AZAM RAHIMI

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SPECTROSCOPIC STUDIES
OF METAL COMPLEXES IN SOLUTION

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
AZAM RAHIMI
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This is to certify that the

thesis entitled

SPECTROSCOPIC STUDIES OF METAL COMPLEXES

IN SOLUTION

presented by

Azam Rahimi

has been accepted towards fulfillment
of the requirements for

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ABSTRACT

SPECTROSCOPIC STUDIES OF METAL COMPLEXES IN SOLUTION

By

Azam Rahimi

This thesis reports some exploratory studies on the use of scandium-45 and silver-109 nmr probes of the immediate chemical environment of scandium(III) and silver(I) ions in solutions.

Scandium-45 chemical shifts for scandium salt solutions in tetrahydrofuran were found to be strongly dependent on the nature of the counterion. This influence of the anion was not observed for scandium salts in aqueous solutions in the same range of concentration. It is concluded that in the THF solution Sc^{3+} salts exist as ion pairs or higher ionic aggregates while in water Sc^{3+} or $Sc(OH)^{2+}$ ion is completely solvated by the solvent molecules. Studies of ^{45}Sc chemical shifts in water-THF mixtures confirmed the above conclusions.

Attempts were made to study Sc(III) complexes with crown and cryptands by ^{45}Sc nmr. The results were largely inconclusive due to very low solubilities of the Sc(III) complexes and the relatively low sensitivity of ^{45}Sc signal.

Azam Rahimi

Silver-109 nmr studies were first carried out on aqueous solutions of $AgNO_3$ and $AgClO_4$. The ^{109}Ag chemical shifts moved upfield with increasing concentration of the two salts. The shifts were somewhat anion-dependent but extrapolated to the same frequency at infinite dilution. This frequency is indicative of ^{109}Ag resonance of a completely hydrated Ag^+ ion.

Similar studies were carried out in several nonaqueous solvents and, in particular, in acetonitrile. Again an upfield shift with increasing salt concentrations was observed. The ^{109}Ag chemical shift for solvated Ag^+ ion in acetonitrile is considerably further downfield than in water, indicative of stronger interaction of Ag^+ ion with acetonitrile. The results from ^{109}Ag nmr studies in mixtures of these two solvents supported the above conclusion.

Silver-109 nmr was also used to study complexation reaction of Ag^+ ion with benzene, pyridine and their derivatives, in several nonaqueous solvents. Measurements were carried out in acetone, methanol, tetrahydrofuran, propylene carbonate, pyridine and acetonitrile solutions. Solvent dependence of these complexation reactions was observed. The effect of substituents on the complexation reaction and the effect of temperature on complexation of pyridine with Ag^+ ion was also studied. It was found that the Ag^+-pyridine complex is more stable at lower temperature.

In view of the low solubility of the scandium salts and extremely weak sensitivity of the ^{109}Ag resonance, only qualitative information could be obtained with the instruments used in this study.

SPECTROSCOPIC STUDIES
OF METAL COMPLEXES IN SOLUTION

By

Azam Rahimi

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY
Department of Chemistry

1977

To my parents
as a symbol of
my endless appreciation

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LIST OF ABBREVIATIONS

AC	Acetone
ACN	Acetonitrile
PC	Propylene Carbonate
THF	Tetrahydrofuran
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
Bz	Benzene
To	Toluene
Py	Pyridine
L	Ligand
M	Molarity

PART I

CHAPTER I

HISTORICAL

Chemistry of Scandium

Scandium was one of the missing elements in the original periodic table of Mendeleev published in 1871. Mendeleev called this element "eka-boran" and estimated its atomic weight to be 45. In 1879, Mendeleev's predictions of this missing element were confirmed by its discovery by Nilson. The element was named scandium, because the minerals containing it were found in Scandinavia. This new rare earth was different from the lanthanons by its weak basicity, atomic weight of less than 131 and by its spark spectrum. Scandium was obtained in a small quantity from gadolinite and euxenite minerals after separation from lanthanons and fractional crystallization and precipitation. Since scandium was obtained in a very small quantity, Nilson was not able to study it in detail.

For many years not much attention was paid to this element. Later in 1950, when the problem of obtaining this element and its compounds in a good quantity and high purity was overcome, the interest in scandium and its compounds increased rapidly. During recent years different compounds of scandium have been synthesized and characterized. Many intermetallic compounds and alloys of this metal with interesting properties are available. Application of different instrumental techniques such as neutron activation analysis, flame and emission spectroscopy, made it possible to detect and determine small traces of this element in rocks, biological materials, etc. Different inorganic and organic compounds of scandium were synthesized and characterized by different methods. Stable complexes of scandium in trivalent states with anionic and neutral ligands were prepared in the solid and solution state. A comprehensive review of all aspects of scandium has been provided by Horovitz, Gschneidner, Melson, Youngblood, and Schoch in a recent monograph (1).

Scandium, with electronic configuration of [Ar] $3d^1 4s^2$, is a group III element and the first member of Sc, Y, La Ac group. Its ionic radius is ∿0.7 Å which is smaller than the radii of lanthanides and in its compounds coordination numbers exceeding 6 are not known. Scandium chemical behavior is intermediate between that of aluminum and of the lanthanides. The usual oxidation state of this element in its compound is III. Many inorganic salts of scandium have been synthesized. Organo-scandium compounds which contain scandium-carbon bonds are well characterized. Coordination compounds of scandium containing nitrogen-, oxygen-, phosphorus- and sulphur-donor ligands have been of physicochemical measurements on these systems. Physicochemical studies on scandium complexes in solutions are particularly rare. This fact might be due to the $3d^0$ configuration of scandium in its +3 oxidation state, which makes useless some of the techniques, such as electronic spectroscopy and magnetic susceptibility measurements. Nuclear magnetic resonance spectroscopy seems to be a potentially useful technique for such studies.

Nuclear Magnetic Resonance Studies

During recent years nuclear magnetic resonance (nmr) spectroscopy has been extensively used as a powerful tool for the elucidation of the molecular structure and investigation of environmental effects on a given nucleus. In particular the application of Fourier transform technique to the nmr spectroscopy has introduced the advantage of obtaining spectra in a shorter period of time.

In the past decade the nmr of metallic nuclei with $I > 0$ has become an interesting and useful extension of the more common nmr spectroscopy of nuclei such as ^{1}H, ^{13}C, ^{31}P, and ^{19}F. A lot of work has been done in this area specially on alkali metal nmr (3), but very few reports about other nuclei have been published. Scandium-45 spectroscopy has shown the sensitivity of the chemical shift to the variation of the coordination environment of the Sc(III) ion and suggests that this technique may be useful for such studies.

