)^{2+}$ in a relative ratio of 5:4:1 , respectively .

(ii) A stoichiometric amount of $CoCl_2.6H_2O$ in absolute ethanol was added to a mixture of bipyridine and 4-fluorobipyridine (1:2 mole ratio), which were previously dissolved in ethanol. Using the same procedure described as above, the yellow precipitate was obtained .

The ^{19}F and ^{1}H-NMR spectra of the product show the presence of a mixture of $Co(bpy)_3^{2+}$, $Co(fbpy)(bpy)_2^{2+}$, $Co(fbpy)_2(bpy)^{2+}$ and $Co(fbpy)_3^{2+}$ in a relative ratio of 1:3:4:2 , respectively .

The ^{19}F and ^{1}H-NMR chemical shifts for these mixed ligand complexes are tabulated in Tables 5 and 7 , respectively. These assignments were made by comparison with the NMR spectra of $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{2+}$.

The ^{19}F-NMR spectra of the mixed ligand complexes of Co(II) are shown in Figure 12 .

Preparation of diaquabis(bipyridine)cobalt(II) complexes

(i) The method of Palade, Lin'kova and Chudaeva (69)

$CoCl_2.6H_2O$ (1.0 g, 4.0 mmole) was dissolved in water (10 mL) and the solution was acidified with one drop of concentrated HCl. Bipyridine (1.25 g, 8.0 mmole) and potassium chloride (2.0 g, 27.0 mmole) were added to the solution and the mixture was heated on the water-bath for 10 min. The solution was cooled to give a pink-red crystalline precipitate, which was filtered and washed with a mixture of alcohol and ether (1:1) and then with ether, and dried in air. The complex is formulated as $[Co(bpy)_2Cl_2].3.5H_2O$ (69).

As reported by Palade et al., in aqueous solution $Co(bpy)_2Cl_2$ is rapidly converted into the diaqua complex $Co(bpy)_2(H_2O)_2{}^{2+}$. The ^{1}H-NMR spectrum of the complex in methanol d-4 shows an equilibrium established between $Co(bpy)_3{}^{2+}$, $Co(bpy)_2(H_2O)_2{}^{2+}$ and $Co(bpy)(H_2O)_4{}^{2+}$ species in a relative ratio of 1:9:1 , respectively.

(ii) The method of Jaeger and Van Dijk (70)

A solution of $CoCl_2.6H_2O$ (0.24 g, 1.0 mmole) in absolute ethanol (5 mL) was treated with a solution of bipyridine (0.31 g, 2.0 mmole) in ethanol. The mixture was stirred for 15 min. Diethyl ether was added to this solution to give a grey precipitate. The precipitate was filtered and washed with ether.

The ^{1}H-NMR spectrum of the product in D_2O is similar to that of $Co(bpy)_2Cl_2$ in methanol. A relative ratio of 1:4:4 was found for $Co(bpy)_3{}^{2+}$: $Co(bpy)_2(H_2O)_2{}^{2+}$: $Co(bpy)(H_2O)_4{}^{2+}$.

The diaquabis(4-fluorobipyridine)cobalt(II) complex, $Co(fbpy)_2(H_2O)_2{}^{2+}$, was also prepared by the methods similar to that described for the preparation of $Co(bpy)_2(H_2O)_2{}^{2+}$.

Preparation of tris(2,2′-bipyridine)cobalt(III) hexafluorophosphate

$CoCl_2.6H_2O$ (0.12 g, 0.50 mmole) and 2,2′-bipyridine (0.26 g, 1.7 mmole) were heated with distilled water until complete dissolution had occurred. The yellow solution was treated with hydrogen peroxide 30% (0.5 mL) and hydrochloric acid (0.5 mL). The mixture was then evaporated to a syrupy consistency. 10 mL of water was added and the solution was then treated with a saturated solution of $NaPF_6$. The yellow precipitate was filtered, washed with water, alcohol, then with ether and dried under vacuum .

Preparation of tris(4-fluorobipyridine)cobalt(III) hexafluorophosphate

$Co(fbpy)_3(PF_6)_3$ was prepared by the method similar to that described for the preparation of $Co(bpy)_3(PF_6)_3$.

The proton chemical shifts for $Co(bpy)_3^{3+}$ and $Co(fbpy)_3^{3+}$ are listed in Table 6 and their spectra are shown in Figure 14. The ^{19}F-NMR data for $Co(fbpy)_3^{3+}$ are summarized in Table 5 and its spectrum is shown in Figure 10b.

Anal. calcd. for $CoC_{30}H_{21}F_3N_6.3PF_6$: C 35.45 , N 8.27 ; found : C 35.05 , N 8.17 .

Preparation of diaquabis(bipyridine)cobalt(III) hexafluorophosphate

Following a reported method (71), $Na_3Co(CO_3)_3.3H_2O$ (1.8 g, 5.0 mmole) and 2,2′-bipyridine (1.6 g, 10 mmole) were dissolved in 20 mL of water. The solution was allowed to stand for 8 hrs. Addition of $NaPF_6$ solution precipitated a brown solid. After filtration, the solid was washed with acetone to remove any $Co(bpy)_3(PF_6)_3$ present. The complex obtained was then dissolved in water and cooled in an ice bath. $HClO_4$ (70% in H_2O) was added dropwise until CO_2 evolution ceased. After 72 hrs, the resultant precipitate was filtered and washed with ether.

Table 6. The proton chemical shifts of Co(II) and Co(III) complexes containing bpy and fbpy as ligands (a)

	$Co(bpy)_3^{2+}$	$Co(fbpy)_3^{2+}$	$Co(bpy)_3^{3+}$	$Co(fbpy)_3^{3+}$
H-3	83.2	78.7 78.5 78.4 78.1	9.03	8.98
H-3′		83.9 83.6 83.4 83.2		9.07
H-4	14.5	----	8.63	----
H-4′		14.8 14.6 14.3 14.2		8.66
H-5	45.8	41.8 41.6 40.6 40.4	7.89	7.94
H-5′		46.5 46.2 45.2 44.9		
H-6	87.7	87.5 86.7 83.8 [2](b)	7.83	7.73
H-6′		92.8 92.2 89.2 88.8		7.84

(a) In acetone d-6 ; the anion was PF_6^-; referenced against protonated acetone (2.04 ppm).

(b) Number in bracket is overlapping peaks ; under H-3′ peaks.

Table 7. The proton chemical shifts of mixed ligand complexes of Co(II) containing bpy and fbpy in CD_3CN [(a)].

	$Co(fbpy)(bpy)_2^{2+}$	$Co(fbpy)_2(bpy)^{2+}$
H-3	76.7	78.0 77.5 77.3 76.9
H-3′	83.5	82.9 82.4 82.2 81.8
H-3″	84.5 84.1 83.9 81.5	85.3 85.0 84.8 84.5
H-4′	14.4	14.4 [4][(b)]
H-4″	15.3 15.1 13.9 13.7	14.8 14.6 13.6 13.1
H-5	40.3	41.9 41.6 40.5 39.1
H-5′	46.1	46.2 [2] 45.9 [2]
H-5″	47.4 47.0 44.6 [2]	47.7 47.4 44.9 43.5
H-6	89.1	90.1 [2] 89.1 [2]
H-6′	87.4	87.4 [2] 86.3 [2]
H-6″	93.1 [2] 90.6 [2]	96.0 93.1 92.5 90.7

(a) The anion was PF_6^-; referenced against protonated acetonitrile (1.93 ppm).
(b) Number in brackets are overlapping peaks.

Proton positions are numbered as in Figure 13.

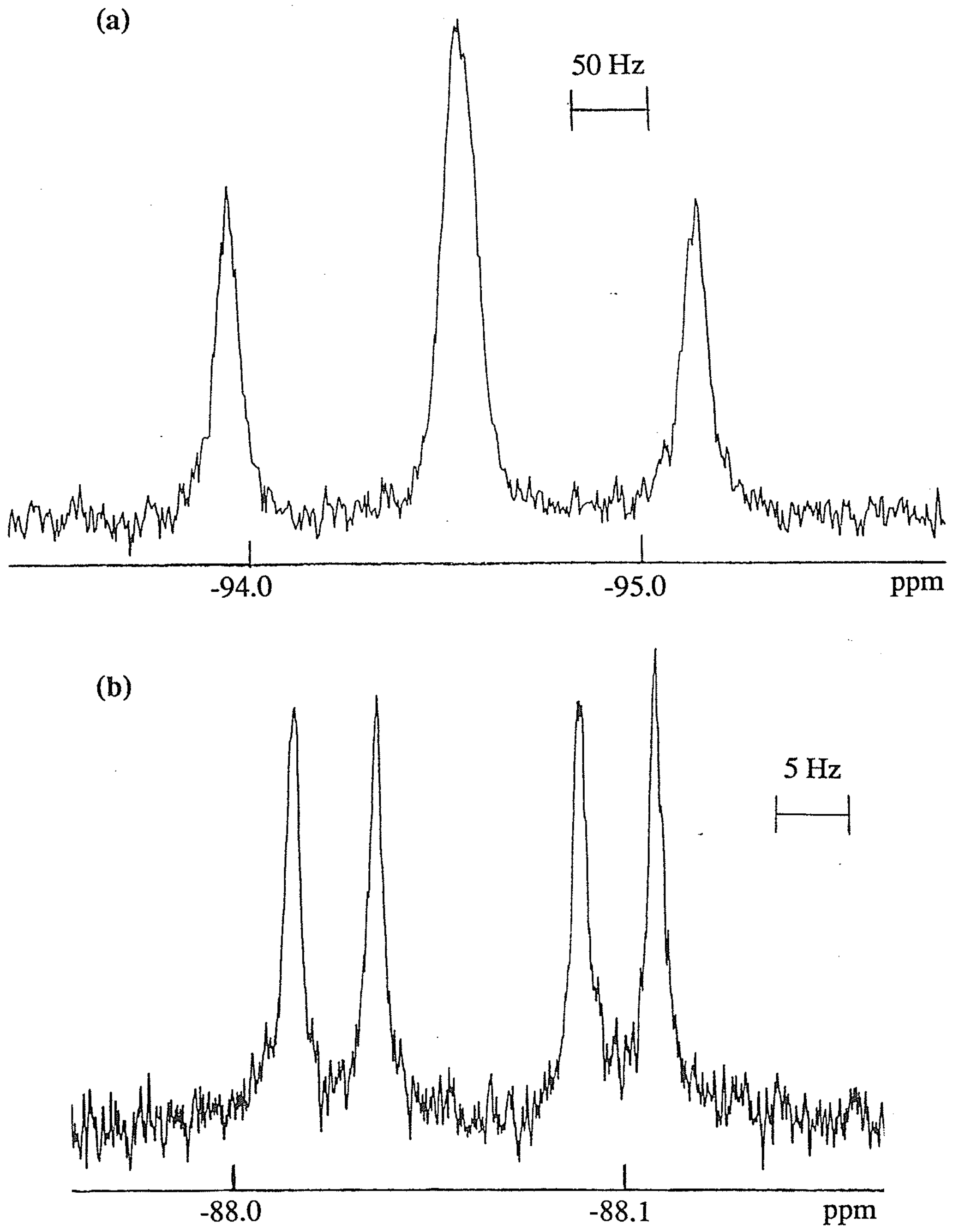


Figure 10. ^{19}F-NMR spectra of tris-fbpy complexes of Co(II) and Co(III) in CD_3CN

(a) $Co(fbpy)_3(PF_6)_2$

(b) $Co(fbpy)_3(PF_6)_3$

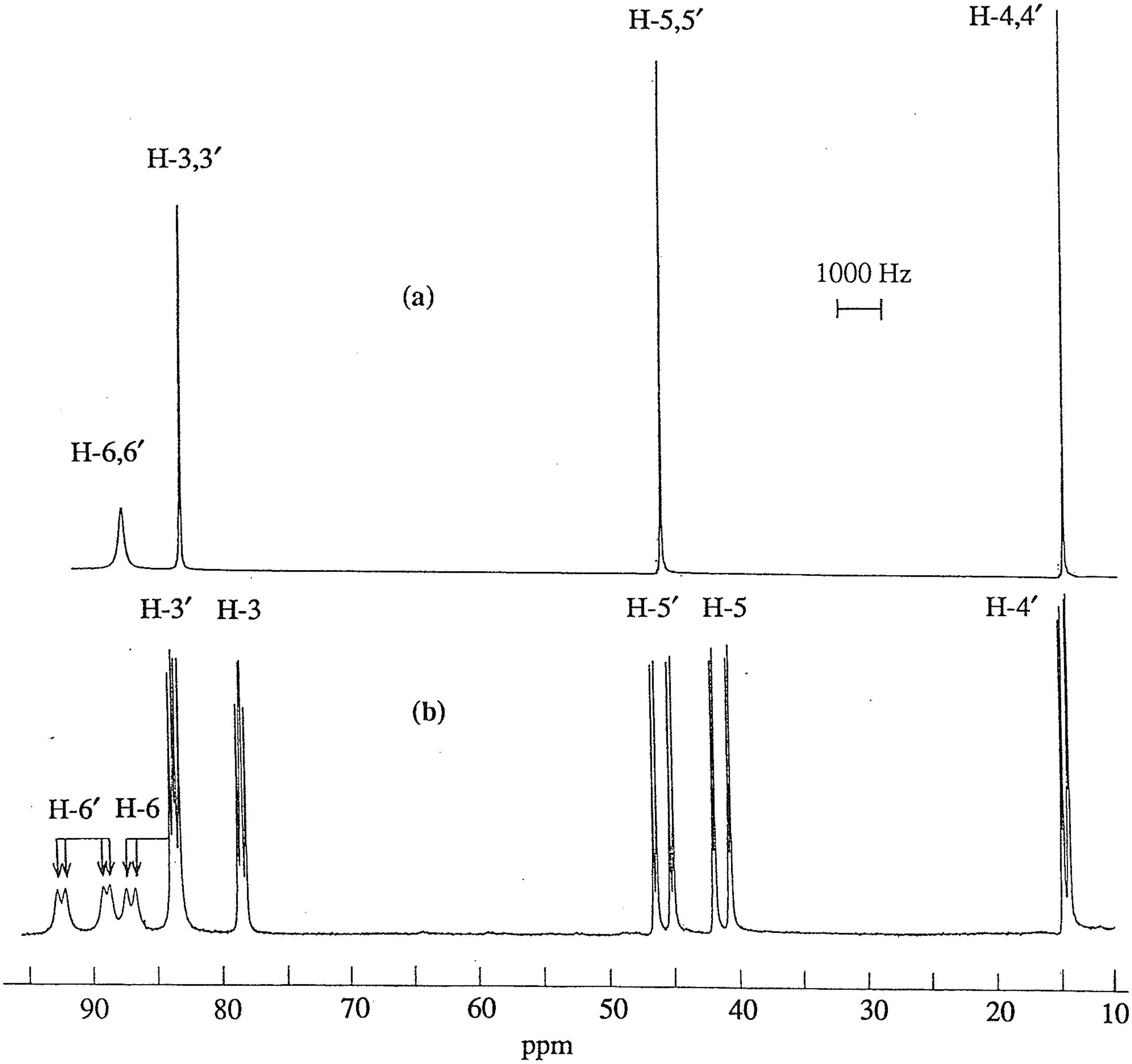


Figure 11. ^{1}H-NMR spectra of Co(II) complexes in acetone d-6 .

(a) $Co(bpy)_3(PF_6)_2$

(b) $Co(fbpy)_3(PF_6)_2$

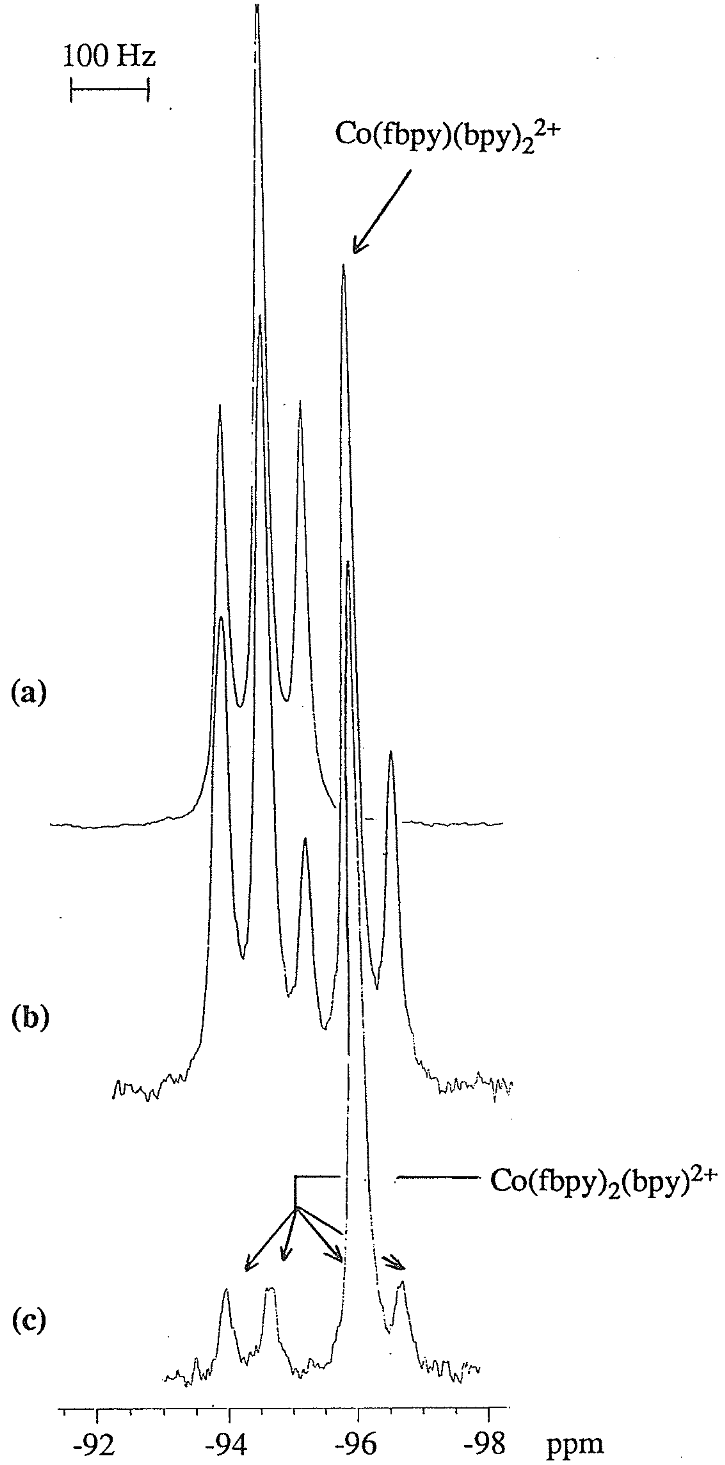


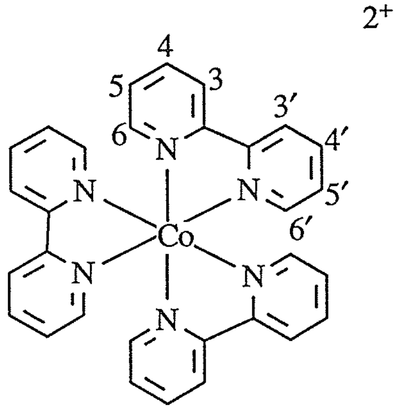
Figure 12. ^{19}F-NMR spectra of mixed ligand complexes of Co(II) containing bpy and fbpy in CD_3CN.