Scandium-45 nuclide with spin of 7/2 has 100% natural abundance and a relative sensitivity of 0.3 compared to an equal number of protons at constant field. Very few reports of the application of ^{45}Sc nmr spectroscopy to the study of the scandium complexes have been published. Proctor and Yu (4) measured the magnetic moment of scandium with a nuclear induction spectrometer. They measured the resonance frequency of ^{45}Sc in an aqueous solution of $Sc(NO_3)_3$. By comparing this frequency with that of ^{23}Na from a saturated aqueous solution of NaCl and taking for the scandium spin the value of 7/2, they calculated the magnetic moment of scandium to be, $\mu_{^{45}Sc}=4.7497\pm0.008$ μN (nuclear magneton). The magnetic moment of scandium was also measured by nuclear magnetic resonance absorption (5). Proton resonance was used for comparison. The value obtained for the magnetic moment was 4.74916 ± 0.00012 which agrees quite well with the previous results. Scandium-45 nucleus has also been used as a secondary standard for measurements of the nuclear magnetic moment of other nuclei (6,7). Lutz (8) measured the Larmor frequency of scandium-45 in a dilute solution of scandium chloride in acidified heavy water and calculated the magnetic moment of scandium to be, $\mu_{^{45}Sc} = 4.748711$ μN. Lutz also investigated the relative chemical shifts of ^{45}Sc in solutions of $Sc(NO_3)_3$, $ScCl_3$ and $Sc(ClO_4)_3$ in heavy water and light water as the solvents. It was found that for acidified solutions of scandium chloride in water, there is no shift as the concentration of the salt is increased, and the observed linewidth was narrow, 28 to 35 Hz. In the case of acidified $Sc(ClO_4)_3$ solution, there was a shift to lower frequency as the concentration of the salt increased, and the linewidth was also narrow, 30 Hz. He also noticed that at low concentration, there is no difference in the scandium chemical shift between acidified solution of $ScCl_3$ and $Sc(ClO_4)_3$. The linewidth for $Sc(NO_3)_3$ solution was broader than that of the above salts. He observed a difference in the Larmor frequencies of scandium-45 in solutions of light and heavy water, which was related to the difference in shielding of the ^{45}Sc nucleus by light and heavy water ("solvent isotope effect"). Buslaev _et_ _al_. (9) investigated the scandium complex formation in aqueous solution. This work was done by study of the magnetic resonance of ^{45}Sc nucleus as a function of the concentration of the salt and the nature of the anion: Cl^-, NO_3^-, and ClO_4^-. It was observed that the linewidth for $Sc(NO_3)_3$ is greater than those of $ScCl_3$ and $Sc(ClO_4)_3$ and related it to the following order of the complexing ability of the anions:

$$NO_3^- > Cl^- \geq ClO_4^-$$

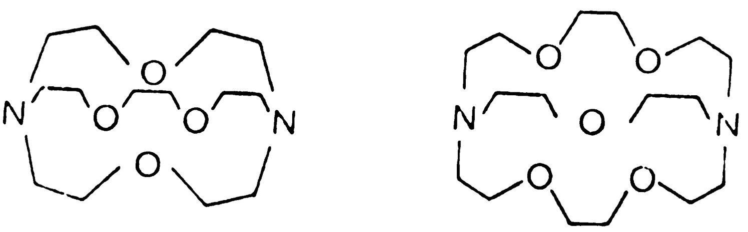
This order is unexpected since Cl^- usually forms stronger complex with metal ions than NO_3^-. More recently, Buslaev _et_ _al_. (10) reported a study on the linewidth and chemical shift of the ^{45}Sc resonance in the solutions of various scandium salts. They found that the linewidth of ^{45}Sc resonance in the nitrate solution depends on the concentration of the salt. In concentrated solutions the line was very broad ($\Delta\nu$ = 2630 Hz for the saturated solution which is 80% by weight of the salt (11)). The line broadening was explained in terms of formation of an outersphere ion pairs and higher aggregate formed in concentrated solution. They did not observe the change in the chemical shift in the concentration range of 2% to saturated solution of $Sc(NO_3)_3$. In an aqueous solution of $(NH_4)_3ScF_6$ in the presence of ammonium fluoride, fine structure in the ^{45}Sc nmr spectrum was observed. The spectrum consists of seven lines whose relative intensities indicate the interaction of ^{45}Sc spin with six equivalent fluorine nuclei in ScF_6^{3-} anion which has an octahedral structure. They also observed a shift of ^{45}Sc resonance toward higher field in HCl solution of $ScCl_3$ relative to an aqueous solution of $ScCl_3$. They suggested that in these solutions various aquochloro complexes of scandium are formed, but the exchange is fast relative to the nmr time scale so that only one resonance is observed. In a solution of $ScBr_3$ in HBr, the exchange is slow and two resonances were observed due to aquo- and bromo complexes of scandium. They also observed a change in the chemical shift of ^{45}Sc resonance with respect to the nature of the counterion. The chemical shift decreased as the anion changed from chlorine to bromine and to iodine.

Melson _et al_ (12) reported scandium-45 nmr spectra for several scandium salts in aqueous solution. They observed the concentration and anion dependence for the chemical shift and linewidth of Sc-resonance in the solutions of the scandium chloride, perchlorate, and nitrate. They noticed that at low concentration for chloride, perchlorate and bromide solutions of scandium, the chemical shifts approach the same value. In other words the limiting chemical shift is independent of the counterion. They suggested that in these solutions with low concentration the species present might be hydrated $[Sc(OH)]^{2+}$ or $[Sc(H_2O)_6]^{3+}$ ions. They also observed the concentration and anion dependence of the chemical shift and linewidth of the Sc-resonance in aqueous solutions of the different scandium salts. In the case of chloride and bromide, the presence of the chloro and bromo species in the solution was suggested. Other investigators (13-15) also studied these systems and identified the presence of the hydrated species of $ScCl^{2+}$, $ScCl_2^{1+}$, $ScBr^{2+}$, and $ScBr_2^{1+}$ in the aqueous solutions. They measured the stability constant of these complexes by various methods such as potentiometry and cation-exchange. Their values do not agree with each other. For perchlorate as anion, the observed changes in the chemical shift and linewidth of Sc-resonance was related to the formation of $[Sc(OH)]^{2+}$ ion at low concentration and polymeric hydroxy species at higher concentration (10). Melson et al. (12) observed different behaviors for $Sc(NO_3)_3$ and $Sc_2(SO_4)_3$ in aqueous solution. The chemical shifts in these cases did not approach the limiting value at lower concentration which indicates that the species present in the solution include the anions. The linewidth increased with increasing concentration of the salts, which was indicative of the formation of a complex (or contact ion pair) of nitrate and sulfate with scandium ion in concentrated solutions. The stability constants for the formation of Sc(III)-nitrate complexes and related thermodynamic parameters have been measured by solvent extraction method (16). For sulfate complexes of scandium in aqueous solution the log k, ΔH° and ΔS° values were also determined calorimetrically (17). These evidences support the conclusion of Melson et al. (12) obtained from ^{45}Sc nmr.

Complexation with Crown and Cryptands Macrocyclic Ligands

The discovery of cyclic polyether (crown) by Pederson (18) and diazapolyoxamacrocyclic (cryptands) by Lehn and his coworkers (19) introduced into different areas of research a new class of compounds with very interesting and unusual binding properties. Figure 1 shows the structure of some of the crowns and cryptands. These macrocycles contain flexible frameworks with different cavity sizes which enable them to bind a wide variety of cations (20).

These compounds form strong complexes with alkali and alkaline earth metal ions (21) and they have been used as models for ion carrier molecules of biological interest. Crown ethers form two dimensional complexes, and cryptands form three-dimensional complexes. The strength of the



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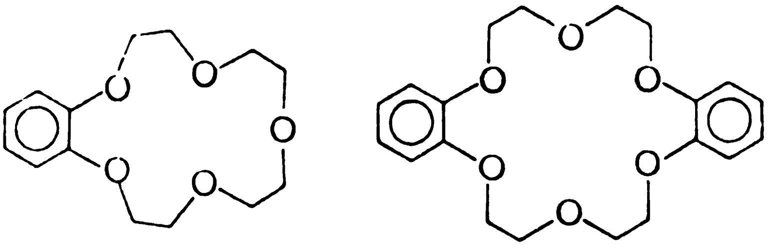
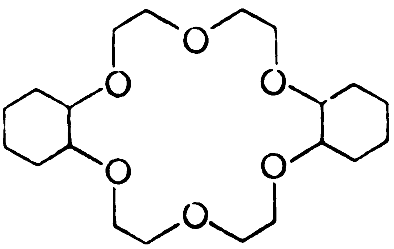


"benzo-15-crown-5" "dibenzo-18-crown-6"



"dicyclohexyl-18-crown-6"

Figure 1. Structure of macrocyclic ligands cryptand and crown.

complexes largely depends on the relation of the cavity sizes of the polyethers to the diameter of the ions. Although these macrocyclic polyethers have been used extensively as complexing agents for a variety of metal ions, the studies on complexation of these ligands with Sc(III) ion has just been started. Olszanski (22) has done some studies on reaction of $ScCl_3$ and $Sc(NCS)_3$ with the benzo-15-crown-5 and dibenzo-18-crown-6. He found that the stoichiometry of the complex is a function of both the salt and the solvent used in the course of the reaction. A more extensive historical discussion of these macrocyclic ligands and their complexes with metal ions in particular alkali metal ions can be found in the Ph.D. thesis of E. H. Mei, Michigan State University (1976).

Conclusion

From the above discussion it is evident that ^{45}Sc NMR spectroscopy may be used as a sensitive probe for the detection and the study of scandium (III) ion solvation and complexation in solution. The first part of this thesis reports an investigation of Sc(III) salt solutions and of complexation of this ion with macrocyclic ligands crowns and cryptands by scandium-45 nmr spectroscopy.

CHAPTER II

EXPERIMENTAL PART

Experimental

Reagents

Scandium oxide was purchased from Research Organic/ Inorganic Chemical Corporation and was 99.9% pure.

Salts

Anhydrous $ScCl_3$ was prepared as described by Stutz and Melson (23); $ScCl_3 \cdot 5H_2O$, $Sc(NO_3)_3 \cdot 3H_2O$, $Sc(ClO_4)_3 \cdot 6H_2O$, and $ScI_3 \cdot 6H_2O$ were prepared from Sc_2O_3 according to the described methods (24-28). These compounds were dried over P_2O_5 under vacuum at room temperature. The Karl Fischer titration method was used to measure the numbers of water molecules accompanying each salt. For the hydrated $ScCl_3$ and $Sc(NO_3)_3$ cases, the number of water molecules is different from that reported earlier (25,26). The difference may be due to differences in drying procedures (reported values for the number of water molecules accompanying $ScCl_3$ is 6 and for $Sc(NO_3)_3$ it is 4).

Solvents

Tetrahydrofuran (THF), (Burdick and Jackson Laboratories, Inc.) was dried over metallic sodium and benzophenone by refluxing. Its water content, measured by the Karl Fischer method, was less than 100 µg/ml.

Ligands

The cryptands C211 and C221 were obtained from E. M. Laboratories, Inc. and were used as received. Crown ethers dibenzo-18-crown-6, dicyclohexyl-18-crown-6 and benzo-15-crown-5 were purchased from Aldrich Chemical Company.

Sample Preparation

Tetrahydrofuran solution of scandium salts were prepared by the following methods:

1. The required amount of anhydrous salt sample was introduced into a volumetric flask and diluted to the mark by tetrahydrofuran or by a mixture of tetrahydrofuran and water in desired ratio.

2. Since the preparation of anhydrous scandium salts was difficult, attempts were made to make tetrahydrofuran solutions of scandium salts by another method. Hydrated scandium salts were dissolved in the dry tetrahydrofuran. The solvent from the solution was refluxed and the condensed solvent was passed through molecular sieves which were in the column of the Soxhlet extraction apparatus. The water concentration during the course of the extraction was monitored by the Karl Fischer method. After a few hours the water concentration was reduced from ∿250-400 μg/ml to ∿20-30 μg/ml. To make solutions with the highest

possible concentrations of the salts (which was still very low, 0.02 M for $ScCl_3$, 0.0017 M for $Sc(NO_3)_3$ and 0.0014 M for $ScBr_3$,) some of the solvent was evaporated.

The IR spectra of the solid dehydrated product (after dehydration process and evaporation of the solvent) did not show any H_2O-bands which are present in the spectra of the hydrated scandium salts. The IR spectra of the product in the $ScCl_3$ case was identical to that of the $ScCl_3 \cdot 3THF$ adduct, first prepared by Herzog et al. (29). The crystal and molecular structure of this compound was recently reported (30). In this compound the scandium ion is hexa-coordinated by three chloride ions and three tetrahydrofuran molecules. The IR spectra of tetrahydrofuran adducts of other scandium salts have bands in common with those of the $ScCl_3 \cdot 3THF$ adduct with some shifts in their positions. Therefore, it is possible that in the dehydration process the H_2O molecules around scandium ion have been replaced by tetrahydrofuran molecules. The above dehydration process was used in other solvents besides tetrahydrofuran, such as acetonitrile (CH_3CN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and acetone (CH_3COCH_3). In CH_3CN hydrolysis took place, and the IR spectrum of the precipitate indicated that it was Sc_2O_3. In DMF, DMSO and CH_3COCH_3 decomposition took place during dehydration process. Therefore, tetrahydrofuran was used as the nonaqueous solvent for this work. Scandium iodide was not used, since the water concentration did not reduce appreciably even after a long dehydration process.

The solutions for study of ^{45}Sc nmr in mixture of solvents were prepared by adding the required volumes of the two solvents to the desired weighted amount of the salt in a volumetric flask.

Instrumental Measurement

Scandium-45 nmr

Continuous wave ^{45}Sc nmr spectra were obtained for some of the experiments with a highly modified NMRS-MP-1000 spectrometer (31,32) operated at 55.1 MHz at a field of 53.3 Kg. The time sharing method of Baker *et al.* (33,34) with frequency sweep was used. Spectra were time averaged for many scans on a Nicolet 1083 computer. Five mm nmr tubes were used. The reference was 3.0 *M* aqueous $Sc(ClO_4)_3$ solution. Increasing chemical shift values (positive chemical shifts) correspond to upfield shift. Magnetic susceptibility correction was not made because of the large chemical shift range. The linewidths are not the natural linewidth since some instrumental line broadening contributes to them. For some of the experiments, the spectrometer was modified to operate in the Fourier transform mode which saved time (since for continuous wave mode, a lot of scans were necessary to see the signal which took as long as $\sim$24 h).

The ^{45}Sc nmr studies in mixed solvents were done in both modes and identical data were obtained.

Infrared

Infrared measurements in the 4000-200 cm^{-1} spectral region were obtained on the Perkin Elmer Model 457 grating spectrophotometer. The mull samples were held between potassium bromide salt plates. Nujol was used for making the mulls.

CHAPTER III

SCANDIUM-45 NMR STUDIES OF SOLVATION AND COMPLEXATION OF SCANDIUM(III) ION IN SOLUTIONS

Introduction

Scandium-45 nmr spectroscopy is shown to be a potentially useful technique for the study of the nature of the chemical species present in the solution. The work done in this area so far deals with ^{45}Sc nmr studies in aqueous solutions . This might be due to low solubility of anhydrous scandium salts in nonaqueous solvents which makes it difficult to see ^{45}Sc-resonance with these solutions. With this in mind this study was initiated to investigate the salt solutions of Sc(III) salts in nonaquous solvents. In addition since there have been no published reports of any studies involving the ^{45}Sc nmr studies of crown and cryptand complexes of this ion in solution, it seemed interesting to study complex formation of these complexing agents with Sc(III) ion by ^{45}Sc nmr spectroscopy.

A: A Scandium-45 NMR Study of Solutions of Scandium Salts in Tetrahydrofuran and in a Mixture of Water and Tetrahydrofuran

The chemical shift and linewidth of the ^{45}Sc resonances for tetrahydrofuran solutions of scandium salts are recorded in Table I. The chemical shifts, "δ", are referred to an aqueous solution of $ScCl_3$ at infinite dilution. Increasing values (positive chemical shifts) correspond to

Table I. ^{45}Sc NMR Data for Some Scandium Salts in Tetra-Hydrofuran Solution.