(a) $Co(fbpy)_3^{2+}$

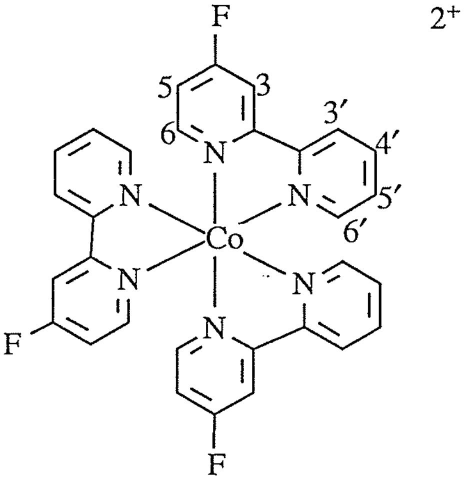
(b) 1:1:2 mole ratio of $CoCl_2$: bpy : fbpy

(c) 1:2:1 mole ratio of $CoCl_2$: bpy : fbpy

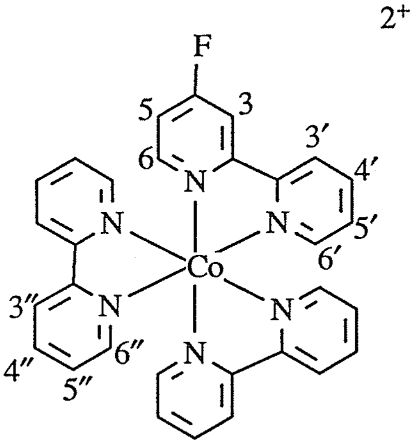
All NMR spectra were recorded on Bruker WH-90 spectrometer.



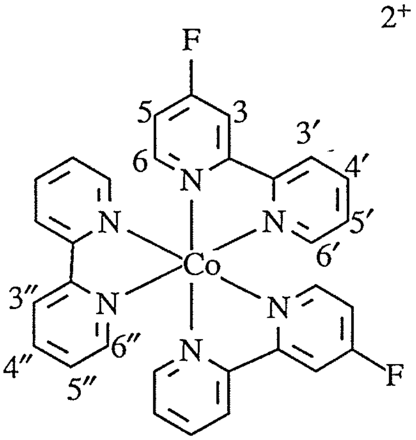
$Co(bpy)_3^{2+}$



$Co(fbpy)_3^{2+}$



$Co(fbpy)(bpy)_2^{2+}$



$Co(fbpy)_2(bpy)^{2+}$

Figure 13. The mixed ligand complexes of Co(II) containing bpy and fbpy

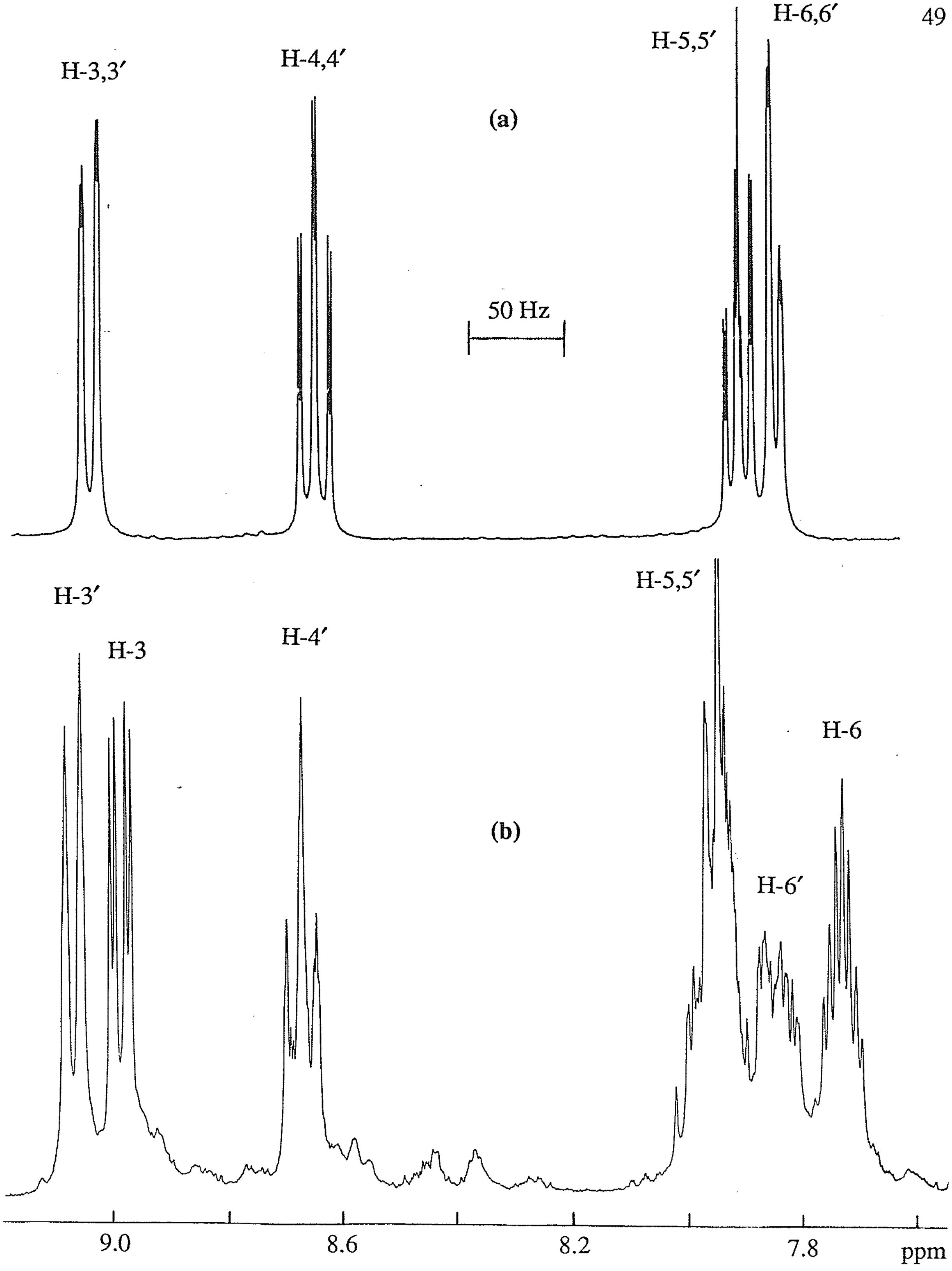


Figure 14. ^{1}H-NMR spectra of Co(III) complexes in acetone d-6

(a) $Co(bpy)_3(PF_6)_3$

(b) $Co(fbpy)_3(PF_6)_3$

3. LIGAND EXCHANGE REACTIONS

Exchange reaction between $Fe(fbpy)_3^{2+}$ and bpy

2,2′-Bipyridine (1.0 mg, 6.4×10^{-3} mmole) was added to tris-fbpy iron(II) (15.0 mg, 17.3×10^{-3} mmole) in 1.0 mL of acetonitrile d-3 . The ^{19}F-NMR spectrum of the sample obtained after 15 min shows a singlet at -102.7 ppm (relative to internal C_6F_6) corresponding to free ligand 4-fluorobipyridine. Also present in the ^{19}F-NMR spectrum is a mixture of mono-, bis- and tris-fbpy complexes of Fe(II). After two weeks, only mono-, bis-fbpy iron(II) and free ligand fbpy in a relative ratio of 2:1:10 , respectively, were observed in the ^{19}F-NMR spectrum .

In the ^{19}F-NMR spectrum of a sample containing $Fe(fbpy)_3^{2+}$ and bpy in 1:1 mole ratio, only a single peak at -102.7 ppm was observed.

Exchange reaction between $Fe(bpy)_3^{2+}$ and fbpy

4-fluorobipyridine (3.2 mg, 1.84×10^{-2} mmole) was added to tris-bpy iron (II) (15.0 mg, 1.84×10^{-2} mmole) in 1.0 mL of acetonitrile d-3. The fluorine NMR spectrum of the sample obtained after 15 min shows a singlet characteristic of free ligand fbpy and a mixture of mono- and bis-fbpy complexes of iron (II), $Fe(fbpy)(bpy)_2^{2+}$ and $Fe(fbpy)_2(bpy)^{2+}$, respectively. A relative value of 4:1:26 was found for the ratio of mono : bis : fbpy . The same observation was found in the ^{19}F-NMR spectrum of the sample after one month.

Exchange reaction between $Fe(fbpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$

A spectrum of a 1:1 mixture of $Fe(fbpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ in CD_3CN was recorded by ^{19}F-NMR . The fluorine NMR spectrum obtained after 1.5 hrs shows the presence of a mixture of mono-, bis- and tris-fbpy complexes of iron (II), $Fe(fbpy)(bpy)_2^{2+}$, $Fe(fbpy)_2(bpy)^{2+}$ and $Fe(fbpy)_3^{2+}$, in a relative ratio of 1:3:6, respectively. After one month, 2:2:1 ratio was found for mono-, bis- and tris-fbpy complexes. There was no free ligand fbpy in the fluorine spectrum. The ^{19}F-NMR spectra are shown in Figure 15 .

Exchange reaction between $Co(fbpy)_3^{2+}$ and bpy

2,2′-Bipyridine (1.2 mg, 7.7×10^{-3} mmole) was added to $Co(fbpy)_3(PF_6)_2$ (20.0 mg, 23.0×10^{-3} mmole) in 1.0 mL of CD_3CN. The fluorine NMR spectrum obtained after 10 min shows a mixture of bis- and tris-fbpy complexes of Co(II), $Co(fbpy)_2(bpy)^{2+}$ and $Co(fbpy)_3^{2+}$, respectively. A relative value of 1:4 was found for the ratio of bis : tris complexes. The same ratio was found in the ^{19}F-NMR spectrum of the sample after 2 weeks. Also present in the ^{19}F-NMR spectrum is a singlet at -102.7 ppm . The ^{19}F-NMR spectrum is shown in Figure 16.

Exchange reaction between $Co(bpy)_3^{2+}$ and fbpy

4-Fluorobipyridine (1.4 mg, 8.0×10^{-3} mmole) was added to $Co(bpy)_3^{2+}$ (20.0 mg, 24.5×10^{-3} mmole) in dried acetone d-6 and the sample was recorded by ^{1}H-NMR . The spectrum obtained after 20 min shows a mixture of $Co(bpy)_3^{2+}$ and $Co(fbpy)(bpy)_2^{2+}$ in a ratio of 3:1 , respectively. Also present in the ^{1}H-NMR spectrum are the free ligands, bpy and fbpy, in a 1:1 ratio. The ^{1}H-NMR spectrum is shown in Figure 17 .

Exchange reaction between $Co(fbpy)_3^{3+}$ and bpy

2,2′-Bipyridine (1.0 mg, 6.4×10^{-3} mmole) was added to $Co(fbpy)_3^{3+}$ (20.0 mg, 19.7×10^{-3} mmole) in 1.0 mL of CD_3CN. The fluorine NMR spectrum obtained after 10 min shows only four peaks with equal intensities at -88.02, -88.04, -88.09 and -88.11 ppm relative to internal C_6F_6 , which are characteristics of $Co(fbpy)_3^{3+}$. Upon standing at room temperature for 2 weeks, a mixture of $Co(fbpy)_3^{3+}$ and $Co(fbpy)_2(bpy)^{3+}$ in a ratio of 2:1, respectively, was observed in the ^{19}F-NMR spectrum. Also present in the fluorine NMR spectrum is a singlet at -102.7 ppm . The ^{19}F-NMR spectra are shown in Figure 18.

Exchange reaction between $Co(fbpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$

A 1:1 mixture of $Co(fbpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ in acetonitrile d-3 was recorded by ^1H and ^{19}F-NMR . The proton and fluorine NMR spectra show signals characteristic of each complex, indicating that there is no ligand exchange between $Co(fbpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ within 15 min. After a week, the mixed ligand complexes of Co(II) and Fe(II) containing bpy and fbpy were observed in the ^1H and ^{19}F-NMR spectra of the sample.

The ^{19}F and ^1H-NMR spectra are shown in Figures 19 and 20 , respectively.

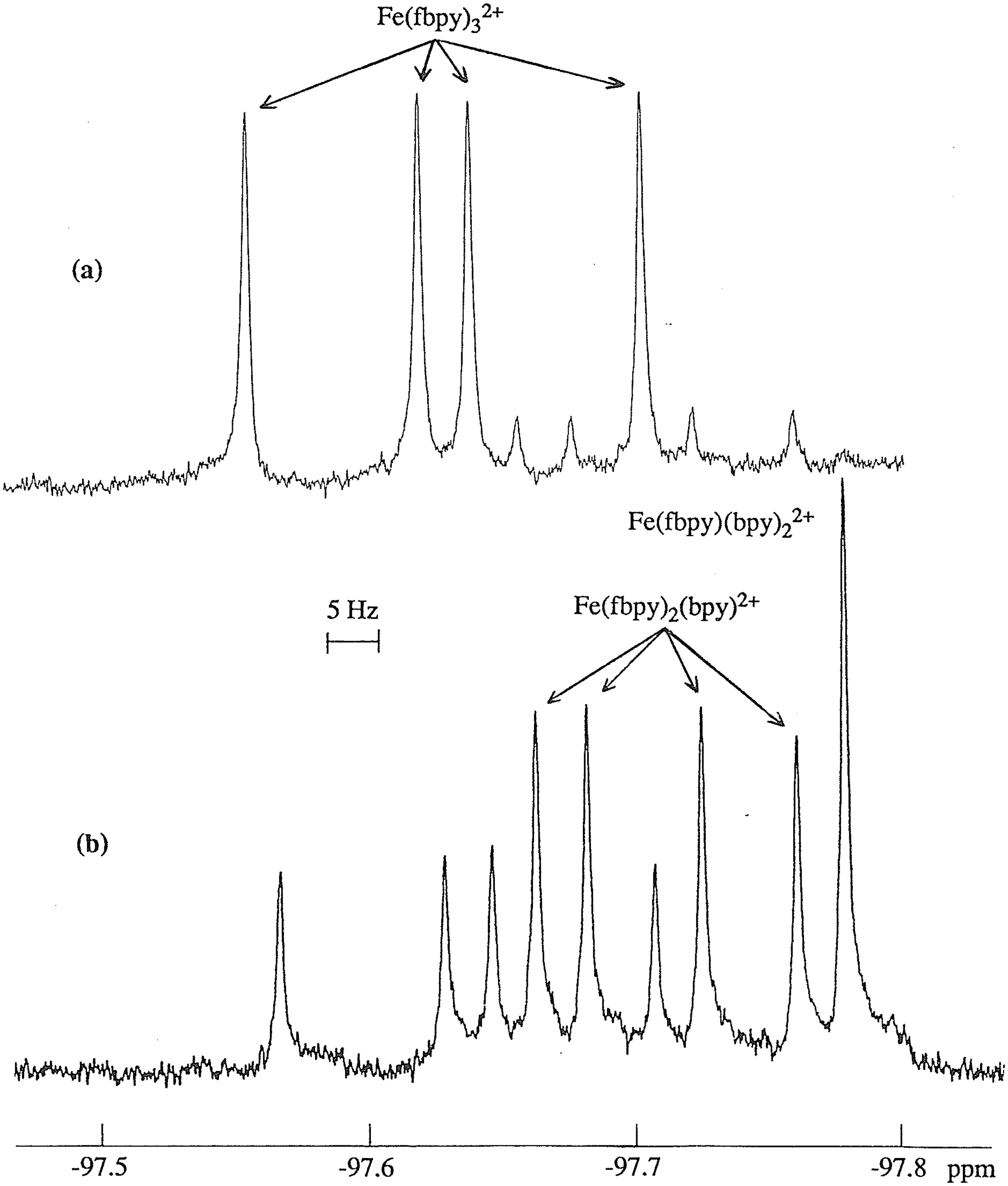


Figure 15. ^{19}F-NMR spectra of $Fe(fbpy)_3^{2+}$ + $Fe(bpy)_3^{2+}$ (1:1 mole ratio) in CD_3CN

(a) after 1.5 hrs.

(b) after one month

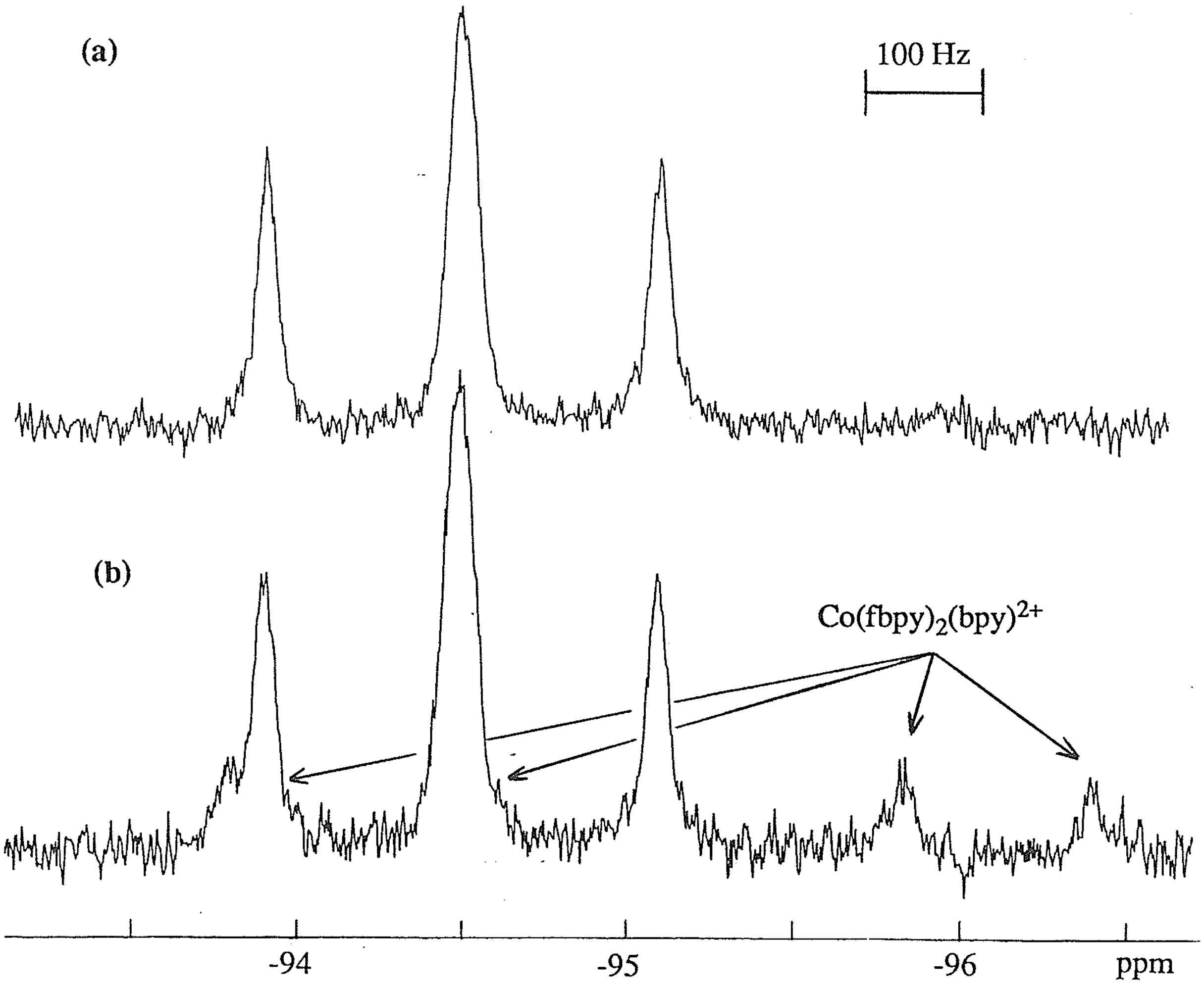


Figure 16. (a) ^{19}F-NMR spectrum of Co(fbpy)$_3^{2+}$ in CD$_3$CN

(b) ^{19}F-NMR spectrum of Co(fbpy)$_3^{2+}$ + bpy (3:1 mole ratio) in CD$_3$CN after 10 min.

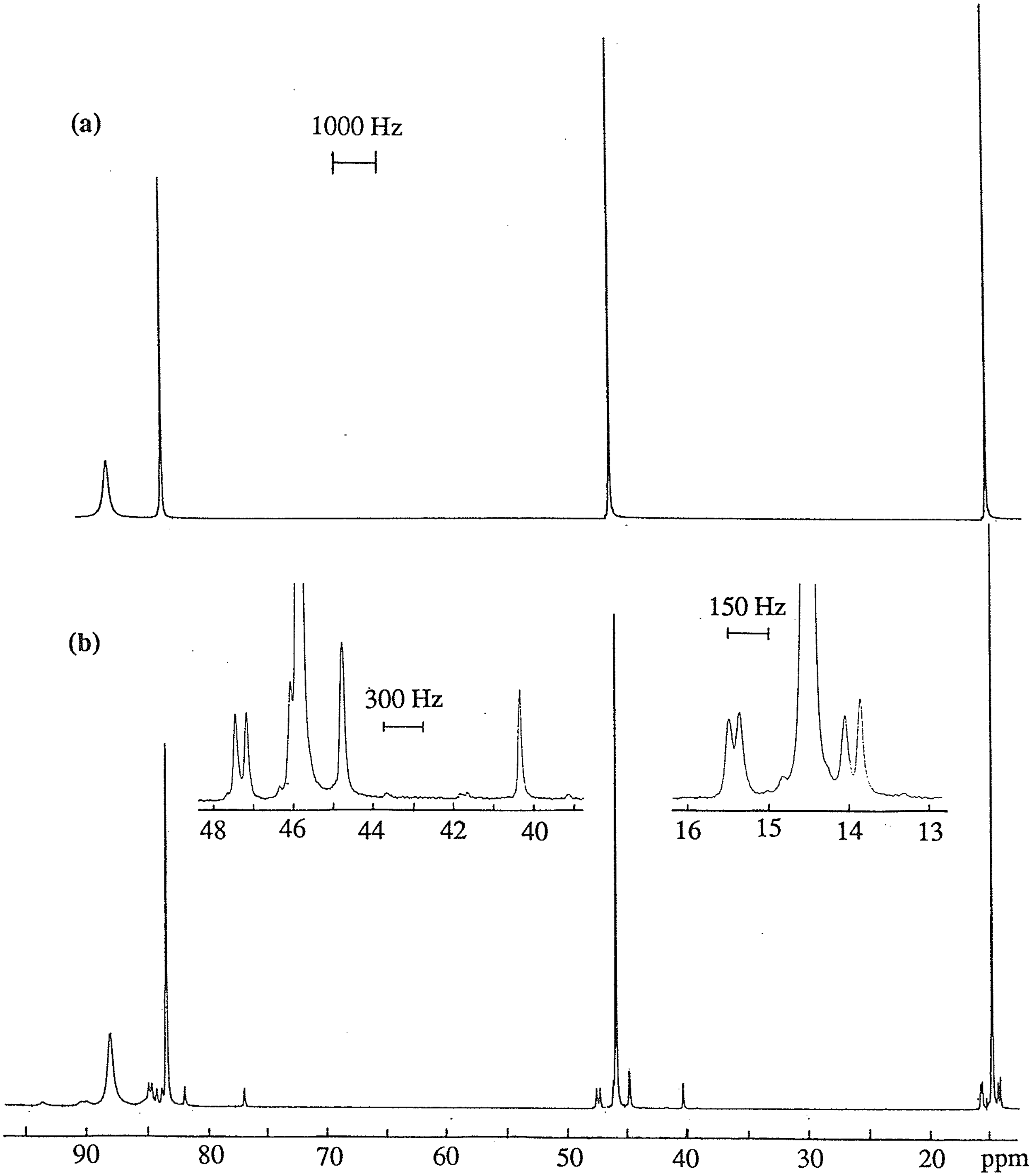


Figure 17. (a) ^{1}H-NMR spectrum of $Co(bpy)_3^{2+}$ in dried acetone d-6

(b) ^{1}H-NMR spectrum of $Co(bpy)_3^{2+}$ + fbpy (3:1 mole ratio) in dried acetone d-6 after 20 min.

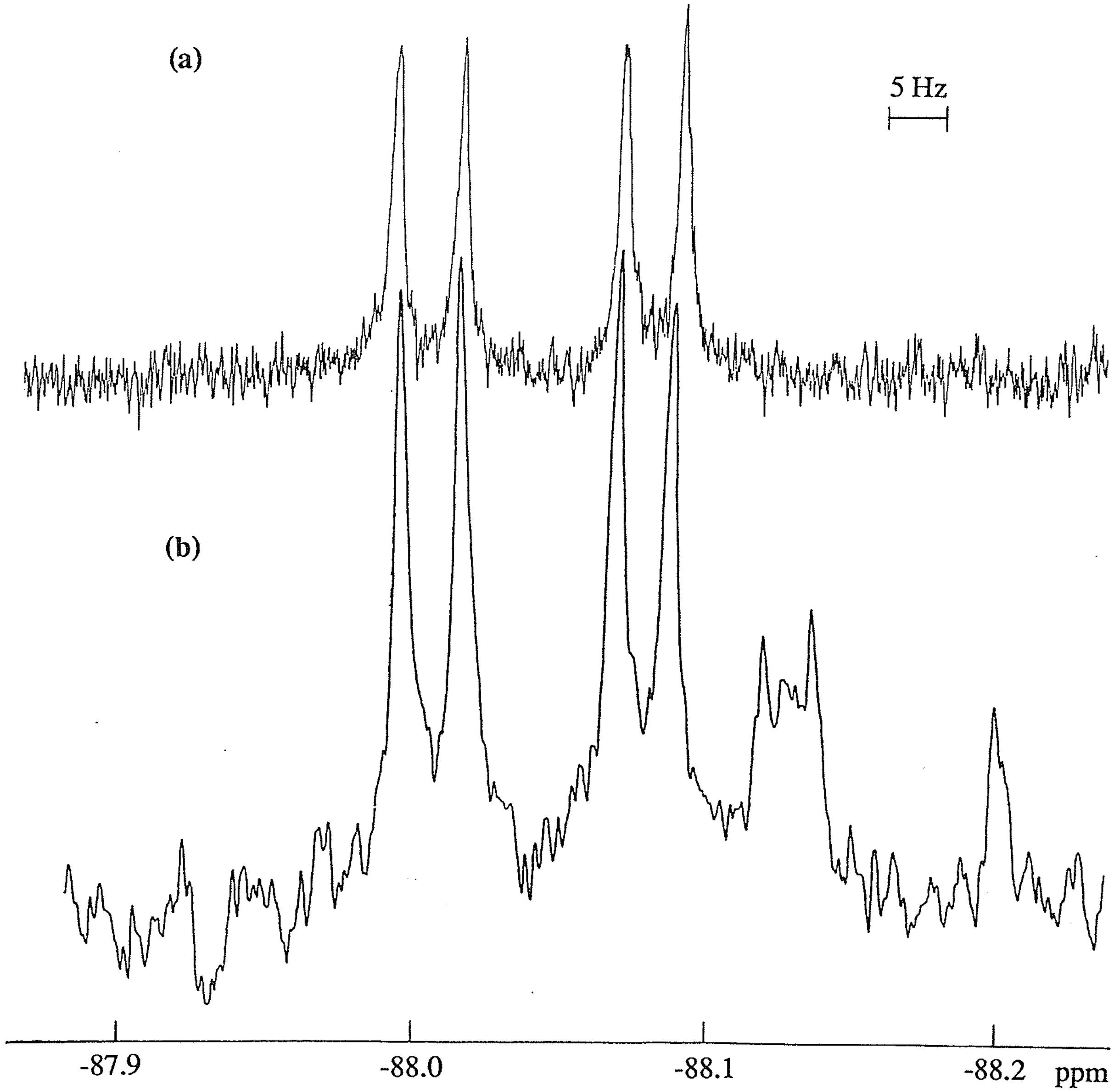


Figure 18. ^{19}F-NMR spectra of $Co(fbpy)_3^{3+}$ + bpy (3:1 mole ratio) in CD_3CN

(a) after 10 min.

(b) after two weeks

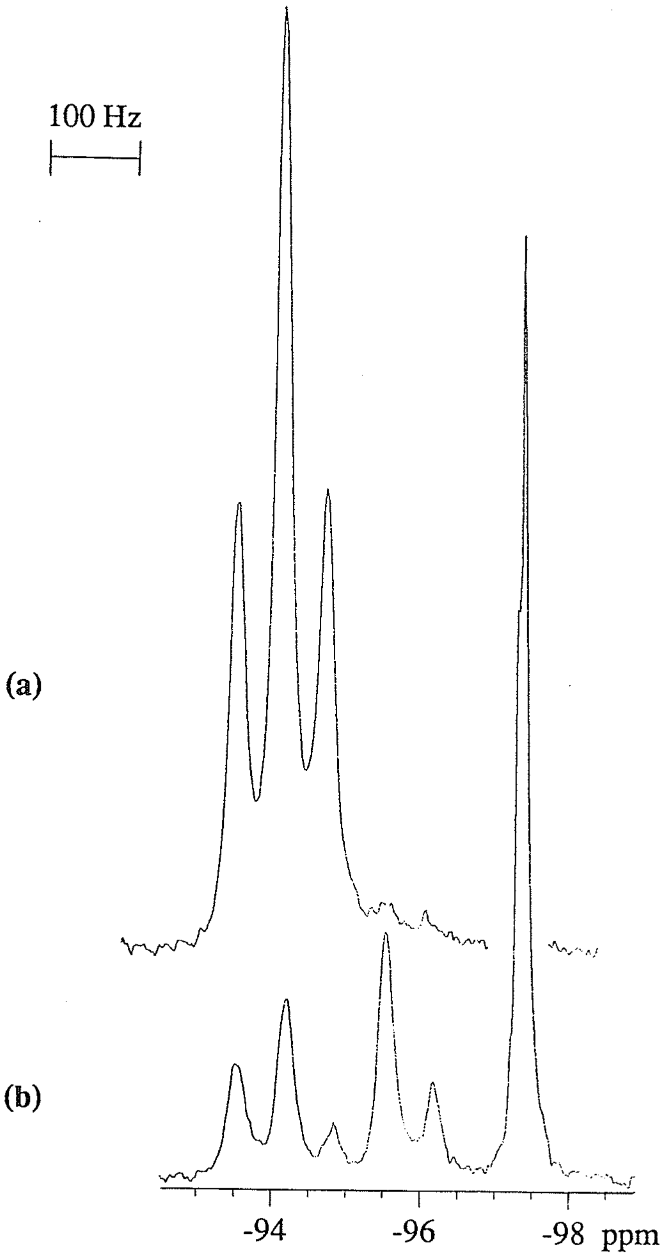


Figure 19. ^{19}F-NMR spectra of $Co(fbpy)_3^{2+}$ + $Fe(bpy)_3^{2+}$ (1:1 mole ratio) in CD_3CN

(a) after 15 – 20 min.

(b) after one week

Both NMR spectra were recorded on Bruker WH-90 spectrometer .

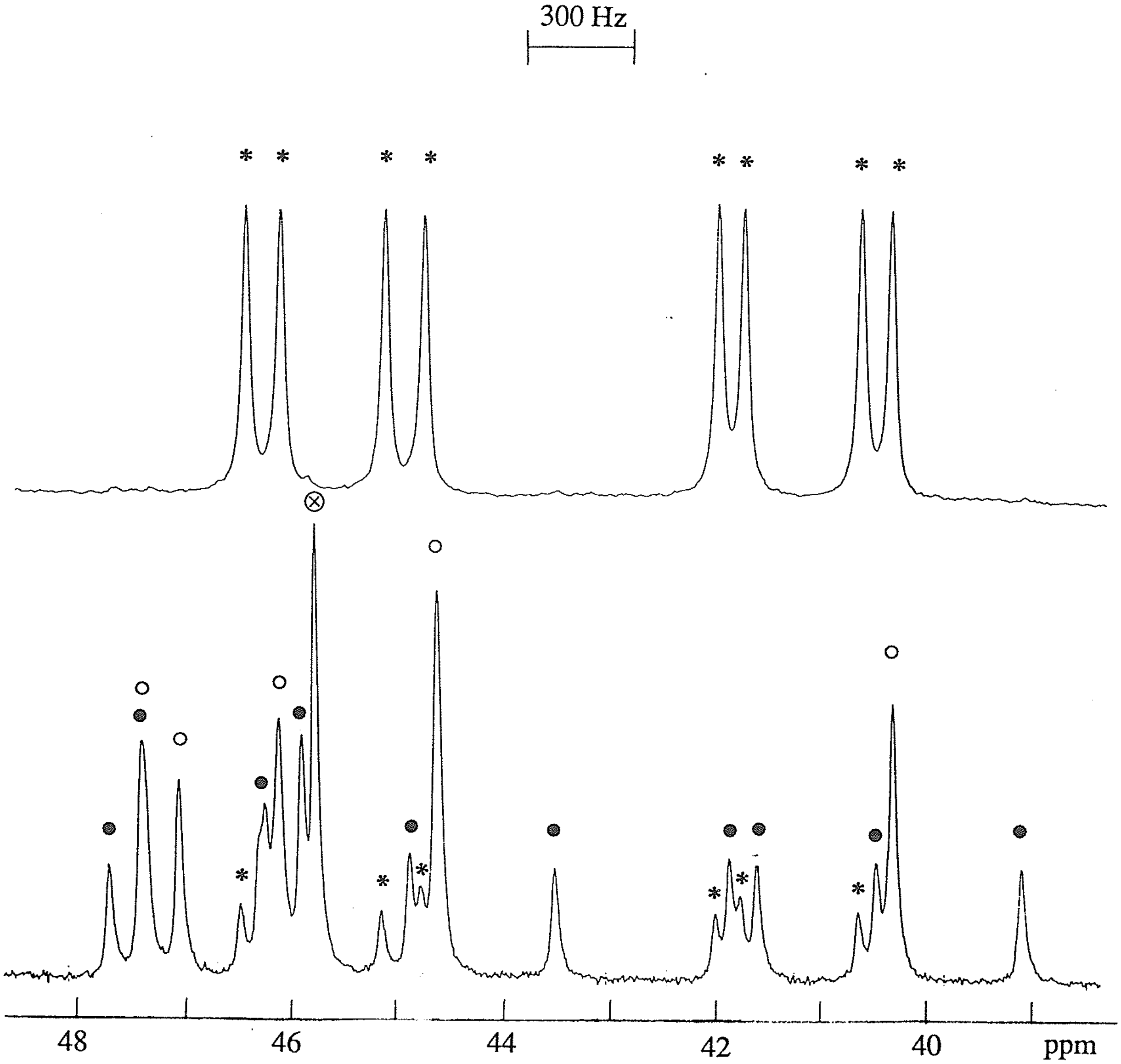


Figure 20. Portion of ^{1}H-NMR spectrum of $Co(fbpy)_3^{2+}$ + $Fe(bpy)_3^{2+}$ in CD_3CN showing only the H-5,5′ region of Co(II) complexes

(a) after 15 – 20 min.

(b) after one week

- * $Co(fbpy)_3^{2+}$
- ● $Co(fbpy)_2(bpy)^{2+}$
- ○ $Co(fbpy)(bpy)_2^{2+}$
- ⊗ $Co(bpy)_3^{2+}$

4. ELECTRON TRANSFER REACTIONS

Reaction between $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$

A spectrum of a 1:1 mixture of $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$ in acetonitrile d-3 was recorded by ^{19}F-NMR at room temperature. The ^{19}F-NMR spectrum shows signals characteristic of $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$, indicating that there is no electron transfer between $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$. After allowing the mixture to stand at room temperature for two weeks, no evidence of any reactions in this system could be detected.

Reaction between $Fe(fbpy)_3^{2+}$ and $Co(bpy)_3^{3+}$

A spectrum of a 1:1 mixture of $Fe(fbpy)_3^{2+}$ and $Co(bpy)_3^{3+}$ in acetonitrile d-3 was recorded by ^{19}F-NMR at room temperature. The ^{19}F-NMR spectrum shows neither electron transfer nor ligand exchange between $Fe(fbpy)_3^{2+}$ and $Co(bpy)_3^{3+}$ within 15 min. Upon allowing the solution to stand at room temperature for 2 weeks, the mixed ligand complexes of Fe(II) and Co(III) containing bpy and fbpy were found in the ^{19}F-NMR spectrum.

Reaction between $Fe(fbpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$

A spectrum of a 1:1 mixture of $Fe(fbpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$ in acetonitrile d-3 was recorded by ^{19}F-NMR at room temperature. The ^{19}F-NMR spectrum obtained after 20 min shows signals characteristic of $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$, indicating that there is electron transfer between $Fe(fbpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$. A trace amount of Co(II) complex was found in the spectrum. There was, however, no signal from Fe(III). The ^{19}F-NMR spectrum is shown in Figure 21 .

Reaction between $Fe(bpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$

A spectrum of a 1:1 mixture of $Fe(bpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$ in acetonitrile d-3 was recorded by ^{19}F-NMR at room temperature. The ^{19}F-NMR spectrum obtained after 30 min shows the presence of $Co(fbpy)_3^{3+}$, indicating that there is only electron transfer, but not ligand exchange, between $Fe(bpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$ within 30 min. There were no signals characteristic of $Co(fbpy)_3^{2+}$ in the ^{19}F-NMR spectrum.

Upon allowing the solution to stand at room temperature for 2 weeks, the mixed ligand complexes of Fe(II) and Co(III) containing bpy and fbpy were found in the solution by its ^{19}F-NMR spectrum, indicating that ligand exchange occurs between $Fe(bpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$ after electron transfer. The ^{19}F-NMR spectrum is similar to that which shows ligand exchange between $Fe(fbpy)_3^{2+}$ and $Co(bpy)_3^{3+}$ and is shown in Figure 22.

Reaction between $Fe(fbpy)_3^{2+}$ and $Fe(bpy)_3^{3+}$

A 1:1 mixture of $Fe(fbpy)_3^{2+}$ and $Fe(bpy)_3^{3+}$ in acetonitrile d-3 was recorded by ^{19}F-NMR at room temperature. There were neither signals characteristic of $Fe(fbpy)_3^{3+}$ nor $Fe(fbpy)_3^{2+}$ in the spectrum. Instead, a very broad peak at -90.5 ppm and a peak at -94.2 ppm (relative to internal C_6F_6) were found.