Scandium Salt	Concentration Sc^{3+} M	Chemical Shift δ, ppm	Line Width Hz
$ScCl_3$	0.020	-202	660
$ScCl_3 \cdot 4H_2O$	0.020	-191	800
$ScCl_3 \cdot 4H_2O$	0.015	-190	890
$ScCl_3 \cdot 4H_2O$	0.010	-193	900
$ScBr_3$	0.007	-273	231
$ScBr_3 \cdot 4H_2O$	0.007	-264	323
$Sc(NO_3)_3$	0.017	- 10	244
$Sc(NO_3)_3 \cdot 3H_2O$	0.017	- 7	216
$Sc(ClO_4)_3 \cdot 6H_2O$	0.020	- 23	492
$Sc(ClO_4)_3 \cdot 6H_2O$	0.010	- 25	494

increasing shielding. For the sake of comparison the data obtained from this study will be discussed in conjunction with those obtained for aqueous solutions by Olzanski et al. (22) as listed in Table II.

It is obvious from the data in Table I, that for tetrahydrofuran solutions of scandium salts a large range of chemical shifts is observed. These shifts can indicate that there is a significant change in the coordination environment of the scandium(III) ion in these solutions compared to the aqueous solutions. A study of concentration dependence of the chemical shift was not possible because of (a) low solubility of scandium salts in the tetrahydrofuran and (b) limitation of the instrument sensitivity for observing the signal at lower concentrations. However, in the concentration range in which nmr observations were possible, the chemical shifts were anion dependent and did not approach a limiting value as was observed in aqueous solution of $ScCl_3$, $ScBr_3$ and $Sc(ClO_4)_3$ (22). These results indicate that even at such low salt concentrations the concentration of free and solvated Sc(III) ion is very small and the anion is still interacting with the Sc(III) ion. This difference between the two systems might be explained in terms of the dielectric constant of tetrahydrofuran ($D = 7.58$ at 25°C) with respect to water ($D = 78.54$ at 25°C). The large chemical shifts observed for $ScCl_3$ and $ScBr_3$ tetrahydrofuran solutions also indicate that there is strong interaction between the anions and Sc(III) ion and that the

Table II. ^{45}Sc NMR Data for Some Scandium Salts in Aqueous Solution[a].

Scandium Salt	Concentration Sc^{3+} M	Chemical Shift, ppm[b]	Line Width Hz[c]
$ScCl_3$	3.0	-18.8	220
	2.5	-10.4	200
	2.0	- 3.6	178
	1.5	- 1.5	52
	1.0	- 0.5	50
	0.6	- 0.1	48
	0.3	+ 0.2	56
	0.1	+ 0.1	50
	0.03	0.0	58
$ScBr_3$	3.0	+ 6.5	181
	2.0	+ 5.4	183
	1.0	+ 2.5	176
	0.6	+ 1.1	148
	0.3	+ 0.8	146
	0.1	0.0	93
	0.03	+ 0.2	71
$Sc(ClO_4)_3$	3.0	+14.8	139
	2.5	+11.9	114
	2.0	+ 8.7	85
	1.5	+ 5.7	65
	1.0	+ 3.6	59
	0.6	+ 2.2	43
	0.3	+ 1.0	47
	0.1	0.0	45

These data are from Olzanski's thesis and the sign of the chemical shifts were changed to follow our convention.

Table II. Continued

Scandium Salt	Concentration Sc^{3+} M	Chemical Shift δ, ppm[b]	Line Width Hz[c]
$Sc(NO_3)_3$	2.0	+ 0.1	1655
	1.0	- 0.9	1004
	0.6	- 1.6	739
	0.3	- 4.3	656
	0.1	- 4.3	456
	0.03	- 5.0	440
$Sc_2(SO_4)_3$	2.0	- 6.7	454
	1.2	- 7.3	272
	0.6	- 8.6	220
	0.2	- 9.1	197
	0.06	- 9.3	190
	0.02	- 9.4	181
ScI_3	3.0	+ 5.7	1185
	2.5	+ 1.8	964
	2.0	- 1.4	751
	1.5	- 2.5	671
	1.0	- 4.2	604
	0.6	- 4.3	504
	0.3	- 3.3	377
	0.1	- 2.8	295

[a] Data obtained at ambient temperature.

[b] Relative to aqueous $ScCl_3$ solution at infinite dilution. Error limits ±1 ppm.

[c] Not corrected for instrumental broadening.

species present in the solution are contact ion pairs rather than solvent separated ion pairs.

The linewidths in tetrahydrofuran solutions are much broader at equal concentrations (Table I) than those found in dilute aqueous solutions (Table II), indicating that the environment of Sc(III) ion is not symmetrical which may be due to contact ion pair formation. In dilute aqueous solutions, the species present is suggested to be predominantly $[Sc(H_2O)_6]^{3+}$ ion or the hydrated $[Sc(OH)]^{2+}$ (35,36).

Solutions of hydrated scandium salts in tetrahydrofuran were also studied and the results indicate that there is a change in the chemical shift with respect to the anhydrous salt solutions. This study was carried out to understand the role of water in these solutions and the competition between tetrahydrofuran and water for the Sc(III) ion. The ^{45}Sc nmr spectra were obtained on a series of the solutions of $ScCl_3$ in a mixture of tetrahydrofuran with water. The variation of ^{45}Sc resonances as a function of solvent composition is shown in Table III and Figure 2. From these data a smooth transition of the Sc-resonance from its value in one pure solvent to the other is observed. The rate of this transition is dependent on the relative solvation ability of the two solvents.

The isosolvation point has been defined as a point in which the chemical shift lies midway between the values for pure solvents and where the two solvents compete equally

Table III. ^{45}Sc nmr Data for $ScCl_3$[a] in Water-Tetrahydrofuran Solutions.

Mole Fraction H_2O	Chemical Shift δ, ppm[b]
0.000	-204
0.001	-200
0.004	-186
0.008	-178
0.011	-177
0.020	-170
0.039	-150
0.134	-119
0.206	- 88
0.314	- 52
0.529	- 12
0.818	- 3
0.976	0
0.988	0
1.000	0

[a] $[Sc^{3+}] = 0.010M$

[b] ±2 ppm.

for the cation in question. Frankel, et al. (37) and Bloor and Kidd (38) have examined preferential solvation of Co^{3+} and ^{23}Na respectively in solvent mixtures. Greenberg (39) has studied ^{23}Na nmr in mixtures of several solvents and has used the isosolvation point as a measure of the preferential solvation of the solvents in question.

In our case, a change in the concentration of the H_2O-THF mixture affects not only the solvation shell of the Sc(III) ion but also the ion pair dissociation. Therefore the isosolvation criterion cannot be used in this case. However, from the curvature of the plot of chemical shifts vs mole fraction of tetrahydrofuran (Figure 2) it is obvious that the change in the chemical shift is large, even in solvent mixtures with low mole fraction of H_2O. These results indicate that the interaction of H_2O with Sc (III) ion is strong and Sc(III) ion is preferentially solvated by H_2O which is in accord with the donor number of the two solvents: $DN_{H_2O} > DN_{THF}$. Donor number which can represent the donor ability of a solvent has been defined empirically by Gutmann (40) as the enthalpy of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solution. It has been shown by Gutmann that the donor number is very useful in predicting the trends of complexation reaction in nonaqueous solvents.

A comparison of the shifts for the anhydrous and hydrated

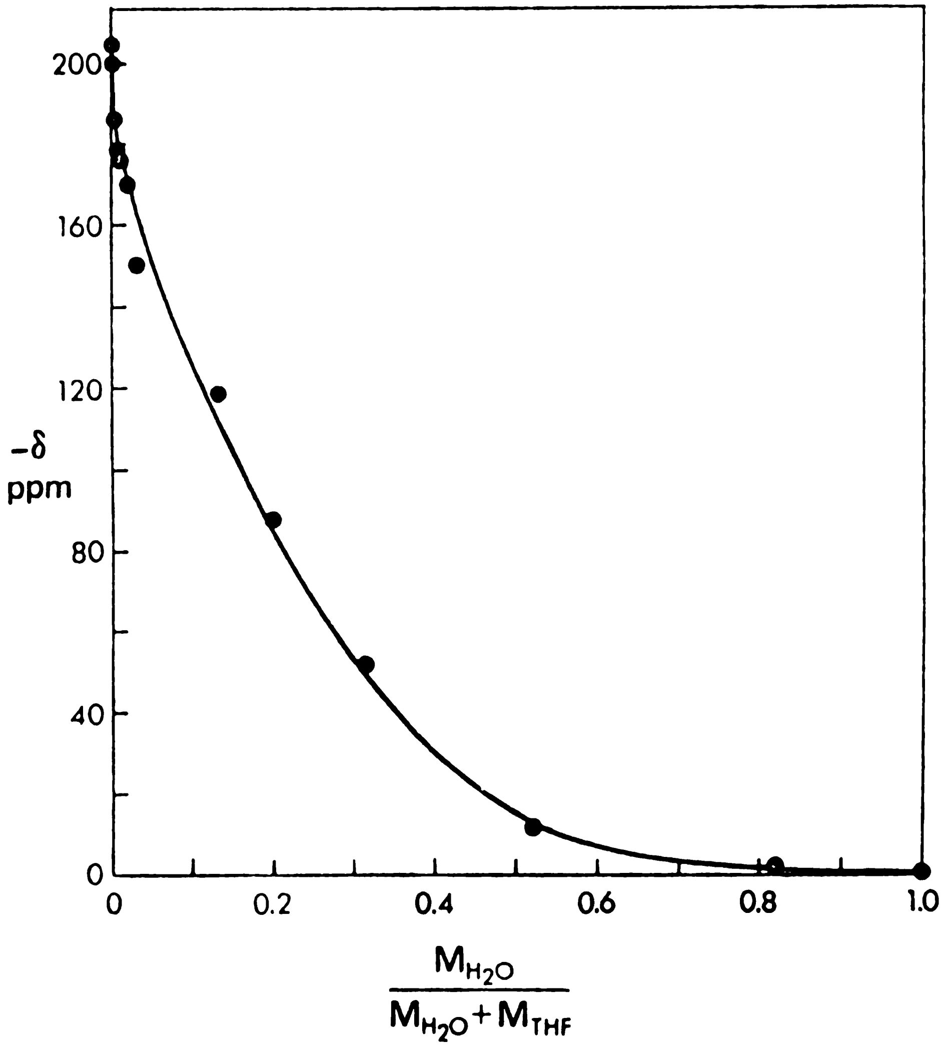


Figure 2. Variation of the chemical shift of the scandium-45 resonance as a function of solvent composition for binary solvent water and tetrahydrofuran.

salts (Table I), leads to the following observations: the chemical shift for anhydrous $ScBr_3$ (0.007$\underline{M}$) in tetrahydrofuran is -273 ppm, for $ScBr_3$, $4H_2O$ (0.007$\underline{M}$) it is -264 ppm, for anhydrous $Sc(NO_3)_3$ (0.017$\underline{M}$) it is -10 ppm, and for $Sc(NO_3)_3$, $3H_2O$ (0.017$\underline{M}$) it is -7 ppm. The apparent shift of the hydrated salt toward the chemical shift of Sc(III) ion in water indicates the partial solvation of Sc(III) ion by water in these solutions.

In all these experiments only one scandium resonance is observed because the rate of exchange of tetrahydrofuran with water in the coordination sphere of Sc(III) ion is very fast with respect to nmr time scale. Therefore, the observed resonance signal corresponds to the average of all the species present in the solution.

B: Scandium-45 NMR Studies on Complexation Reactions of Scandium With Crown Ethers and Cryptands in Solution

Scandium-45 nmr spectra were obtained for a series of solutions of the $Sc(ClO_4)_3 \cdot 6H_2O$ in water at varying mole ratios of ligand to metal. Different crown ethers and cryptands were used.

Cryptands C211 and C221 (Figure 1) were used, as ligands, because of their cavity radii (C221, 0.8 Å; C221, 1.15 Å). Table IV records the chemical shifts and linewidths of scandium resonance as a function of ligand to metal mole ratio. As the ligand is added to the solution

Table IV. ^{45}Sc NMR Data for $Sc(ClO_4)_3 \cdot 6H_2O$/cryptand Mixtures in Aqueous Solution

	Conc. Cryptand M	Conc. Sc(III) M	Chemical Shift δ, ppm	Line Width Hz
Cryptand C211	0.000	0.03	0	120
	0.003	0.03	0	160
	0.009	0.03	-6	488
	0.018	0.03	-22	>2000
Cryptand C221	0.000	0.05	0	150
	0.005	0.05	0	260
	0.015	0.05	-10	583

the chemical shifts increase as well as the linewidths, which can serve as an indication for complexation of the Sc(III) ion with cryptands. Formation of these kinds of complexes distorts the spherically symmetrical electric field around the scandium ion and results in a very appreciable broadening of the scandium resonance. This line broadening is due to the interaction of the quadrupole moment of this nucleus with the fluctuating electric fields around the nucleus. In the case of C211, at mole ratios above 0.6 the signal becomes so broad that the line disappears. In all these cases only one resonance is observed because of the rapid exchange between the coordinated and the free Sc(III) ion in the solution. The ^{45}Sc resonance observed is the average for Sc(III) ions in all different sites. For cryptand C221 at a mole ratio above 0.3, a white precipitate was formed which precluded the study of the complexation at higher mole ratios. This precipitate was found to be the perchlorate of the protonated ligand. This conclusion was based on elemental analysis and the IR spectrum of the solid which remained after the solvent was evaporated and the residue was dried over P_2O_5 under vacuum. Results from elemental analysis are as follows: Calculated for C221$\cdot$ $2HClO_4$: C, 36.02; H, 6.37; N, 5.25; Cl, 13.32. Found: C, 35.664; H, 6.12; N, 5.17; Cl, 12.97. The IR spectrum of this solid product shows a NH band at 3140 cm^{-1} and ClO_4^- bands at 1080 cm^{-1} and 620 cm^{-1}.

The above data indicate that complexation takes place in the solution but it is very weak because in aqueous solution, water molecules coordinate strongly to the Sc(III) ion and compete with the ligand. The formation constants of the complexes could not be evaluated because of following experimental difficulties: (a) broadening of the ^{45}Sc resonance line which causes the disappearance of the signal at higher mole ratios (in case of C211). (b) Protonation of the ligand in aqueous solution (in case of C221). (c) Low solubility of the Sc salts in other solvents of interest. The combination of low solubility of scandium salts in nonaqueous solvents such as tetrahydrofuran and broad line width results in signal-to-noise ratios below a usable limit.

Crown ethers dicyclohexyl-18-crown-6, benzo-15-crown-5 and dibenzo-18-crown-6 (Figure 1) were used as complexing agent for Sc(III) ion. To study complexation of dicyclohexyl-18-crown-6 a series of aqueous solution of $Sc(ClO_4)_3 \cdot 6H_2O$ with varying mole ratios of ligand to metal was prepared. The ^{45}Sc nmr spectra of these solutions were obtained. This experiment was done at different concentrations of $Sc(ClO_4)_3 \cdot 6H_2O$. Results are shown in Table V. No appreciable changes in the chemical shifts or linewidths of the Sc-resonance in these solutions were observed. This shows that no complexation reaction has taken place in the solution. Similarly no evidence for complexation of benzo-15-crown-5 with Sc(III) ion was obtained for aqueous solution of $Sc(ClO_4)_3 \cdot 6H_2O$.