The same sample was examined again after 12 days by ^{19}F-NMR. Two broad peaks present in a ratio of 1:1 were observed at -94.2 and -97.6 ppm in the spectrum. The fluorine-19 NMR spectra of the mixture are shown in Figure 23.

Reaction between $Fe(bpy)_3^{2+}$ and $Fe(fbpy)_3^{3+}$

The same fluorine-19 NMR spectra were obtained for a 1:1 mixture of $Fe(bpy)_3^{2+}$ and $Fe(fbpy)_3^{3+}$. An examination of the spectrum obtained within 15 min showed the presence of broad peaks at about -90.0 and -94.2 ppm. Again, two broad peaks in 1:1 ratio were found at -94.2 and -97.6 ppm in the ^{19}F-NMR spectrum of a twelve-day old sample.

Reaction between $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$

$Co(bpy)_3(PF_6)_2$ (16.0 mg, 2.0×10^{-2} mmole) was dissolved in acetone d-6 (0.5 mL) in a dry box under nitrogen atmosphere. A NMR tube containing this solution was quickly connected to the vacuum rack and immersed in liquid nitrogen. A solution of $Co(fbpy)_3(PF_6)_3$ (20.0 mg, 2.0×10^{-2} mmole) in acetone d-6 (0.5 mL) was added as quickly as possible to this NMR tube while it was still kept in liquid nitrogen. The NMR tube was then sealed under dynamic vacuum. The sample was kept in liquid nitrogen until it was transferred to the NMR spectrometer for recording the first spectrum. The ^{1}H-NMR spectrum was studied over the temperature range from -83° to +27°C .

At -83° the ^{1}H-NMR spectrum showed separate signals characteristic of $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$. At -53°, in addition to the characteristic resonances of $Co(bpy)_3^{2+}$, four peaks of equal intensity for each particular ligand proton in the $Co(fbpy)_3^{2+}$ complex were observed. The signals characteristic of the mixed ligand complexes of Co(II) did not begin to appear until -33°. These peaks then increased as the temperature was raised to +27°. Portions of the ^{1}H-NMR spectra showing only the region of H-5,5′ of Co(II) complexes are shown in Figure 24 .

The temperature studies showed that all peaks of Co(II) complexes shifted upfield with increasing temperature. This is probably indicative of a decrease in the "rigidity" of the complexes as the temperature is increased.

The ^{19}F-NMR spectrum was also studied over the temperature range -73° to +27°. Only characteristic resonances of $Co(fbpy)_3^{3+}$ were found in the ^{19}F-NMR spectrum at -73°. The appearances of the mixed ligand complexes of Co(II) were observed at -33° after the formation of $Co(fbpy)_3^{2+}$ at -53°. These peaks gradually increased as the temperature was raised to +27°, whereas the peaks corresponding to $Co(fbpy)_3^{2+}$ decreased with increasing temperature.

Miscellaneous : Preparation of SiF_4(bpy) and SiF_4(fbpy)

Silicon tetrafluoride (3.0 mmoles) was condensed over a solution of bipyridine (0.28 g, 2.0 mmoles) in distilled, dried CH_2Cl_2 in a reaction tube connected to the vacuum rack. The mixture was slowly warmed to room temperature and a white solid was found to form within 5 min. After evaporating dichloromethane under vacuum and without further purification, a spectrum of the product was recorded by ^{19}F and ^{29}Si-NMR in dimethyl sulfoxide d-6.

(4-fluoro-2,2′-bipyridine)silicon tetrafluoride was prepared by the same procedure.

The ^{19}F-NMR chemical shifts and coupling constants for SiF_4(bpy), SiF_4(fbpy) and SiF_4(phen) are tabulated in Table 8.

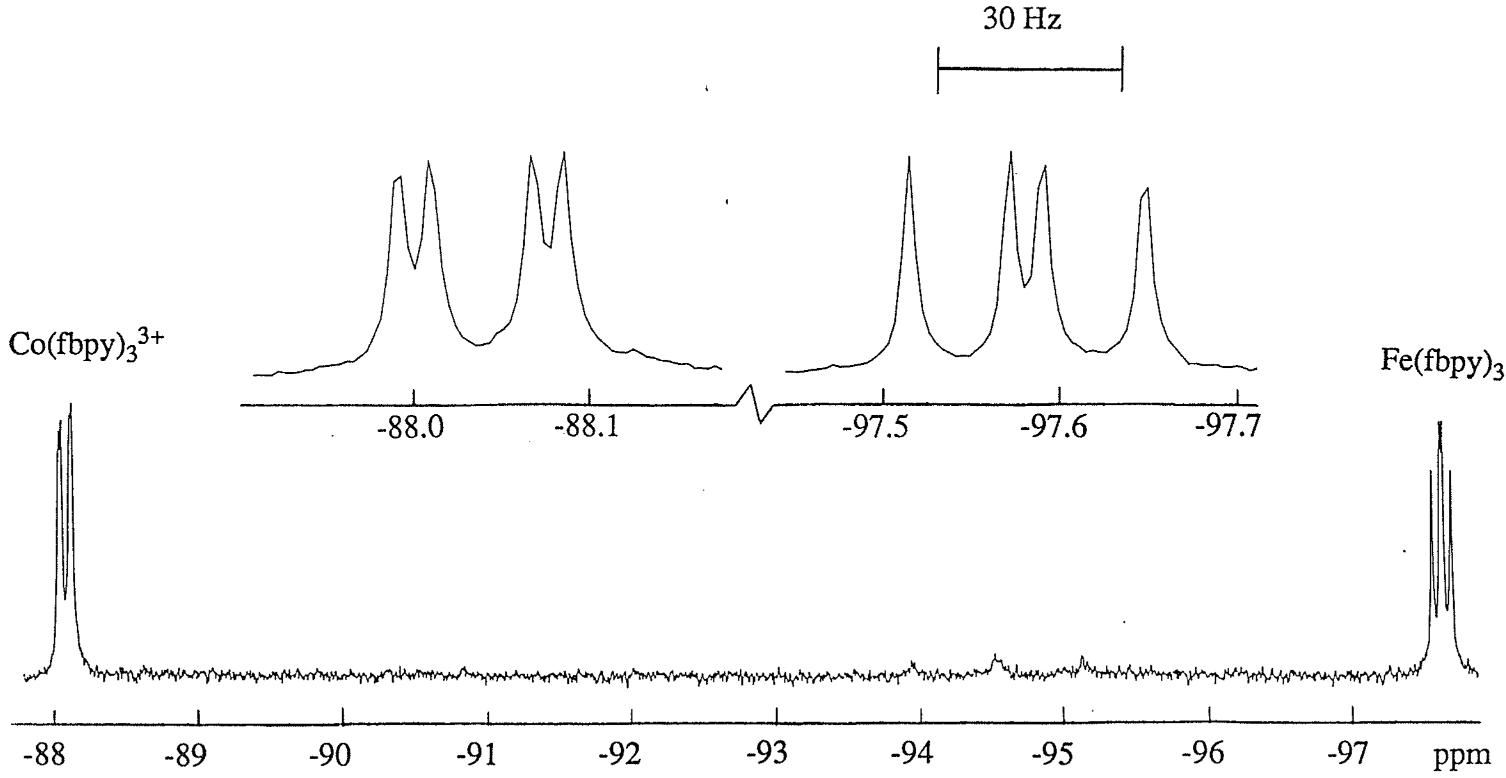


Figure 21. ^{19}F-NMR spectrum of Fe(fbpy)$_3^{3+}$ + Co(fbpy)$_3^{2+}$ (1:1 mole ratio) in CD_3CN

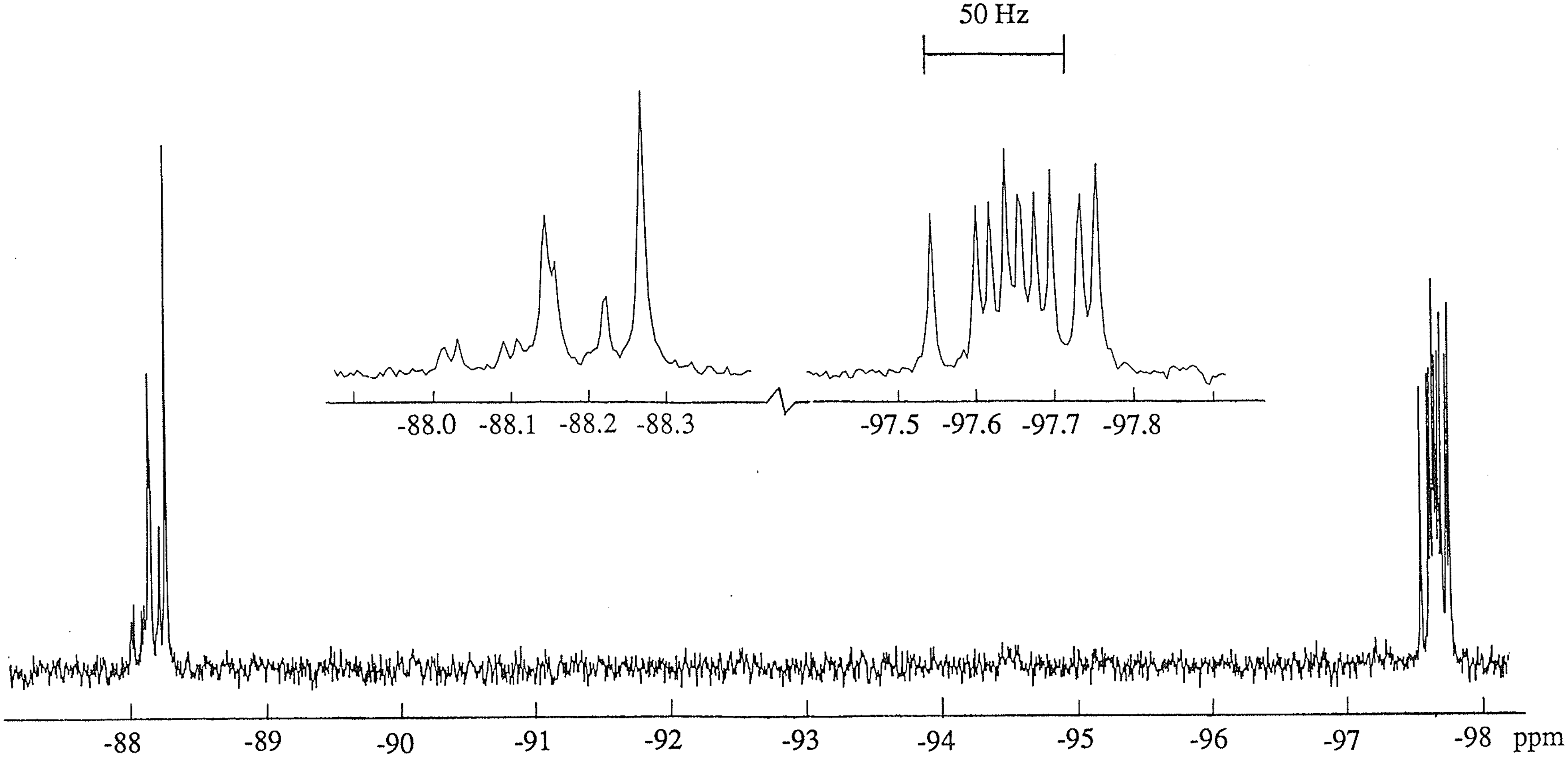


Figure 22. ^{19}F-NMR spectrum of $Fe(bpy)_3^{3+}$ + $Co(fbpy)_3^{2+}$ (1:1 mole ratio) in CD_3CN after two weeks

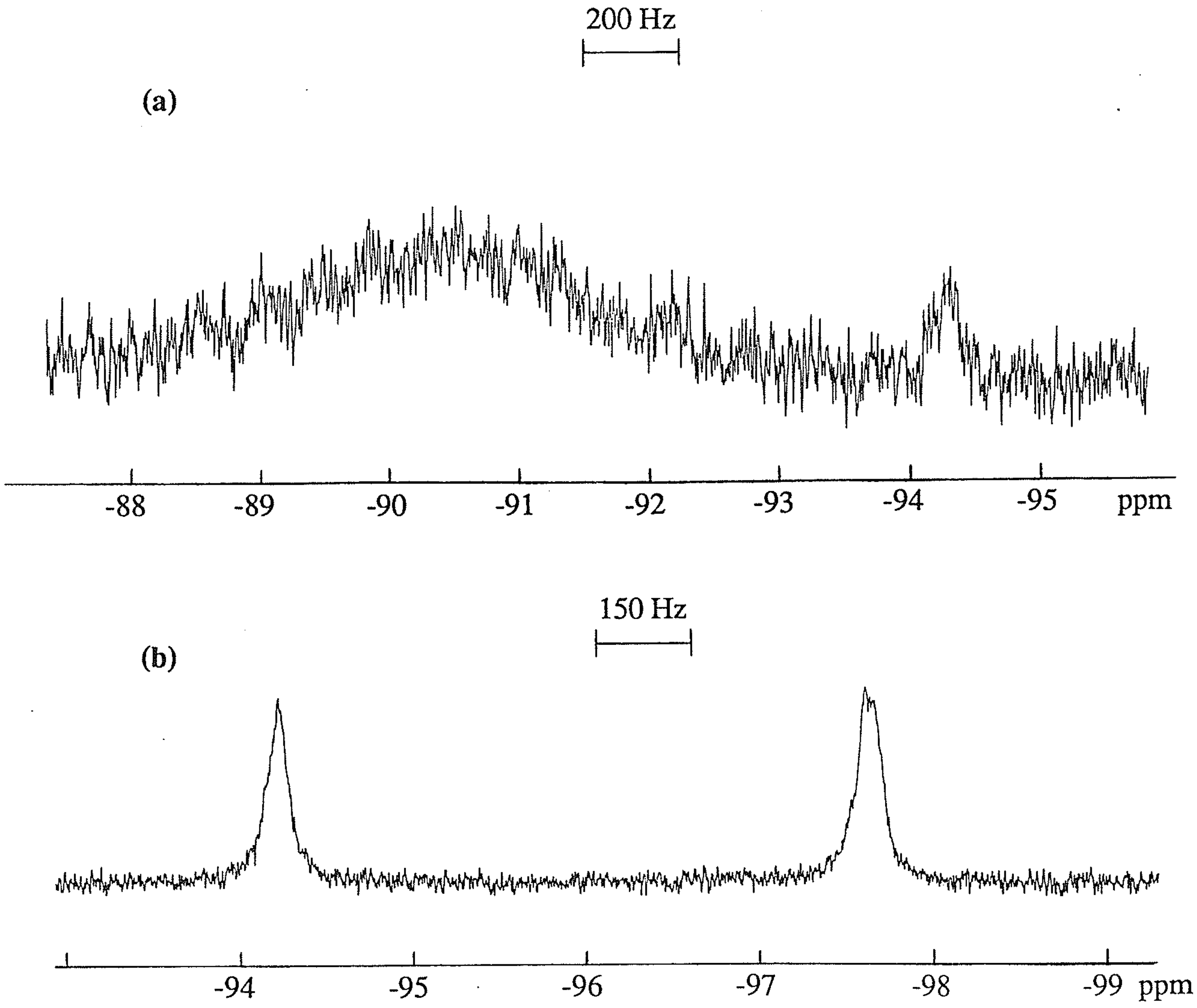
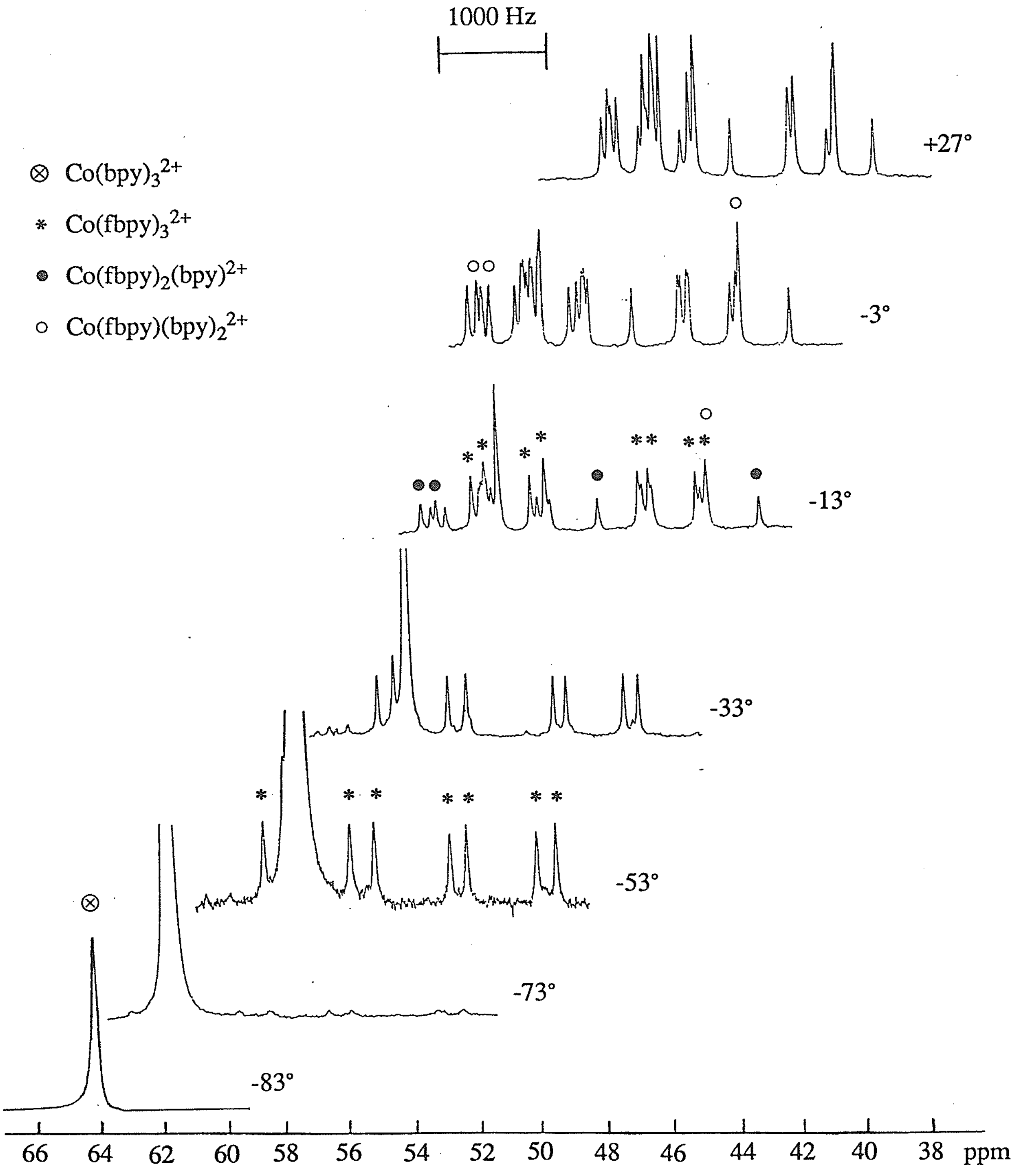


Figure 23. ^{19}F-NMR spectra of Fe(fbpy)$_3^{2+}$ + Fe(bpy)$_3^{3+}$ (1:1 mole ratio) in CD$_3$CN

(a) after 15 min.

(b) after 12 days



<u>Figure 24</u>. Portion of ^{1}H-NMR spectra of Co(bpy)$_3^{2+}$ + Co(fbpy)$_3^{3+}$ (1:1 mole ratio) in acetone d-6 at various temperature, showing only the H-5,5′region of Co(II) complexes.

Table 8. ^{19}F-NMR data for SiF_4(bpy), SiF_4(fbpy) and SiF_4(phen) (a)

	SiF_4(bpy)	SiF_4(fbpy)	SiF_4(phen)
F_a	-120.4	-120.1	-120.1
F_b	-143.9	-143.3	-144.9
F_c	----	-144.0	----
fbpy	----	-91.4	----
$J(F_aF_b)$	14	14	17
$J(F_aF_c)$	----	14	----
$J(F_bF_c)$	----	27	----
$J(F_aSi)$	161	161	158
$J(F_bSi)$	141	140	142
$J(F_cSi)$	----	140	----

(a) NMR spectra recorded on Bruker AM-300 spectrometer in DMSO d-6 ; C_6F_6 as internal reference (-162.9 ppm) , coupling constants in Hz .

IV. RESULTS AND DISCUSSION

1. CHARACTERIZATION OF IRON AND COBALT COMPLEXES

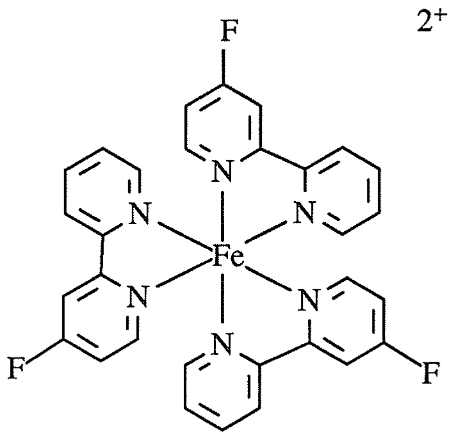
Free ligand 4-fluoro-2,2′-bipyridine

The ^{1}H-NMR spectrum of the free ligand fbpy is shown in Figure 2. The resonances were assigned by inspection and comparison with the ^{1}H-NMR spectrum of 2,2′-bipyridine (72). Similarly, assignments for the ^{13}C-NMR spectrum of fbpy (Figure 3) were made by comparison with that of bpy (73). Spectral assignments were thus straightforward for fbpy and all NMR data are listed in Table 2. One singlet ("pyridyl") and one doublet ("fluoropyridyl") were also observed in the ^{15}N-NMR spectrum for two non-equivalent nitrogens in fbpy (Figure 4b).

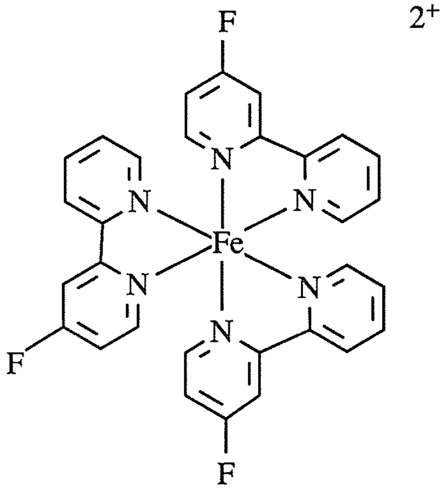
Fe(II) complexes

The ^{1}H-NMR spectrum of $Fe(bpy)_3^{2+}$ in acetonitrile is similar to that reported in the literature (74). The switch of the resonances of the protons 5,5′ and 6,6′, however, was observed as the ^{1}H-NMR spectrum of $Fe(bpy)_3^{2+}$ was recorded in acetone solution (Figure 5a). In the ^{15}N-NMR spectrum of $Fe(bpy)_3^{2+}$ (Figure 6a), a single peak was observed for six equivalent nitrogens in this symmetrically octahedral complex.

For the tris unsymmetrical 4-fluorobipyridine iron(II) complex, the ^{19}F-NMR spectrum shows four resonance peaks with equal intensities. Obviously, two geometrical isomers, namely fac- and mer-isomers, exist for this complex and the concentrations of the two isomers are established statistically resulting in a ratio of fac:mer = 1:3 . The ^{19}F-NMR spectrum was recorded on 300 MHz spectrometer (proton-decoupled) and is shown in Figure 7a .



fac-Fe(fbpy)$_3^{2+}$



mer-Fe(fbpy)$_3^{2+}$

In order to assign which one of four peaks in the fluorine NMR spectrum belongs to the fac-isomer, it was attempted to separate the isomers by High Performance Liquid Chromatography (HPLC) using a μ-Bondapak-CN (R.P.) column with methanol-water mixture as the mobile phase. It was, however, unsuccessful.

The ^{1}H-NMR spectrum of Fe(fbpy)$_3^{2+}$ was also recorded but proved to be less informative than ^{19}F-NMR. The chemical shift difference in the two isomers or within the mer-isomer was small and it was not possible to observe the expected four peaks for each particular proton in the complex, except the protons 6 and 6′ (Figure 5b) .

The presence of the two isomers was also confirmed in the ^{15}N-NMR spectrum of Fe(fbpy)$_3^{2+}$ (Figure 6d) . Three singlets ("pyridyl") and three doublets ("fluoropyridyl") were observed for the six non-equivalent nitrogens in mer-Fe(fbpy)$_3^{2+}$, and one singlet and one doublet for the two sets of non-equivalent nitrogens in fac-Fe(fbpy)$_3^{2+}$.

By varying the mole ratio of bpy:fbpy, assignments for the ^{19}F-NMR spectra of the mixed ligand complexes of Fe(II) containing bpy and fbpy were made unambiguously. As shown in Figure 8, a single peak at -97.76 ppm relative to internal C_6F_6 , corresponds to mono-fbpy complex and the remaining four peaks of equal intensity (-97.65, -97.67, -97.71 and -97.74 ppm) belong to the bis-fbpy complex.

Fe(III) complexes

In neutral or very dilute acid solutions, the blue complex $Fe(bpy)_3^{3+}$ showed significant changes of colour after a few minutes. The only solvent in which this complex is stable for any length of time is concentrated H_2SO_4 .

The ^1H-NMR spectrum of $Fe(bpy)_3^{3+}$ was recorded in CD_3CN at room temperature (Figure 9a), since the complex was more stable in acetonitrile than in the other solvents investigated. The spectrum is in close agreement with the spectrum in D_2SO_4 obtained by DeSimone and Drago (75) .

In the ^1H-NMR spectrum of $Fe(fbpy)_3^{3+}$ (Figure 9b), it was only possible to observe two equally intense peaks for H-3 and two equally intense peaks for H-3′. This demonstrated that both the fac- and mer-isomers were present in solution. It was not possible to assign the sets of peaks arising from H-4′ and H-5,5′since they were overlapped under the solvent peak (protonated acetonitrile). The broad peak at -44.4 ppm arising from H-6,6′ was assumed to consist of eight lines. These assignments were made by comparison with the proton NMR spectrum of $Fe(bpy)_3^{3+}$.

The ^{19}F-NMR spectrum of $Fe(fbpy)_3^{3+}$ (Figure 7b) shows four broad peaks at -57.9, -58.4, -61.2 and -61.7 ppm relative to internal C_6F_6 , indicating the presence of fac- and mer-isomers in the statistical ratio of 1:3 . Also, a peak which was assumed to be protonated 4-fluorobipyridine was found at -94.2 ppm . The same observation was found in the fluorine NMR spectrum of $Fe(fbpy)_3^{3+}$ after the sample was kept at 0°C and in a dark place for one week. Upon standing at room temperature and exposing under sunlight, however, the blue solution of $Fe(fbpy)_3^{3+}$ became colourless and only one peak at -94.2 ppm was found in the ^{19}F-NMR spectrum.

It was attempted to confirm the peak at -94.2 ppm arising from protonated 4-fluorobipyridine. The ^{19}F-NMR spectrum of a mixture of $Fe(fbpy)_3^{3+}$ and fbpy (1:2

mole ratio) in CD_3CN showed the presence of a single peak at -101.8 ppm, whereas the broad peaks which are characteristics of $Fe(fbpy)_3^{3+}$ remained unchanged. This indicated that there is an equilibrium in which a rapid proton transfer occurred between $fbpyH^+$ and fbpy, since no signal of fbpy was observed at -102.7 ppm.

Another attempt using a 3:1 mixture of $Fe(fbpy)_3^{3+}$ and bipyridine in CD_3CN was tried. The ^{19}F-NMR spectrum showed a single peak at -98.5 ppm and the broad peaks at the region of -60.0 ppm. After a week, these broad peaks disappeared and an increase in the single peak was observed at a downfield shift of -95.4 ppm. Further addition of bipyridine resulted in a further increase in this peak as well as an upfield shift to -102.1 ppm was observed . These results again confirmed the presence of an equilibrium in which a rapid proton transfer occurred between $fbpyH^+$ and bpy.

Co(II) complexes

The ^1H-NMR spectrum of $Co(bpy)_3(PF_6)_2$ in acetone d-6 is shown in Figure 11a . The spectrum is similar to that reported by Huang and Brewer (68). The protons in the paramagnetic complex show large shifts and their lines are broad, the width being greatest for the lines with the largest shifts.

From integration available, the amount of $Co(bpy)_3^{3+}$ was found to be about 2% in the fresh sample and about 4% in the five-day old sample of $Co(bpy)_3^{2+}$. The presence of $Co(bpy)_3^{3+}$ was confirmed by comparison with the ^1H-NMR spectrum of an authentic sample.

The ^{19}F-NMR spectrum of the complex $Co(fbpy)_3^{2+}$ (Figure 10a) shows three peaks at -93.95, -94.54 and -95.15 ppm (relative to internal C_6F_6) with a ratio of 1:2:1 . It is possible to state that both fac- and mer-isomers of the complex are present in the statistical ratio of 1:3 . The presence of both isomers was also confirmed in the ^1H-NMR spectrum as shown in Figure 11b . The spectrum shows four resonance peaks with equal intensities for each particular proton. The proton chemical shifts for $Co(fbpy)_3^{2+}$ complex are tabulated in Table 6 . These assignments were made by comparison with the ^1H-NMR spectrum of $Co(bpy)_3^{2+}$ complex.

The presence of $Co(fbpy)_3^{3+}$ (about 2 - 6%) in the sample of $Co(fbpy)_3^{2+}$ was confirmed by comparison with the ^{19}F and ^1H-NMR spectra of an authentic sample.

By varying the mole ratio of bpy:fbpy, assignments for the ^{19}F-NMR spectra of the mixed ligand complexes of Co(II) containing bpy and fbpy were made unambiguously. A single peak at -96.0 ppm relative to internal C_6F_6 , as shown in Figure 12, corresponds to mono-fbpy complex. For the bis-fbpy complex, only three peaks of equal intensity (-93.95, -94.54 and -96.60 ppm) were observed in the ^{19}F-NMR spectrum (Figure 12c). The fourth peak was assumed to be overlapped under the single peak from the mono-fbpy complex (-96.0 ppm).

Co(III) complexes

Compared with the spectra of the paramagnetic complexes, the protons in the diamagnetic complexes occur within a few ppm. The ^1H-NMR spectrum of $Co(bpy)_3(PF_6)_3$ is shown in Figure 14a and the ^1H chemical shifts are listed in Table 6 . Assignments for the complex with symmetric ligands, $Co(bpy)_3^{3+}$, were made by examination of the splitting patterns and comparison with the literature (75) .

The ^{19}F-NMR spectrum of the tris unsymmetrical 4-fluorobipyridine Co(III) complex (Figure 10b) shows four peaks with equal intensities at -88.02, -88.04, -88.09 and -88.11 ppm relative to internal C_6F_6 . This demonstrates that both fac- and mer-isomers are present in the statistical ratio of 1:3 .

In the ^1H-NMR spectrum of $Co(fbpy)_3^{3+}$ (Figure 14b), distinction between isomers was impossible. The chemical shift difference between corresponding signals for the two isomers or within the mer-isomer was small and it was not possible to observe the expected four lines for any ligand proton in the complex .

For the diaqua-complex of Co(III), the ^{1}H-NMR spectrum of the product in D_2O (Figure 25) shows the presence of cis-$Co(bpy)_2(H_2O)_2^{3+}$ species. Eight sets of non-equivalent protons were observed for the cis-configuration of $Co(bpy)_2(H_2O)_2^{3+}$. Also two singlets were found in the ^{15}N-NMR spectrum as expected for cis and trans-nitrogens.

The ^{15}N-NMR spectrum of cis-$Co(bpy)_2(H_2O)_2^{3+}$ is shown in Figure 6b and chemical shifts are tabulated in Table 3.

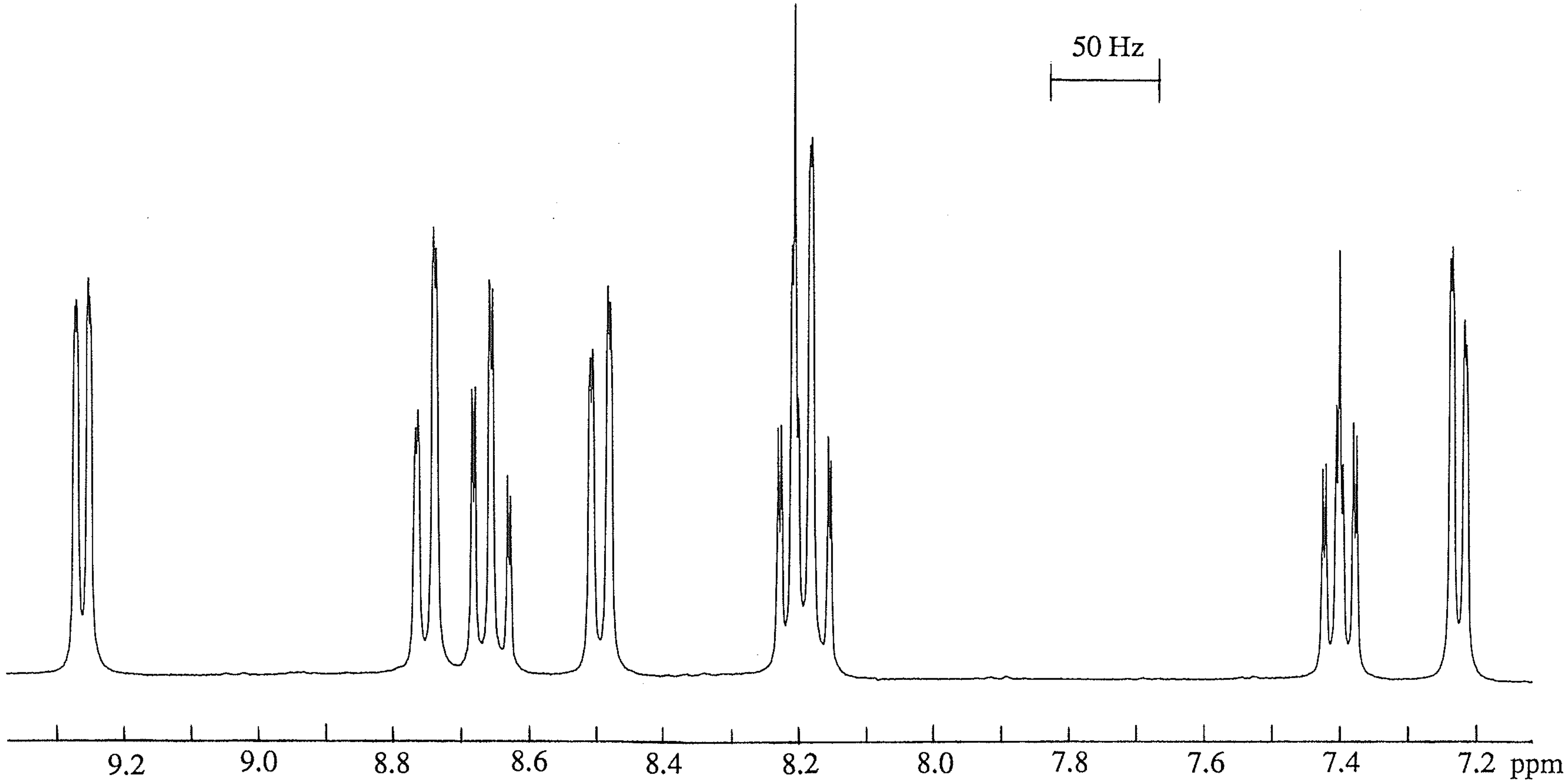


Figure 25. ^{1}H-NMR spectrum of cis-Co(bpy)$_2$(H$_2$O)$_2$(PF$_6$)$_3$ in D$_2$O

2. ELECTRON TRANSFER BETWEEN CO(II) AND CO(III) COMPLEXES

A fluorine label may serve as a sensitive probe for investigating stereochemical changes in transition metal and main group complexes (76)-(78). A new compound 4-fluoro-2,2′-bipyridine (fbpy) was thus synthesized and its suitability as a probe of reaction mechanisms was investigated, since the analogous 2,2′-bipyridine (bpy) ligand is often present in complexes undergoing rapid hydrolysis, racemization, electron transfer, etc.

A 1:1 mixture of $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$ in acetone d-6 was studied at various temperatures by ^1H and ^{19}F-NMR. At the lowest temperature (-83°) there is neither electron transfer nor ligand exchange between $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$. However, electron transfer was observed in this system at -53°, which was indicated by the presence of $Co(fbpy)_3^{2+}$. Four peaks of equal intensity for each ligand proton are characteristics of a 3:1 mixture of mer- and fac-$Co(fbpy)_3^{2+}$, whose proton resonance lines spread over 100 ppm. At higher temperatures (-13° to room temperature) the mixed ligand complexes of Co(II) containing bpy and fbpy were clearly seen in the ^1H and ^{19}F-NMR spectra, indicating that ligand exchange occurred after the electron transfer step, as shown in Figure 24 .

From experimental evidence, a new mechanism which involves bond cleavage during electron transfer is proposed for the $Co(bpy)_3^{2+}$ – $Co(fbpy)_3^{3+}$ system. The overall reaction consists of ligand exchange (hydrolysis) of Co(II) complex as the first step, followed by acid-base equilibrium, and then electron transfer via a hydroxo-bridged intermediate (Scheme 5).