Table V. ^{45}Sc NMR Data for $Sc(ClO_4)_3 \cdot 6H_2O$/Crown Mixtures in Aqueous Solution

Conc. Sc(III) M	L/M*	Chemical Shift δ, ppm	Line Width Hz
0.02	0.00	-19	138
0.02	0.20	-17	136
0.02	0.25	-16	129
0.02	0.30	-18	
0.02	0.50	-17	127
0.02	1.00	-17	134
0.02	2.00	-17	102
0.03	0.00	-17	137
0.03	0.20	-16	120
0.03	0.75	-17	110
0.03	0.50	-17	117
0.03	1.00	-16	85
0.01	0.00	-20	
0.01	0.20	-19	183
0.01	0.25	-19	159
0.01	0.50	-20	207
0.01	1.00	-19	156
0.01	2.00	-20	158

*L/M = [Dicyclohexyl-18 crown 6]/[Sc(III)].

Since the solubility of dibenzo-18-crown-6 was very low in water, the complexing ability of this ligand toward Sc(III) ion could not be measured. From above data it can be concluded that these ligands cannot displace water molecules which surround the Sc(III) ion. This indicates the coordination abilities of these ligands are lower than those of water.

Conclusion

This study shows that ^{45}Sc spectroscopy is very useful technique in directly providing qualitative information about the nature of the chemical environment about Sc(III) ion in its solutions. However due to low solubility of the salts quantitative data could not be obtained. The sensitivity of scandium resonance to the variation of the coordination environment of the Sc(III) ion makes this technique useful for study of Sc(III) ion solvation, ion pair formation, and complexation of this ion with different ligands in solution. In particular the range of the chemical shift for ^{45}Sc-resonance is large, on the order of hundreds of part per million, which makes it more sensitive to detect small changes in the chemical environment of this nucleus.

PART II

CHAPTER I

HISTORICAL

Chemistry of Silver

Silver with electronic configuration of $[Kr]4d^{10}5s^{1}$ is a group B element and the second member of Cu, Ag, Au group. Its normal and dominant oxidation state in its compounds is +1. Oxidation states of +2 and +3 have also been identified in many silver compounds.[41]

Silver ion shows a great tendency to form complexes with a wide variety of ligands. Organosilver compounds in which silver interacts with one or more carbon atoms have been characterized. In these compounds the organic moiety can be σ-bonded to Ag^{+} ion as in alkyl , alkenyl, and alkynyl silver compounds, or σ- and π-bonded as in alkene-, alkyne-, and arene-silver coordination complexes.[42-44]

Coordination complexes of Ag(I) with aromatic and heteroaromatic compounds have been a subject of interest for many years. In these compounds there is an interaction between the silver ion and the π-electronic system of the aromatic moiety. This interaction includes both σ- and π-type bonding. The σ-type bonding is as a result of donation of π-electrons from ligand to metal ion and the π-type bonding is as a result of back donation of d-electrons of metal to ligand.

In 1922 the first silver arene complex, $C_6H_6Ag^{+}$,was detected and isolated from a solution of $AgClO_4$ in benzene.[45] Silver-arene complexes with other stoichiometries have also been reported.[46]

Equilibrium constants for predominant stoichiometries of complexes of Ag^+ ion with benzene have been determined from solubility measurements of benzene in aqueous silver nitrate solutions[47] and from measurements of the chemical shift of the benzene resonance in aqueous solution of benzene in the presence of varying excess concentrations of silver nitrate.[48] The following numerical values of equilibrium constants from the two measurements are similar but cannot be compared directly because the two types of measurements were made at different temperatures:

	K_1	K_2
from solubility[47]	2.41 1-mol^{-1} (25.0°)	0.212 1-mol^{-1}(25.0°)
from nmr[48]	2.30 kg/mol^{-1}(33.5°)	0.48 kg-mol^{-1}(33.5°)

In 1/1 and 1/2 (benzene/Ag^+) complexes Ag^+ ion was suggested to be on the six-fold symmetry axis of the aromatic ring at one or both sides respectively.[47] This idea was supported by the results of Raman spectroscopic studies.[49] But from theoretical considerations based on symmetries of quantum-mechanical wave functions an unsymmetrical geometrical configurations of these complexes was suggested. In these complexes silver ions lie away from the symmetry axis of the aromatic ring and above and between adjacent carbon atoms.[50] This conclusion was supported by the results from x-ray diffraction studies on the solid complex of $C_6H_6AgClO_4$ which shows the silver ion interacts primarily with the two nearest ring carbons.[51] Further x-ray investigation suggested[52] that the discrete carbon atoms undergo a small amount of thermal motion and the benzene molecules possibly undergo some type of reorientation (highly hindered rotation). From proton nmr studies on the benzene-silver perchlorate complex at 77 K and 298 K,[53] it was concluded that at lower temperatures the benzene molecule in the complex is more or less rigidly held in the crystal lattice, while at room temperature it is rotating more or less freely about the six-fold molecular symmetry axis. The apparent conflicting result from x-ray and proton nmr studies was attributed[54] to the relative time scales involved in the two types of experiments.

The proton nmr spectrum of the aqueous solution of $AgNO_3$ with benzene exhibits one single absorption due to aromatic protons.[55] The observation was explained in terms of rapid exchange between several different species in equilibrium with one another, and it was not established whether or not all protons are equivalent.

Complexation of several substituted benzene derivatives with silver ion has also been studied and the equilibrium constants of these complexes have been determined from solubility measurements of these aromatic compounds in aqueous solutions of silver nitrate.[55-58] The results of these studies indicate that the stability of the complexes increases with increasing electron donating abilities of the substituent groups and suggest that σ-type bonding is more significant than π-type bonding in the formation of these complexes.

The complexation reaction of silver ion with heterocyclic aromatic compounds such as pyridine and its substituted derivatives has also been studied by many investigators. In pyridine and its derivatives, the electron pair present on the heterocyclic atoms is more available for interaction with Ag^+ ion than are the aromatic π-electrons. In these complexes there will be a donation of electrons from the ligand to silver ion, i.e., σ-bonding and donation from silver to ligand, i.e., π-bonding.

Formation constants, enthalpy and entropy of the complex formation between silver ion and pyridine (pyridine/Ag^+: 1/1 or 2/1) have been measured by different techniques such as calorimetry,[59,60] ultraviolet absorption spectroscopy[61] and potentiometry.[62,63]

The obtained values from different methods are in good agreement.

	log K_1	log K_2	$-\Delta H_1$ (kcal/mol.)	$-\Delta H_2$ (kcal/mol)	$-\Delta S_1$(e.u.)	$-\Delta S_2$(e.u.)
From calorimetric[59,60] measurement (at 25°, in H_2O)	2.00±0.04	2.11±0.08	4.83±0.05	6.51±0.06	7.0 ±0.3	12.2±0.5

	log K_1[a] ($l\ mol^{-1}$)	$-\Delta H_1$(kcal/mol)	$-\Delta S_1$(e.u.)
From UV absorption[61] measurement (at 26° in CH_3CN)	2.037	4.5	5.8

a) The K_1 was reported[61] to be 109 but is tabulated here as log K_1 for comparison.

	log K_1	log K_2
from potentiometric measurement[62] (at 25° in H_2O)	1.97	2.38

Above values are for following reactions

$$Ag^+ + PY \rightleftarrows Ag(PY)^+ \qquad (K_1,\ \Delta H_1,\ \Delta S_1)$$

$$Ag(PY)^+ + PY \rightleftarrows Ag(PY)_2^+ \ (K_2,\ \Delta H_2,\ \Delta S_2)$$

Formation constant and thermodynamic data for complexes of silver ion with substituted pyridine have been determined[62-64] from potentiometric and calorimetric measurements and a linear relationship between the logarithm of formation constants and basicity of the ligands was obtained.[63]

Nuclear Magnetic Resonance Studies

In recent years the use of magnetic resonance of metallic nuclei provided a sensitive probe in the study of metal ion reactions in solutions. In particular the range of the chemical shift for many metal nuclides is very large, on the order of hundreds to thousands ppm, which makes the chemical shift of metallic nuclei very sensitive to small changes in the chemical environment of the metal nucleus. The major disadvantage of the use of magnetic resonance of metal ion for chemical studies is the lower sensitivity of the resonances compared to the proton or fluorine.