Scheme 5. The proposed mechanism

Step 1. Ligand exchange of Co(II) complex (hydrolysis)

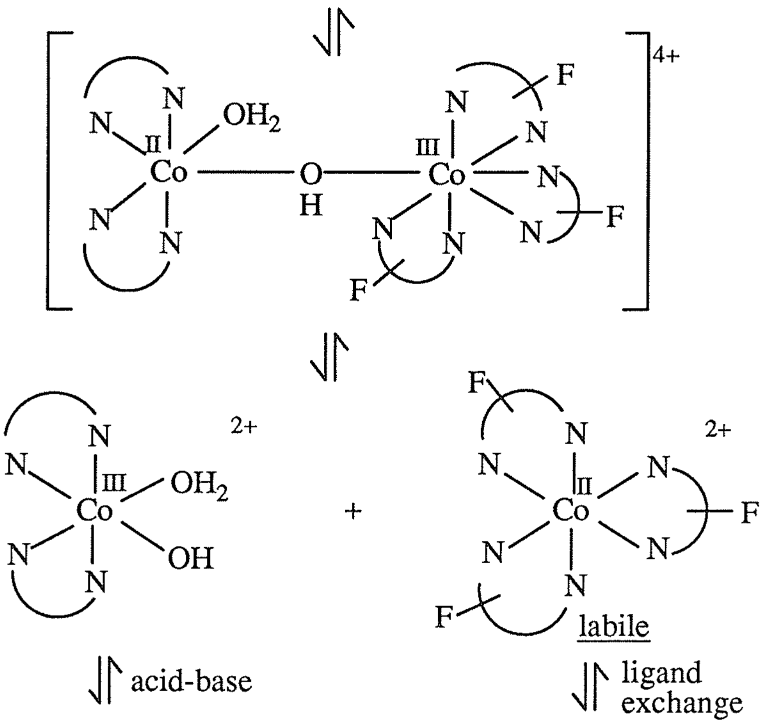
$$\underset{\text{labile}}{\mathrm{Co^{II}(bpy)_3^{2+}}} + 2\,\mathrm{H_2O} \overset{\text{fast}}{\rightleftharpoons} \underset{\text{labile}}{\mathrm{Co^{II}(bpy)_2(H_2O)_2^{2+}}} + \mathrm{bpy}$$

Step 2. Acid-base equilibrium

$$\underset{\text{labile}}{\mathrm{Co^{II}(bpy)_2(H_2O)_2^{2+}}} \overset{\mathrm{H_2O}}{\rightleftharpoons} \underset{\text{labile}}{\mathrm{Co^{II}(bpy)_2(H_2O)(OH)^{+}}} + \mathrm{H^+}$$

Step 3. Electron transfer by inner-sphere mechanism

$$\mathrm{Co^{II}(bpy)_2(H_2O)(OH)^{+}} + \mathrm{Co^{III}(fbpy)_3^{3+}}$$



$$\mathrm{Co^{III}(bpy)_2(H_2O)_2^{3+}} \qquad \mathrm{Co^{II}(fbpy)_2(H_2O)_2^{2+}} + \mathrm{fbpy}$$

Step 4. Ligand exchange (bpy – fbpy complexes)

$$Co^{II}(bpy)_2(H_2O)_2^{2+} + fbpy \rightleftharpoons Co^{II}(bpy)_2(fbpy)^{2+} + 2\,H_2O$$

The NMR spectra presented here are considered sufficient proof for the above-proposed mechanism and the following discussion is given for each step.

Ligand exchange of Co (II) complexes
(bpy – H_2O , bpy – solvent or bpy – fbpy)

Bipyridine is known to form paramagnetic d^7 complexes with cobalt (II) and the lability of the cobalt (II) complexes has been reported in the literature, as pointed out in the introduction. This is again confirmed in the studies presented in this work.

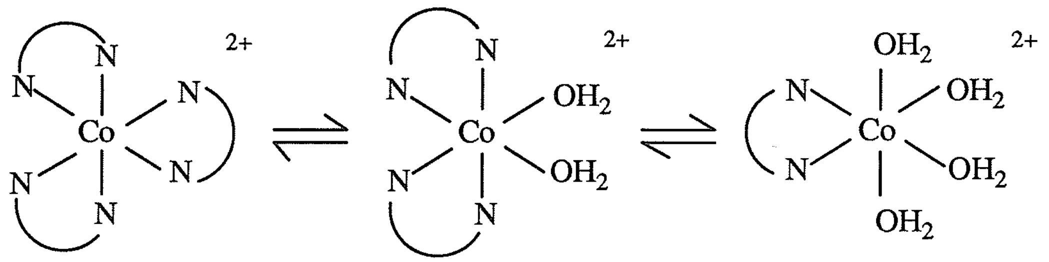
The non-rigidity of the cobalt (II) complexes was detected in the ^{19}F and ^1H-NMR spectra. The ^{19}F-NMR spectrum, as shown in Figure 16, of a 3:1 mixture of $Co(fbpy)_3^{2+}$ and bpy showed the presence of $Co(fbpy)_3^{2+}$, $Co(fbpy)_2(bpy)^{2+}$ and fbpy, indicating that the exchange is slow on the NMR time scale. Similar behaviour was also observed in the ^1H-NMR spectrum of a 3:1 mixture of $Co(bpy)_3^{2+}$ and fbpy (Figure 17).

The question of how ligand exchange in these samples took place immediately arose. The possibility that initial attack of water leads to the formation of intermediate diaqua-complexes, $CoL_2(H_2O)_2^{2+}$ (L = bpy or fbpy), was examined. As observed by Sykes et al. (40), the formation of such complexes is certainly possible, since species with partly dissociated form, i.e. monodentate bipyridine, are assumed to be short lived.

An aquation would require the formation of the free ligand, however, its presence was not observed in the NMR spectrum. It might be assumed that such an equilibrium takes place at a rate faster than that detectable by NMR measurements and would be in favor of the formation of tris-complexes CoL_3^{2+} since the diaqua-complexes are very labile. Although the possibility of aquation of Co(II) complexes, $Co(bpy)_3^{2+}$ and $Co(phen)_3^{2+}$, in aqueous solution was admitted by Berkoff, Krist and Gafney (51), their findings of free ligand were negative. Certainly it seems plausible that such a rapid equilibrium could be established in the presence of water. This assumption receives strong support from the experimental results.

The presence of tris-bpy, diaquabis-bpy and tetraaquamono-bpy complexes of Co(II) in an equilibrium was observed in the ^{1}H-NMR spectrum of an authentic sample of $Co(bpy)_2(H_2O)_2^{2+}$ (Figure 26a).

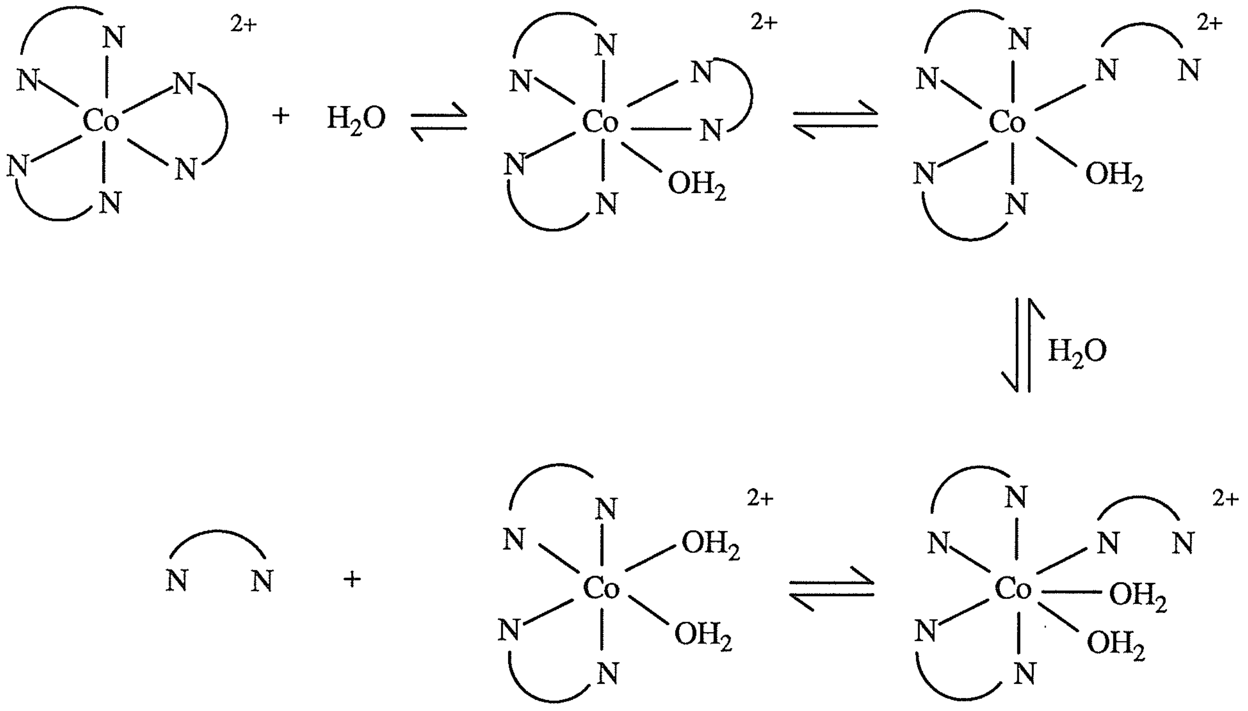
Addition of bpy in a stoichiometric amount to this sample rapidly shifted the equilibrium to the formation of $Co(bpy)_3^{2+}$.



The possibility that the presence of $Co(bpy)_3^{2+}$ in the equilibrium is introduced during the preparation of $Co(bpy)_2(H_2O)_2^{2+}$ was also checked. Removal of tris-complex, if any, in the sample of diaqua-complex was carried out by washing the sample with acetone, since $Co(bpy)_3^{2+}$ is very soluble in acetone. However, the same equilibrium was found in the solution by recording the NMR spectrum. Also, the ^{1}H-NMR spectrum of the acetone washings showed that there was no $Co(bpy)_3^{2+}$ present. Thus, there was no doubt as to the authenticity of the samples of $Co(bpy)_2(H_2O)_2^{2+}$.

If hydrolysis was the mechanism of ligand exchange, then removal of water from the solvent used and from hydrated $Co(bpy)_3^{2+}$ complexes should stop the exchange reaction. However, ligand exchange between $Co(bpy)_3^{2+}$ and fbpy still occurred rapidly after the water was removed from acetone (Figure 17). It is certainly possible that water is still present in the sample of $Co(bpy)_3^{2+}$, since removal of water from hydrated Co(II) complexes is difficult and may not be completely effective.

It appears that hydrolysis may be the mechanism of ligand exchange in Co(II) complexes. The following mechanism is possible to explain the role of water in ligand exchange.



Seven-coordinated cobalt (II) complexes with one water molecule occupying the seventh site (79) or with two water molecules at sixth and seventh sites (80) have been revealed in X-ray structural investigations. It is also known that complex ions of the form $[Co(bpy)_2X_2]^{n+}$ and $[Co(phen)_2X_2]^{n+}$ exist in only the cis-configuration (81). Earlier works (82),(83) have demonstrated that there are good steric reasons for expecting the trans-configuration of the type $[M(bpy)_2X_2]^{n+}$ and $[M(phen)_2X_2]^{n+}$ to be unstable with respect to the cis-configuration. The exchange between the tris-complex $Co(bpy)_3^{2+}$ and dimethyl sulfoxide (DMSO) as solvent was also observed in the ^{1}H-NMR spectrum of $Co(bpy)_3^{2+}$ in DMSO. It again confirms the non-rigidity of these complexes in solution.

$$\begin{tikzcd}
\mathrm{Co(bpy)_3^{2+}} + 2\,\mathrm{DMSO} \arrow[r, shift left] & \mathrm{Co(bpy)_2(DMSO)_2^{2+}} + \mathrm{bpy} \arrow[l, shift left] \arrow[d, shift right] \\
\mathrm{Co(DMSO)_6^{2+}} + \mathrm{bpy} \arrow[r, shift left, "\mathrm{DMSO}"] & \mathrm{Co(bpy)(DMSO)_4^{2+}} + \mathrm{bpy} \arrow[l, shift left] \arrow[u, shift right, "\mathrm{DMSO}"']
\end{tikzcd}$$

Acid-base equilibria

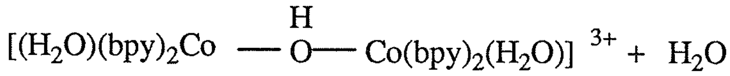
The diaqua- and aquahydroxobis(bipyridine)cobalt(III) complexes, as reported by Kenley et al. (71), are related by the acid-base equilibrium shown below.

$$\mathrm{Co(bpy)_2(H_2O)_2^{3+}} \rightleftharpoons \mathrm{Co(bpy)_2(H_2O)(OH)^{2+}} + \mathrm{H^+}$$

Such an equilibrium has also been suggested by Palade, Lin′kova and Chudaeva (69) for the diaquabis(bipyridine)cobalt(II) complex. They reported that the neutralization of the diaquabis(bipyridine)-cation with alkali is followed by the formation of a binuclear complex with a bridging OH group according to the equations :

$$\mathrm{Co(bpy)_2(H_2O)_2^{2+}} \rightleftharpoons \mathrm{Co(bpy)_2(H_2O)(OH)^{+}} + \mathrm{H^+}$$

$$\mathrm{Co(bpy)_2(H_2O)_2^{2+}} + \mathrm{Co(bpy)_2(H_2O)(OH)^{+}} \rightleftharpoons$$



$$[\mathrm{(H_2O)(bpy)_2Co} - \overset{\mathrm{H}}{\mathrm{O}} - \mathrm{Co(bpy)_2(H_2O)}]^{3+} + \mathrm{H_2O}$$

As shown in Figure 26, a rather rapid equilibrium between various cobalt(II)-bpy complexes was found in the ^{1}H-NMR spectrum of the diaqua-complex in methanol. Addition of water to the same sample resulting in the changes in the proton chemical shifts of $\mathrm{Co(bpy)_2(H_2O)_2^{2+}}$ and $\mathrm{Co(bpy)(H_2O)_4^{2+}}$ were observed in the NMR spectrum. At pH ~11, obtained by adding NaOD, only four broad peaks were seen in the region of Co(II). Assuming this corresponds to the formation of the hydroxo-dimer, as suggested by Palade et al. for this pH range, it is expected that the spectrum of $Co(bpy)_2(H_2O)_2^{2+}$ will reappear upon adding deuterated acid DCl. However, no signals were observed in the Co(II) region after the solution was adjusted to pH ~1 by adding DCl. Instead, the presence of $Co(bpy)_2(H_2O)_2^{3+}$ was found from the ^{1}H-NMR spectrum of the solution.

In a study of complexes of the general type $Co(bpy)_2X_2$ (84) , Vlcek reported that these complexes undergo a very easy oxidation and that they can be used as starting material for the preparation of the corresponding Co(III) complexes. This may be an explanation for the results obtained with diaqua-complexes. It is entirely possible that upon acidification of the hydroxo-dimer complex, $Co(bpy)_2(H_2O)_2^{2+}$ was re-formed and under this acidic condition, the diaqua-complex rapidly oxidized to $Co(bpy)_2(H_2O)_2^{3+}$.

The experiments with diaqua-complex $Co(bpy)_2(H_2O)_2^{2+}$ went no further than that discussed above. Further supporting facts for the acid-base equilibria may be gained by careful perusal of the literature. Though evidence obtained for the acid-base equilibrium of $Co(bpy)_2(H_2O)_2^{2+}$ in this work was scanty, it is certainly a possibility.

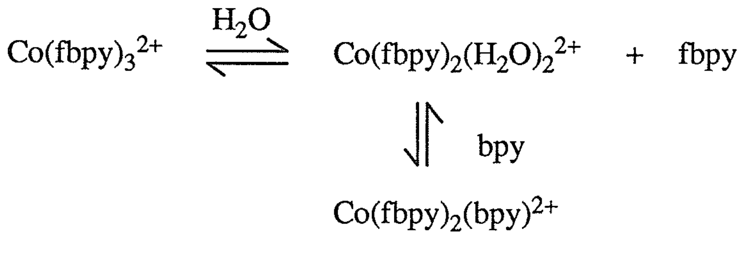
Electron transfer by inner-sphere mechanism

The ^{1}H-NMR spectrum of $Co(bpy)_3^{2+}$ – $Co(fbpy)_3^{3+}$ mixture at -53° showed four equally intense peaks for each particular proton in the cobalt (II) region, which indicated the presence of 3:1 mixture of mer- and fac-$Co(fbpy)_3^{2+}$. Since it is well-known that hydroxide ligands form excellent bridges in transition metal complexes, it is reasonable to suggest that the formation of $Co(fbpy)_3^{2+}$ must occur via an inner-sphere electron-transfer process involving the hydroxo-bridged intermediate, as shown in Step 3 of Scheme 5.

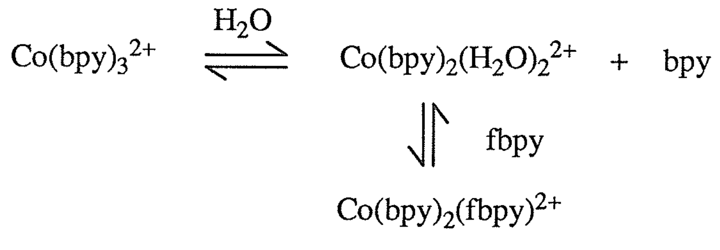
If electron transfer occurred via an outer-sphere pathway, in which complexes remain intact and rigid, a large amount of $Co(fbpy)_3^{2+}$ (as well as a small amount of $Co(bpy)_3^{2+}$, if any) should be observed in the NMR spectra. However, only a small amount of $Co(fbpy)_3^{2+}$ was found in the ^{1}H-NMR spectra. This can be explained by an inner-sphere electron-transfer process, in which only a small amount of $Co(bpy)_2(H_2O)(OH)^+$ is involved.

The presence of the diaquabis(bipyridine)cobalt(III) complex, $Co(bpy)_2(H_2O)_2^{3+}$, formed after the electron transfer step is difficult to detect in the ^1H-NMR spectra due to a small chemical shift range of about 1 ppm for all Co(III) complexes. Proton resonance spectra thus may be more useful in studying paramagnetic complexes in solution. Large shifts in the resonance positions of protons in ligand molecules, along with sharp separate lines arising from every different type of proton have been observed for $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{2+}$.

Since only the changes in the region of the Co(II) complexes were easily observable in the ^1H-NMR spectra, as well as in the ^{19}F-NMR spectra, it was decided to monitor these changes in the low temperature studies. At -33°, ligand exchange of bpy – fbpy in the Co(II) complexes began to appear due to the lability of the newly formed $Co(fbpy)_3^{2+}$ complex. An attack of H_2O and consequent liberation of free ligand fbpy is assumed to be the cause of ligand exchange.



$$\begin{tikzcd}
Co(fbpy)_3^{2+} \arrow[r, shift left, "H_2O"] & Co(fbpy)_2(H_2O)_2^{2+} + fbpy \arrow[l, shift left] \arrow[d, shift right] \\
& Co(fbpy)_2(bpy)^{2+} \arrow[u, shift right, "bpy"']
\end{tikzcd}$$



$$\begin{tikzcd}
Co(bpy)_3^{2+} \arrow[r, shift left, "H_2O"] & Co(bpy)_2(H_2O)_2^{2+} + bpy \arrow[l, shift left] \arrow[d, shift right] \\
& Co(bpy)_2(fbpy)^{2+} \arrow[u, shift right, "fbpy"']
\end{tikzcd}$$

Although the detection of all Co(III) complexes present after electron transfer and ligand exchange processes was uncertain because of a small chemical shift range, evidence presented here is considered sufficient proof for the proposed mechanism of electron transfer. Since $Co(bpy)_2(H_2O)_2^{3+}$ would be formed in a small quantity, it is possible that its signals are "overlapped" under the other peaks in the Co(III) region. Unfortunately, better resolved spectra for this region were not obtained.

One feature of the spectra of $Co(bpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$ is temperature dependent. As stated above, only Co(II) complexes were observable in the ^{1}H-NMR spectrum, all resonance lines of Co(II) complexes moved upfield as temperature was increased, with the largest upfield shift for H-3,3′. Although this aspect was not pursued in this work, it is certainly worth a closer examination in the future. The large upfield shift of H-3,3′ with increasing temperature may involve a partially dissociated Co(II) species. With the bipyridine ligand where a pyridine moiety can rotate about the C–C linkage, a monodentate bipyridine ligand is possible.

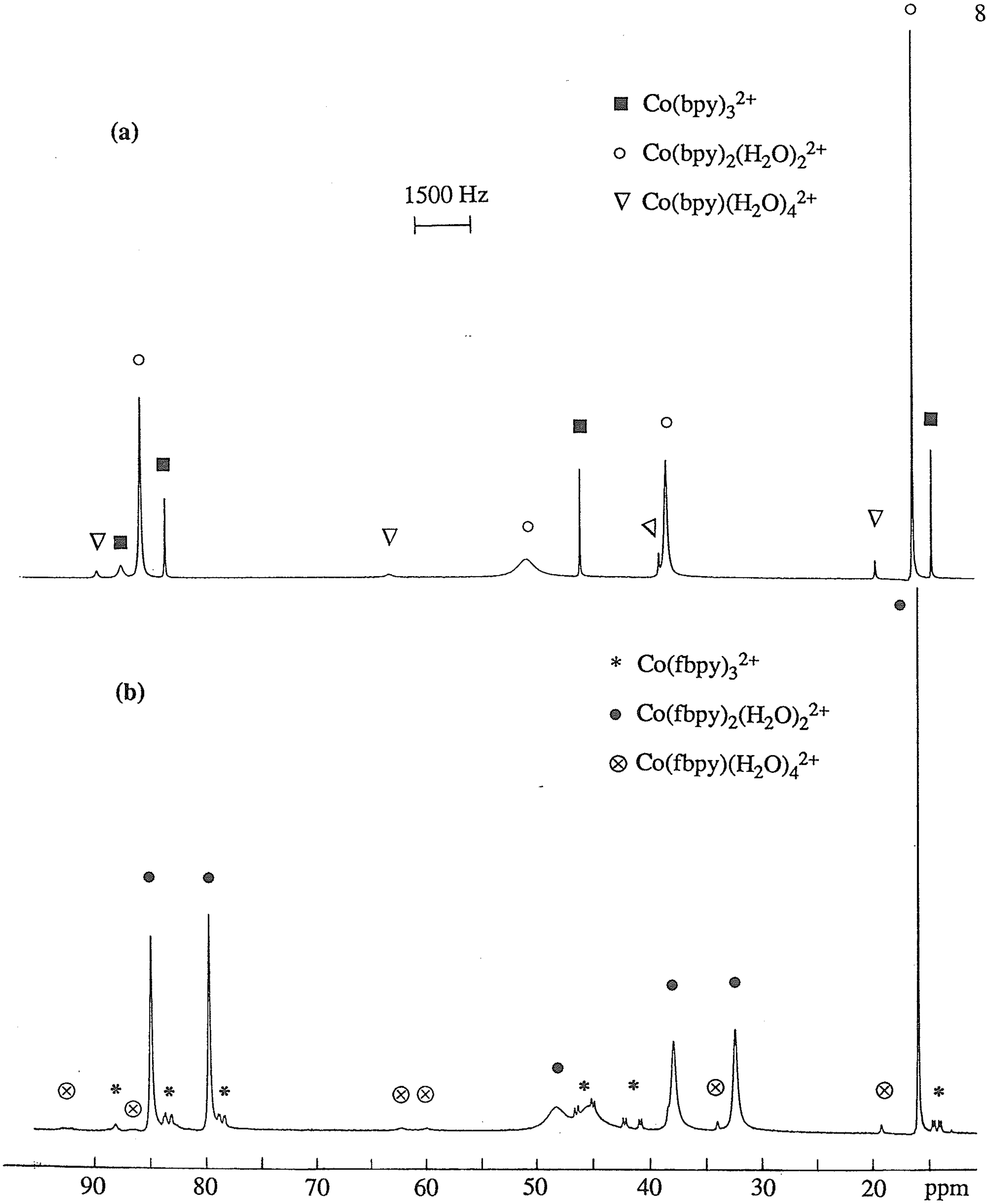


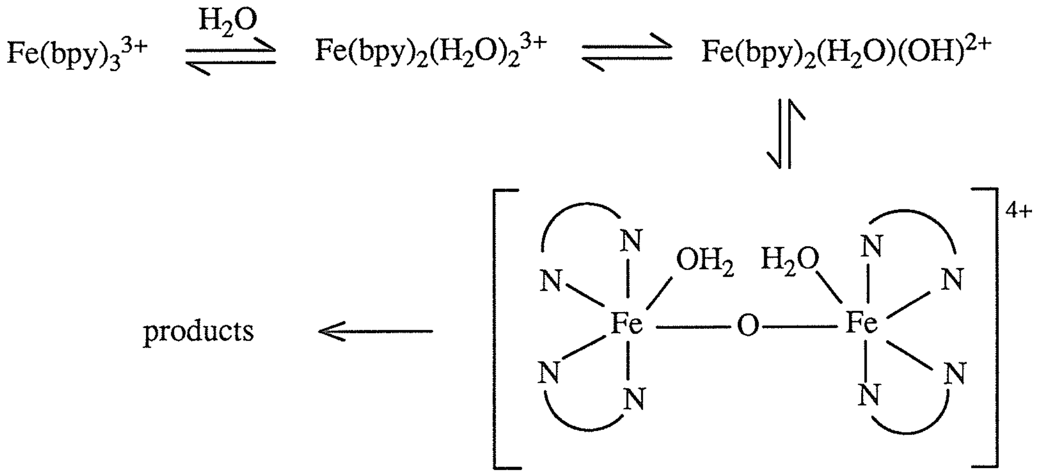
Figure 26. (a) ^{1}H-NMR spectrum of $Co(bpy)_2Cl_2$. $3.5H_2O$ in methanol d-4

(b) ^{1}H-NMR spectrum of $Co(fbpy)_2Cl_2$. $3.5H_2O$ in methanol d-4

3. ELECTRON TRANSFER BETWEEN FE(II) AND FE(III) COMPLEXES

The ^{19}F-NMR spectrum of a 1:1 mixture of Fe(fbpy)$_3$$^{2+}$ and Fe(bpy)$_3$$^{3+}$ in acetonitrile, as shown in Figure 23, consisting of a broad peak at -90.5 ppm and a peak at -94.2 ppm were observed within 15 min at room temperature. Neither signal characteristic of Fe(fbpy)$_3$$^{2+}$ nor Fe(fbpy)$_3$$^{3+}$ was found in the spectrum. After two weeks, two broad peaks at -94.2 and -97.6 ppm appeared in the ^{19}F-NMR spectrum of the same sample in a ratio of 1:1 . Since the nature of the paramagnetic d^5 complexes Fe(bpy)$_3$$^{3+}$ and Fe(fbpy)$_3$$^{3+}$ is not completely understood, the appearance of the spectrum could not be explained with certainty.

As proposed by Ehman and Sawyer (25), the blue Fe(bpy)$_3$$^{3+}$ complex rapidly hydrolyzes to a binuclear species with an oxygen bridge, $[Fe_2(bpy)_4O(H_2O)_2]^{4+}$. This complex could be obtained by direct addition of Fe(III) salt to a bipyridine solution in water (33),(34). The crystal structure of the binuclear iron complex $[Fe_2(phen)_4O(H_2O)_2]^{4+}$, which was prepared by direct interaction of $FeCl_3.6H_2O$ and phenanthroline in water in a mole ratio of 1:2, has also been reported (85). As noted in the introduction, Fe(bpy)$_3$$^{3+}$ can not be prepared by direct interaction of the metal ion and ligand, but by the oxidation of the corresponding Fe(II) complex. It is thus reasonable to suggest that the hydrolysis hypothesis in the cobalt (II) complexes could be extended to the iron (III) complexes as well.



A careful examination of the ^{19}F-NMR spectra of Fe(fbpy)$_3^{3+}$ in acetonitrile showed that there was no evidence of a reduction of Fe(fbpy)$_3^{3+}$ to Fe(fbpy)$_3^{2+}$. Instead, only the presence of protonated fbpy at -94.2 ppm was found in the spectrum of a colourless solution of the complex. It is possible that since both components are very labile, the binuclear species will dissociate to products rather than exist independently for any length of time.

With the presence of the Fe(II) complex, however, an inner-sphere electron-transfer process involving the hydroxo-bridged intermediate is possible for the Fe(fbpy)$_3^{2+}$ – Fe(bpy)$_3^{3+}$ system. The appearance of the peak at -94.2 ppm, which is always observed in the ^{19}F-NMR spectrum of Fe(fbpy)$_3^{3+}$, gave support to this assumption. It is clear that since fbpyH$^+$ could not possibly be produced from Fe(fbpy)$_3^{2+}$, it must arise from Fe(fbpy)$_3^{3+}$ which was formed after the electron transfer process. The newly formed Fe(fbpy)$_3^{3+}$ complex, as the analogous Fe(bpy)$_3^{3+}$, undergoes a rapid hydrolysis leading to the formation of protonated free ligand.

On the assumption of an outer-sphere electron-transfer pathway, Dietrich and Wahl (36),(37) reported that the proton NMR spectra of Fe(phen)$_3^{2+}$ – Fe(phen)$_3^{3+}$ mixtures contain only one set of averaged peaks on addition of small portions of Fe(phen)$_3^{3+}$ to Fe(phen)$_3^{2+}$. Their studies showed that the changes in linewidths and positions of the proton NMR peaks for the diamagnetic species are due to rapid electron transfer between Fe(II) and Fe(III) complexes. This is obviously not the case in the studies presented in this work, since if electron transfer occurred by an outer-sphere mechanism, signals characteristic of $Fe(fbpy)_3^{3+}$ or four averaged peaks should be observed in the ^{19}F-NMR spectra. It thus appears that hydrolysis might be a reasonable hypothesis to explain the results obtained for the Fe(II) – Fe(III) system, in which rapid reversible reactions may be involved.

Though electron transfer between Fe(II) and Fe(III) complexes was just briefly investigated, these preliminary results indicated that the postulated "inner-sphere" mechanism is certainly a possibility if the"non-rigidity" of the iron complexes could be taken as evidence against the outer-sphere mechanism.

4. ELECTRON TRANSFER BETWEEN IRON AND COBALT COMPLEXES

For the $Fe(fbpy)_3^{2+}$ – $Co(fbpy)_3^{3+}$ system, no electron transfer was observed in the ^{19}F-NMR spectrum at room temperature. This result demonstrates that both $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$ are kinetically and thermodynamically stable. The question of whether or not a slow ligand exchange may occur in this system also arises.

An examination of the ^{19}F-NMR spectrum of a 1:1 mixture of $Fe(fbpy)_3^{2+}$ and $Co(bpy)_3^{3+}$ obtained after the solution stood at room temperature for two weeks revealed that indeed a ligand exchange reaction occurred between the two complexes. The same was also observed for the $Fe(bpy)_3^{2+}$ – $Co(fbpy)_3^{3+}$ system. In view of the excellent results obtained with these systems in this work, it seemed highly possible that water is the cause of ligand exchange.

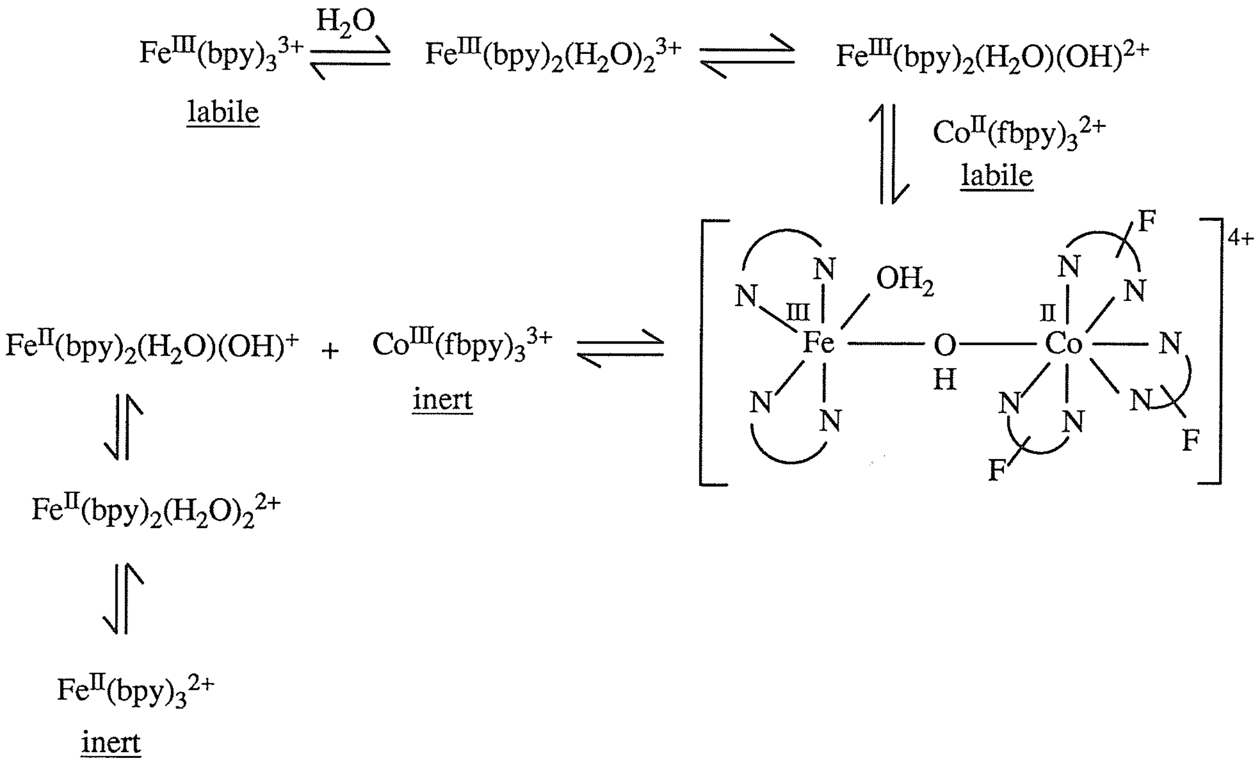
In separate experiments, ligand exchange between $Fe(fbpy)_3^{2+}$ and bpy, as well as between $Fe(bpy)_3^{2+}$ and fbpy, occurred within 15 min whereas no significant change was observed in the ^{19}F-NMR spectra of 3:1 mixtures of Co(III) complexes and the free ligands within the same period of time. This observation indicates that the reactive species in the ligand exchange reaction between Fe(II) and Co(III) complexes should be the Fe(II) species.

It is interesting to note that ligand exchange between these two complexes, Fe(II) and Co(III), resulted in the favorable formation of the mixed ligand complexes of Fe(II). Qualitatively, this implies that the order of thermodynamic stability of metal–nitrogen bond is Fe > Co , whereas the order of kinetic stabilty is Fe < Co .

In contrast to the Fe(II)–Co(III) system, a fast electron-transfer reaction between $Fe(fbpy)_3^{3+}$ and $Co(fbpy)_3^{2+}$ at room temperature was found in the ^{19}F-NMR spectrum of the mixture (Figure 21), which was indicated by the presence of $Fe(fbpy)_3^{2+}$ and $Co(fbpy)_3^{3+}$. This again demonstrates that the favorable driving force in these systems is the formation of kinetically and thermodynamically stable Fe(II) and Co(III).

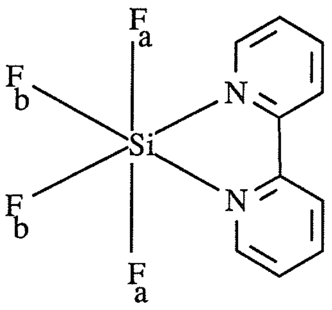
$$\mathrm{Fe(fbpy)_3^{3+}} + \mathrm{Co(fbpy)_3^{2+}} \xrightarrow{\text{fast}} \mathrm{Fe(fbpy)_3^{2+}} + \mathrm{Co(fbpy)_3^{3+}}$$

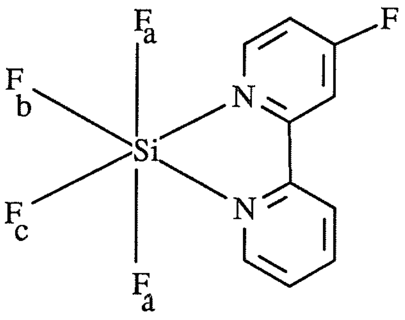
The evidence of slow ligand exchange after the electron transfer step became apparent in the ^{19}F-NMR spectrum of a 1:1 mixture of $\mathrm{Fe(bpy)_3^{3+}}$ and $\mathrm{Co(fbpy)_3^{2+}}$ (Figure 22). The experiments with the Fe(III)–Co(II) systems seemed to suggest that electron transfer occurred via an outer-sphere pathway. However, the possibility of an inner-sphere mechanism catalyzed by water is entirely feasible. Since hydrolysis was the apparent mechanism of ligand exchange in iron and cobalt complexes, it is possible that it might also be responsible for the electron transfer process between Fe(III) and Co(II) complexes. As pointed out in the previous section, the reactive $\mathrm{Fe(bpy)_3^{3+}}$ easily undergoes a rapid hydrolysis with liberation of protonated free ligand and, in fact, this is one of the difficulties of handling the complex. However, with the presence of $\mathrm{Co(fbpy)_3^{2+}}$, an inner-sphere electron transfer involving the hydroxo-bridged intermediate may take place. The following mechanism is possible to explain the role of water in the electron-transfer process.


Fe^III(bpy)_3^3+
H_2O
labile
Fe^III(bpy)_2(H_2O)_2^3+
Fe^III(bpy)_2(H_2O)(OH)^2+
Co^II(fbpy)_3^2+
labile
N
OH_2
III
Fe
O
H
II
Co
F
4+
Fe^II(bpy)_2(H_2O)(OH)^+ + Co^III(fbpy)_3^3+
inert
Fe^II(bpy)_2(H_2O)_2^2+
Fe^II(bpy)_3^2+
inert

V. MISCELLANEOUS

It was attempted to extend the study to the complexes of silicon with 2,2′-bipyridine and 4-fluorobipyridine. Bipyridine is known to form a stable 1:1 adduct with silicon tetrafluoride. Adley, Gilson and Onyszchuk (86) have reported the ^{19}F-NMR spectrum of SiF_4(bpy) which consisted of two triplets of equal intensity at -121.5 and -143.9 ppm. An X-ray structure determination of SiF_4(bpy) has also been carried out (87). These results have confirmed the presence of the cis-structure of SiF_4(bpy). However, its a_2b_2 ^{19}F-NMR spectrum can not be assigned with certainty to cis and trans fluorines. Since such an assignment would be essential in any study of stereoselective fluorine exchange (78), the corresponding SiF_4(fbpy) adduct was prepared, and its spectrum was recorded by ^{19}F-NMR.





The ^{19}F-NMR spectrum of SiF_4(fbpy) (Figure 27b) shows peaks at -120.1 (2F), -143.3 (F) and -144.0 (F). From the symmetry of the adduct, the peaks at -120.1 ppm must be assigned to the trans fluorines in SiF_4(fbpy). The assignment of F_b and F_c, however, remains uncertain.