Both silver isotopes ^{107}Ag and ^{109}Ag have weak nmr signals which makes the measurements practically difficult. Silver-109 has a slightly higher sensitivity than ^{107}Ag which makes it preferable for nmr studies. Silver-109 nuclide with the spin of 1/2 has 49.65% natural abundance and the low sensitivity at constant field of 1.01×10^{-4} compared to proton (assuming sensitivity of 1 for proton). In addition silver-109 has very low resonance frequency of 2.7916 MHz at a field of 1.4092 Tesla.

Further difficulty of ^{109}Ag nmr studies is its extremely long relaxation times (T_1 on the order of minutes) due to small magnetic moment and zero quadrupole moment ($I = 1/2$) which results in very weak interaction of the silver nucleus with its surroundings. As a result of the experimental difficulties described above very few reports have been published on ^{109}Ag nmr studies. Most of the work done in this area carried out by various investigators report either studies on silver alloys,[65,66] solid solutions,[67,68] silver metal[69] or on measurement of the magnetic moment or Larmor frequency of this nucleus.[70-73] To our knowledge there are only two published papers on silver-109 nmr studies in solutions. One is by Burges, *et al.*[74] and the other one is by Jucker *et al.*[76] In addition some studies are being carried out at this time by Maciel and his group[75] but have not been published as yet.

Burges *et al.* measured the ratio of T_1/T_2 for ^{109}Ag in 9.1 molal aqueous solution of $AgNO_3$:$T_1/T_2 = 12$. They found that the addition of a paramagnetic ion decreases this ratio. They measured relaxation times for 8.3 molal aqueous solution of AgF ($T_1/T_2 = 6\pm1$) were $T_1 = (49\pm20)$ sec and $T_2 = (8.2\pm2)$ sec. They also measured the shift of the ^{107}Ag Larmor frequency due to paramagnetic ion in a 9.1 molal aqueous solution of $AgNO_3$ with varying concentration of a paramagnetic ion as $Fe(NO_3)_3$ from 0-1.2 molal. The maximum observed shift was 8.3 ppm and the shift of ^{107}Ag resonance was not a monotonous function of the concentration of paramagnetic ions.

The concentration dependence of the Larmor frequencies of the ^{107}Ag and ^{109}Ag was determined in $AgClO_4$, $AgNO_3$ (^{107}Ag) and AgF (^{109}Ag) in the range from 0.4 molal to nearly saturated solutions. For $AgClO_4$ and $AgNO_3$ an upfield shift was observed with increasing the concentration but for AgF, the shifts were toward lower field with increasing the concentration.

Jucker and his group very recently reported[76] the ^{109}Ag nmr studies of some silver complexes. They investigated solutions of silver salts in acetonitrile, propionitrile, pyridine, and ethylenediamine and also in aqueous solutions of $Na_2S_2O_3$ and ethylamine. From the data the formation of several complexes in these solutions were suggested. They also observed that the chemical shifts of mixtures of AgCl and AgBr and also of AgCl and AgI dissolved in 70% aqueous solutions of ethylamine are linear functions of anion mole fraction.

Maciel and his group[75] simultaneously with our work used ^{109}Ag nmr spectroscopy to study complexation of thiourea and tetramethyl thiourea with Ag^+ ion in DMSO solution. They examined solutions containing 1 M silver nitrate in dimethylsulfoxide with varying ligand concentration. The addition of the ligand to the silver ion solution results in a downfield shift of the ^{109}Ag resonance. Thus the existence of the sulfur bonded Ag(I) complexes was postulated. From the study of the curvature of the plot of mole ratio of ligand to metal ion vs chemical shifts, complex species including highly aggregated forms with different stoichiometries were suggested.

This group has also studied solution chemistry of high concentrations of $AgNO_3$ in dimethylsulfoxide, acetonitrile, water and binary mixtures of these solvents using ^{109}Ag

nmr technique . The concentration and anion dependence of the ^{109}Ag chemical shift was measured. The observed upfield shift with increasing the salt or anion concentration in the solution was related to the strong cation-anion interactions. They also found evidence for Ag(I) complexes with dimethylsulfoxide and acetonitrile from ^{109}Ag nmr studies in these systems.

Conclusions

Thus it is apparent that in spite of experimental difficulties that one encounters in silver-109 nmr measurements, this technique showed some promise for the studies of silver ion complexes in solution. The second part of this thesis reports the use of this technique in the study of (A) silver salt solutions and (B) complexation reaction of this cation with aromatic and heteroaromatic compounds, such as benzene, pyridine and their derivatives.

CHAPTER II

EXPERIMENTAL PART

Experimental

Salts

Silver nitrate (Fisher, certified reagent) was dried under vacuum in an oven at 65°C. Silver perchlorate was purchased as hydrated or as anhydrous salt (G. Frederick Smith Chemical Co.). Both salts were of reagent grade quality. The hydrated salt was first recrystallized from an aqueous solution and then dried over P_2O_5 under vacuum at room temperature. The anhydrous salt was also dried by the same procedure. All the salts were kept in the dark to prevent decomposition.

Solvents

Acetone (Fisher) was distilled over Drierite and further dried over molecular sieves. Acetonitrile (Matheson Coleman & Bell)) was refluxed over calcium hydride and then fractionally distilled over granulated barium oxide. Dimethylformamide (Fisher) was vacuum distilled over P_2O_5. Dimethyl sulfoxide (Fisher) was dried over molecular sieves for two days. Methanol (Fisher) was first fractionally distilled from calcium hydride and then from magnesium turnings in a nitrogen atmosphere. Propylene carbonate (Aldrich) was dried over activated molecular sieves for two days. Molecular sieves used were activated by heating them at 500°C under dry argon in an oven (Lindberg) for 12 hours. Water content of salts and solvents were measured by an automatic Karl Fischer titrator Aquatet II from Photovolt Corp.

Ligands

Benzene (Matheson Coleman & Bell) and toluene (Analytical reagent, Mallinckodt) were purified and dried by refluxing and fractionally distillating over sodium metal and benzophenone under nitrogen atmosphere. Pyridine (Fisher) was refluxed over granulated barium oxide and then fractionally distilled under nitrogen atmosphere. Ligand 2-cyanopyridine (Aldrich) was purified by fractional freezing technique.[77] The purity of 2,5-dibromopyridine (Aldrich), 2,6-dichloropyridine (Aldrich), 4-cyanopyridine (Aldrich) and 2,5-dichloropyridine (K and K Laboratories) were checked by their melting points (94-95°C, 87-88°C, 78-79°C and 59-60°C, respectively), which were in agreement with literature values.

Instrumental Measurement

Silver-109 NMR

Silver-109 nmr measurements were made on a Fourier transform instrument using the magnet of a Varian DA-60 nmr spectrometer equipped with a wide-band probe, computer[78] controlled rf pulse generation and data collection as described previously.[78-80] An external ^1H field lock was used to maintain field stability.