The ^{29}Si-NMR spectra of SiF_4(bpy) and SiF_4(fbpy) were also recorded (Figure 28). However, the silicon-29 NMR spectrum of SiF_4(fbpy), in which the coupling between Si and two non-equivalent fluorines F_b and F_c was not detected, proved to be less informative than ^{19}F-NMR.

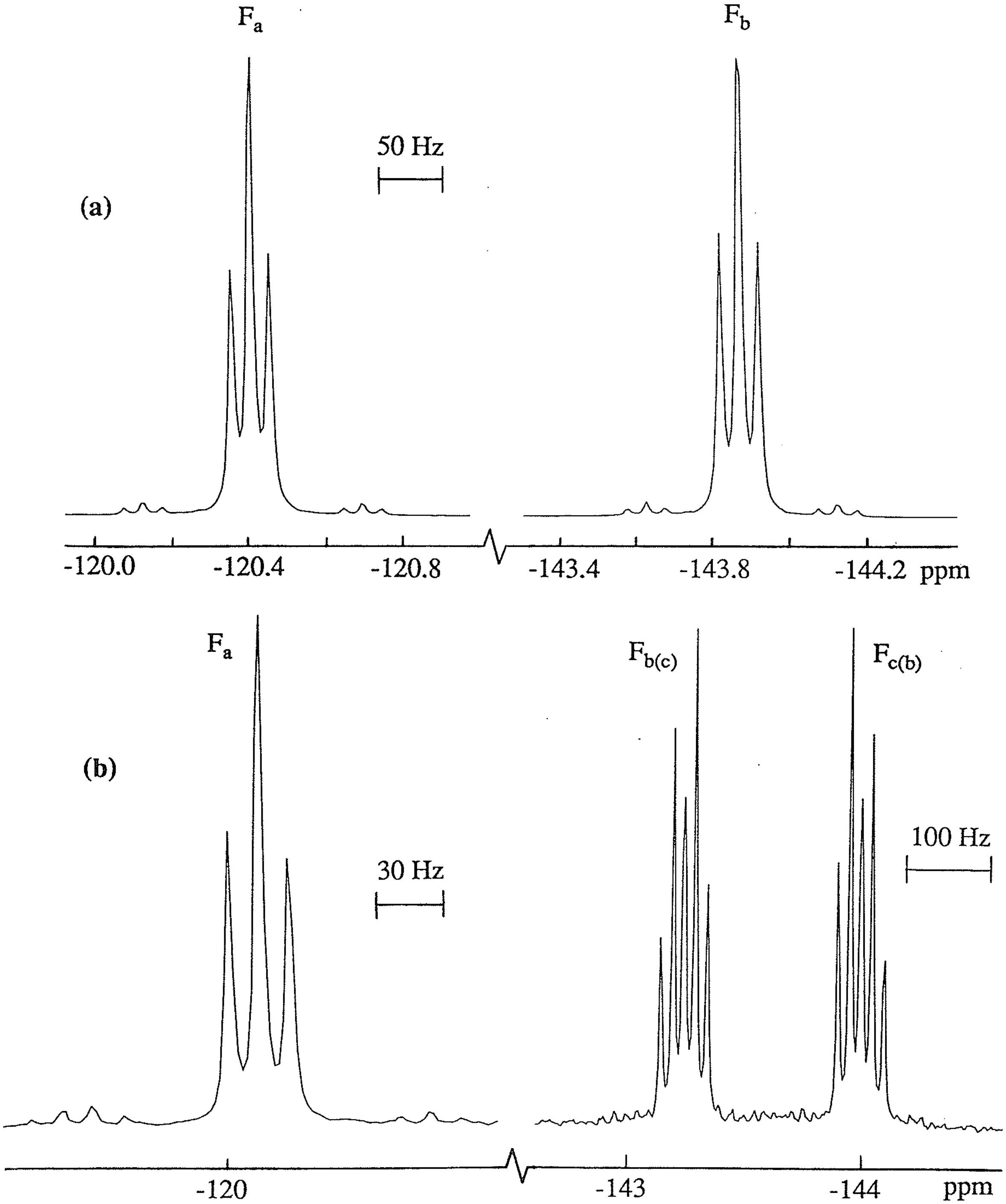


Figure 27. ^{19}F-NMR spectra of Si complexes in DMSO d-6 .

(a) SiF_4(bpy)

(b) SiF_4(fbpy)

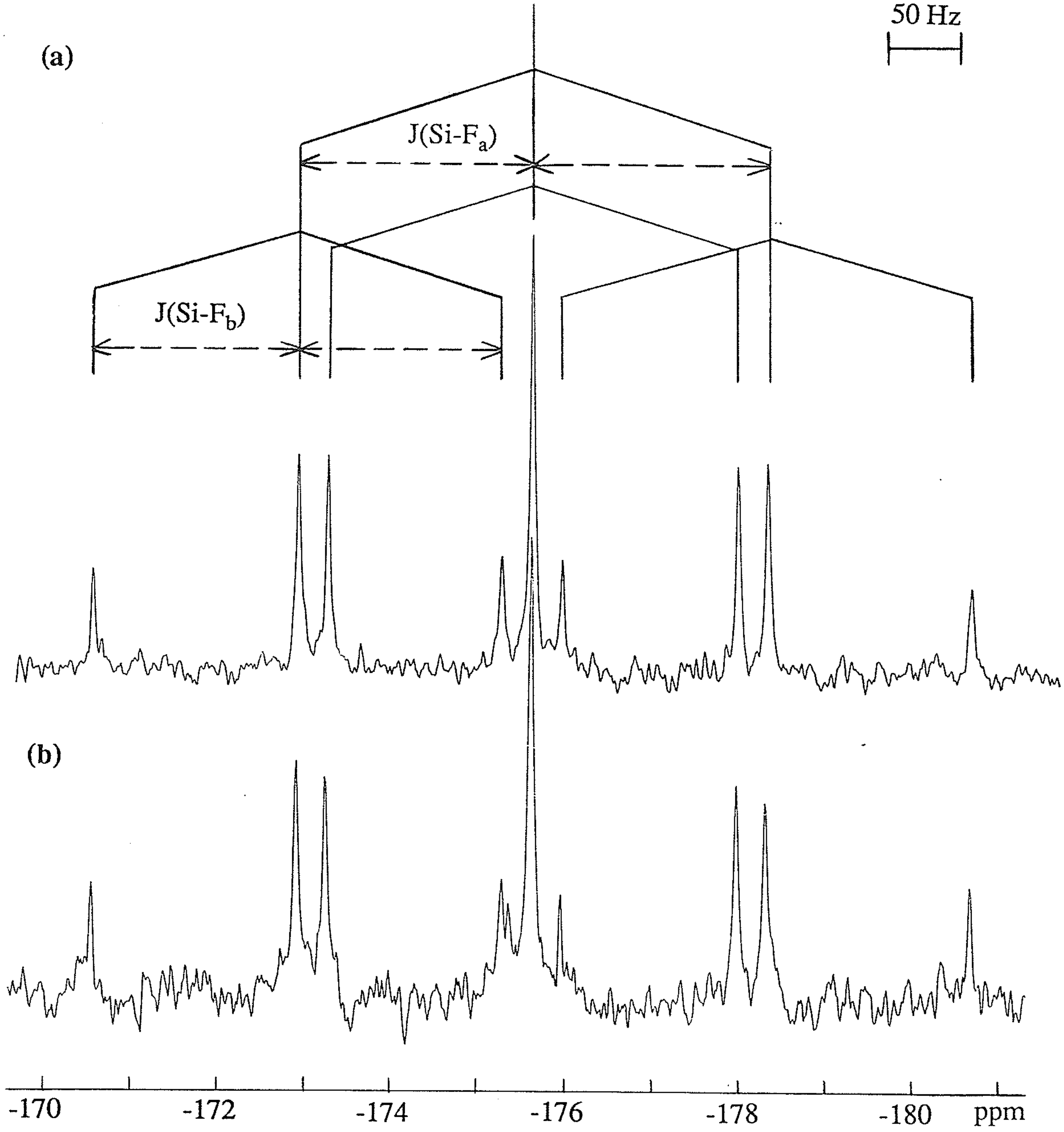


Figure 28. ^{29}Si-NMR spectra of Si complexes in DMSO d-6 .

(a) SiF$_4$(bpy)

(b) SiF$_4$(fbpy)

VI. CONCLUSIONS

Evidence which strongly suggests that hydrolysis is the mechanism of ligand exchange in iron and cobalt complexes, and consequently provides an inner-sphere pathway of electron transfer in these complexes has been presented in this thesis.

The proposed mechanism for the Co(II) – Co(III) systems, in which an electron transfer process occurs via the formation of a hydroxo-bridged intermediate, could be possibly extended to the Fe(II) – Fe(III) and Co(II) – Fe(III) systems as well.

The most important point to note is the non-rigidity of these octahedral complexes in solution. If this was taken as evidence against the outer-sphere mechanism, in which the complexes are assumed to remain intact and rigid during the electron transfer step, the alternative inner-sphere electron transfer pathway is entirely possible.

The hypothesis that hydrolysis is responsible for ligand exchange in the cobalt complexes was presented. The extension of the hydrolysis mechanism to the iron (III) complexes was also presented, however, no proof was obtained.

If hydrolysis was the mechanism of ligand exchange, then removal of water would slow down, and eventually stop the exchange reactions. However, the technique of reducing hydrolysis proved to be difficult.

Therefore, unless removal of traces of water has been effectively carried out, the possibility that hydrolysis provides an inner-sphere pathway for electron transfer in these complexes must be considered.

REFERENCES

1. R. G. Wilkins, The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes, Allyn and Bacon Inc., Boston, p.254 (1974)
2. H. Taube, H. Myers and R. L. Rich, J. Amer. Chem. Soc., **75** , 4118 (1953)
3. H. Taube and H. Myers, J. Amer. Chem. Soc., **76** , 2103 (1954)
4. T. J. Williams and C. S. Garner, Inorg. Chem., **9** , 2058 (1970)
5. H. Taube, Electron Transfer Reactions of Complex Ions in Solution, Academic Press, p.28 - 37 (1970)
6. D. W. Carlyle and J. H. Espenson, J. Amer. Chem. Soc., **91** , 599 (1969)
7. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th Edition, John Wiley and Sons Inc., p.1206 - 1215 (1980)
8. J. P. Birk, Inorg. Chem., **9** , 125 (1970) , quoted in ref.1
9. H. Taube and E. S. Gould, Acc. Chem. Res., **2** , 321 (1969)
10. R. B. Jordan, A. M. Sargeson and H. Taube, Inorg. Chem., **5** , 1091 (1966)
11. E. S. Gould, J. Amer. Chem. Soc., **89** , 977 (1967)
12. F. M. Burstal and R. S. Nyholm, J. Chem. Soc. 3570 (1952)
13. Y. Yamamoto, T. Tarumoro and T. Tarui, Bull. Chem. Soc. Japan, **46** , 1466 (1973)
14. H. Sato and T. Tominaga, Bull. Chem. Soc. Japan, **49** , 697 (1976)
15. J. H. Baxendale and P. George, Trans. Faraday Soc., **46** , 697 (1976)
16. C. C. Deb, D. K. Hazra and S. C. Lahiri, Z. Phys. Chemie., Leipzig, **267** , 769 (1986)
17. F. Basolo, J. C. Hayes and H. M. Neumann, J. Amer. Chem. Soc., **76** , 3807 (1954)
18. P. Krumholtz, J. Amer. Chem. Soc., **71** , 3654 (1949)
19. L. Seiden, F. Basolo and H. M. Neumann, J. Amer. Chem. Soc., **81** , 3809 (1959)
20. F. M. Van Meter and H. M. Neumann, J. Amer. Chem. Soc., **98** , 1388 (1976)
21. R. D. Gillard, L. A. P. Kane-Maguire and P. A. Williams, J. Chem. Soc., Dalton Trans., 1792 (1977)

22. F. P. Dwyer and E. C. Gyarfas, J. Amer. Chem. Soc., **74** , 4699 (1952)

23. G. H. Walden, L. P. Hammet and R. P. Chapman, J. Amer. Chem. Soc., **53** , 3909 (1931)

24. F. P. Dwyer and H. A. McKenzie, J. Proc. Roy. Soc., N.S.W., **81** , 97 (1947)

25. D. L. Ehman and D. T. Sawyer, Inorg. Chem., **8** , 900 (1969)

26. T. S. Lee, I. M. Kolthoff and D. L. Leussing, J. Amer. Chem. Soc., **70** , 3596 (1948)

27. J. E. Dickens, F. Basolo and H. M. Neumann, J. Amer. Chem. Soc., **79** , 1286 (1957)

28. R. K. Murmann and E. A. Healy, J. Amer. Chem. Soc., **83** , 2092 (1961)

29. F. Pantani and G. Ciantelli, J. Electroanal. Chem., **14** , 423 (1967)

30. (a) G. Nord and O. Wernberg, J. Chem. Soc., Dalton Trans., 866 (1972)

    (b) G. Nord and O. Wernberg, J. Chem. Soc., Dalton Trans., 845 (1975)

31. G. Nord, B. Pedersen and E. Bjergbakke, J. Amer. Chem. Soc., **105** , 1913 (1983)

32. P. A. Lay and W. H. F. Sasse, Inorg. Chem., **24** , 4707 (1985)

33. W. M. Reiff, W. A. Baker,Jr. and N. E. Erickson, J. Amer. Chem. Soc., **90** , 4794 (1968)

34. G. Anderegg, Helv. Chim. Acta, **45** , 1643 (1962)

35. E. Eichler and A. C. Wahl, J. Amer. Chem. Soc., **80** , 4145 (1958)

36. M. W. Dietrich and A. C. Wahl, J. Chem. Phys., **38** , 1591 (1963)

37. M. S. Chan and A. C. Wahl, J. Phys. Chem., **82** , 2542 (1978)

38. C. R. Bruce, R. E. Norberg and S. I. Weissman, J. Chem. Phys., **25** , 307 (1956)

39. P. Ellis, R. G. Wilkins and M. J. G. Williams, J. Chem. Soc., 4456 (1957)

40. R. Davies, M. Green and A. G. Sykes, J. Chem. Soc., Dalton Trans., 1171 (1972)

41. A. G. Sykes, Kinetics of Inorganic Reactions, Pergamon Press, London, p.242 (1966)

42. H. Taube, Chem. Rev., **50** , 69 (1952)

43. V. P. Pleiffer and B. Werdelmann, Z. Anorg. Chem., **261** , 197 (1950)

44. B. O. West, J. Chem. Soc., 578 (1954)

45. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, 2nd Edition, John Wiley and Sons Inc., New York, p.216 (1967)

46. R. Farina, R. Hogg and R. G. Wilkins, Inorg. Chem., 7 , 170 (1968)

47. B. R. Baker, F. Basolo and H. M. Neumann, J. Phys. Chem., **63** , 371 (1959)

48. D. J. Szalda, C. Creutz, D. Mahajan and N. Sutin, Inorg. Chem., **22** , 2372 (1983)

49. J. H. Baxendale, E. M. Fielden and J. P. Keene, Proc. Roy. Soc. (London), **A 286** , 320 (1965)

50. W. L. Waltz and R. G. Pearson, J. Phys. Chem., **73** , 1941 (1969)

51. R. Berkoff, K. Krist and H. D. Gafney, Inorg. Chem., **19** , 1 (1980)

52. A. Werner, Ber. **45** , 3061 (1912)

53. N. Sutin, J. Phys. Chem., **64** , 1766 (1960)

54. A. G. Maddock, Trans. Faraday Soc., **55** , 1268 (1959)

55. A. F. Janzen, private communication

56. N. V. Sidgwick, The Electronic Theory of Valency, Oxford University Press, p.157 (1927)

57. J. A. Gibson, D. G. Ibbott and A. F. Janzen, Can. J. Chem., **51** , 3203 (1973)

58. R. E. Wasylishen, G. S. Birdi and A. F. Janzen, Inorg. Chem., **15** , 3054 (1976)

59. R. K. Marat and A. F. Janzen, Can. J. Chem., **55** , 3845 (1977)

60. J. F. Coetzee, Pure Appl. Chem., **13** , 429 (1966)

61. A. I. Vogel, A Textbook of Practical Organic Chemistry, 3rd Edition, p.176 (1957)

62. K. S. Mohamed, D. K. Padma, R. G. Kalbandkeri and A. R. V. Murthy, J. Fluorine Chem., **23** , 509 (1983)

63. X. Huang, T. Q. Nguyen and A. F. Janzen, 8th Winter Fluorine Conference, St. Petersburg, Florida, Jan. 25-30, 1987

64. W. Sont and H. Alper, Organic Preparations and Procedures International, **12** , 243 (1980)

65. R. A. Jones, B. D. Roney, W. H. F. Sasse and K. O. Wade, J. Chem. Soc. B, 106 (1967)

66. H. J. Jakobsen, P. I. Yang and W. S. Brey, Org. Magn. Reson., 17 , 290 (1981)

67. F. Qu, private communication

68. T. L. J. Huang and D. G. Brewer, Can. J. Chem., 59 , 1689 (1981)

69. D. M. Palade, V. S. Lin′kova and G. V. Chudaeva, Russ. J. Inorg. Chem., 27 , 1304 (1982)

70. Von F. M. Jaeger and J. A. Van Dijk, Z. Anorg. Allgem. Chem., 227 , 273 (1936)

71. R. A. Kenley, R. H. Fleming, R. M. Laine, D. S. Tse and J. S. Winterle, Inorg. Chem., 23 , 1870 (1984)

72. S. Castellano, H. Gunther and S. Ebersole, J. Phys. Chem., 69 , 4166 (1965)

73. A. Marker, A. J. Canty and R. T. C. Brownlee, Aust. J. Chem., 31 , 1255 (1978)

74. Y. Ohsawa, M. K. DeArmond, K. W. Hanck and C. G. Moreland, J. Amer. Chem. Soc., 107 , 5383 (1985)

75. R. E. DeSimone and R. S. Drago, J. Amer. Chem. Soc., 92 , 2343 (1970)

76. R. C. Fay and T. S. Piper, J. Amer. Chem. Soc., 85 , 500 (1963)

77. R. K. Marat and A. F. Janzen, Inorg. Chem., 19 , 798 (1980)

78. A. S. Secco, K. Alam, B. J. Blackburn and A. F. Janzen, Inorg. Chem., 25 , 2125 (1986)

79. I. Morgenstern-Badarau, Inorg. Chem., 23 , 2725 (1984)

80. G. R. Newkome, V. K. Gupta, F. R. Fronczek and S. Pappalardo, Inorg. Chem., 23 , 2400 (1984)

81. V. K. Joshi, R. Van Eldik and G. M. Harris, Inorg. Chem., 25 , 2229 (1986)

82. S. E. Livingstone and B. Wheelahan, Austral. J. Chem., 17 , 219 (1964)

83. J. V. Rund, Inorg. Chem., 7 , 24 (1968)

84. A. A. Vlcek, Inorg. Chem., 6 , 1425 (1967)

85. J. E. Plowman, T. M. Loehr, C. K. Schauer and O. P. Anderson, Inorg. Chem., **23**, 3553 (1984)

86. A. D. Adley, D. F. R. Gilson and M. Onyszchuk, J. Chem. Soc., Chem. Commun., 813 (1968)

87. A. D. Adley, P. H. Bied, A. R. Fraser and M. Onyszchuk, Inorg. Chem., **11**, 1402 (1972)