The instrument was operated at a field of 1.4092 T (∿14 KG) and at a frequency of 2.7916 MHz for ^{109}Ag. The measurements at room temperature were made with reference to an external standard which was a saturated aqueous silver perchlorate solution (∿12.5 M) doped with Fe^{+3} salt in a 15 mm Wilmad nmr tube. At other temperatures the same reference solution was placed in a dewar type tube (Figure 3) which was used in the -110 to +130°C ranges. The reference solution was in a 10 mm precision Wilmad nmr tube which was concentrically sealed in a 15 mm precision Wilmad nmr tube. The space between the tubes was evacuated to 10^{-6} torr and then sealed. The secondary reference was a 6 M aqueous solution of $AgClO_4$ doped with Fe^{+3}. The mole ratio of Fe^{+3}/Ag^+ was 1/100. The chemical shift of this reference vs that of the primary reference was -59 ppm.

The line width of the ^{109}Ag resonance for the reference was 5.8 - 8.4 Hz and for the sample solutions was 1.1 - 5.8 Hz. No systematic change occurred in the line width for the various experiments that were done.

Since the relaxation time of ^{109}Ag nucleus is extremely long to reduce it the sample solutions were doped with small amounts of paramagnetic ions such as Ni^{+2} (since Fe^{+3} precipitates in acetonitrile solutions of $AgNO_3$).

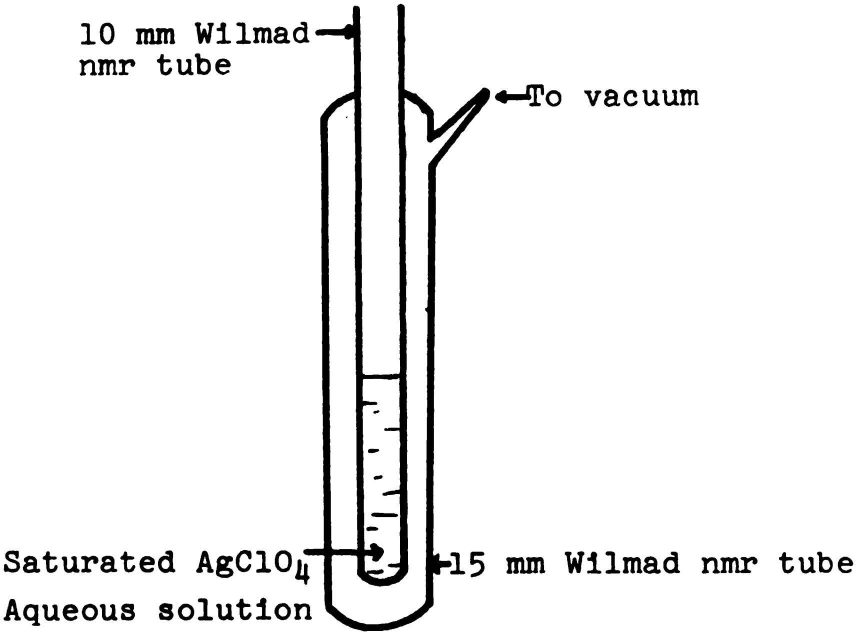


Figure 3. Reference solution in dewar-type tube.

In all cases the ratio of Ag^+ ion to that of paramagnetic ion was at least 50/1. The lower limit of detection with the present instrument is 0.5 M. In our convention the upfield shifts correspond to the positive values. The reported chemical shifts are not corrected for change in diamagnetic susceptibility since the range of chemical shift is so large that it would not produce any problem.

Carbon-13 NMR

Carbon-13 nmr measurements were made on a Varian CFT20 Fourier transform nmr spectrometer equipped with computer controlled pulse generation and data collection. The instrument was operated at a field strength of 18.682 KG and at a frequency of 20 MHz.[81]

For ^{13}C nmr studies on solutions of Ag(I) salts, DMSO was used as an external reference (since TMS has some effect on chemical shift) and D_2O was used for locking the system. Both DMSO and D_2O at 1/1 volume ratio were in a capillary tube which was coaxially centered on the 8 mm nmr tube containing the sample solution.

For ^{13}C nmr studies on complexation reactions, the chemical shifts were referred to the solvent peak which changed the least upon addition of salt (within 0.1 ppm change). The sample solution was in a 5 mm nmr tube which was coaxially centered in the 8 mm nmr tube containing the external reference acetone with D_2O for locking the system.

A positive shift from the reference is downfield. The reported chemical shifts for this case were not corrected for diamagnetic susceptibility because the solvent peak were chosen as a reference.

Proton NMR

Proton nmr measurements were made on Varian A-56/60 D and T60 nmr spectrometers with operating frequency of 60 MHz and magnetic field strength of 14.092 KG.[82,83] The measurements were made with internal reference TMS for acetonitrile solutions and DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) for aqueous solutions. The sample solutions were held in a 5 mm O.D. Wilmad nmr tube. The positive shifts from the reference is downfield..

CHAPTER III

SILVER-109 NMR STUDIES OF SOLVATION AND COMPLEXATION OF SILVER(I) IN SOLUTIONS

Introduction

It was mentioned previously that the NMR of some metal nuclei was shown to be a very useful probe for the study of these ions in solutions. It was of interest to us to explore the possible use of ^{109}Ag nmr for the study of silver chemistry in solutions and in particular, in nonaqueous solvents. It should be mentioned that the experimental difficulties described earlier (page 42) and the low sensitivity of the ^{109}Ag nmr signal did not augur well for the successful use of this technique at least with the previously available instrumentation; nevertheless, a detailed study of the ^{109}Ag chemical shifts in various solvents at different concentrations and in the presence or absence of complexing agents would be a worthwhile initial exploration of silver nmr.

A: NMR Studies of Ag(I) Salts in Solution

1. A Silver-109 NMR Study of Solutions of Silver-salts in Water, Acetonitrile, and Their Mixtures

The chemical shifts of the ^{109}Ag resonance for aqueous solutions of silver nitrate and silver perchlorate were determined. The data are presented in Table VI. The chemical shift "δ" is referred to saturated aqueous solution of $AgClO_4$ doped with Fe^{+3}.

Table VI. ^{109}Ag NMR Data for $AgClO_4$ and $AgNO_3$ in Water

Conc., M		δ(ppm)
0.5	**$AgClO_4$**	-101.5
1.0		- 97.0
2.0		- 89.20
4.0		- 71.7
6.0		- 53.4
8.0		- 34.9
10.0		- 12.24
10.7		- 7.4
	$AgNO_3$	
1.0		- 92.8
2.0		- 81.9
3.0		- 73.8
4.0		- 67.7
5.0		- 62.1
6.0		- 56.8

Figure 4 shows the variation of ^{109}Ag chemical shift as a function of concentration of $AgNO_3$ and $AgClO_4$. As is the case of $Sc(ClO_4)_3$ and $Sc(NO_3)_3$ in aqueous solution (Table II) the chemical shift moves upfield with increasing concentration of silver salt. VanGeet and Templeman[85] observed similar behavior for sodium perchlorate in aqueous solution and they suggested that upfield shifts occur when a water molecule in the cation solvation shell is replaced by an anion which results in a decreased electron density around alkali cation. Deverell and Richards noted[86] the same phenomenon for aqueous alkali metal nitrate solution and suggested a direct interaction between the ions is the predominant cause of the chemical shift of the cation's resonance in the solution. Bloor and Kidd observed similar behavior for aqueous solution of potassium nitrate and they proposed that since the chemical shift arises from the overlapping of the outer electron orbitals of ions during random ionic collisions, the upfield shift of the cation resonance is due to weaker overlap interaction between the anion with cation than water-cation interaction.[87] It is possible that the same explanation applies to the upfield shift observed in aqueous solution of silver salt.

Since the ^{109}Ag chemical shifts reflect changes in the immediate environment (solvation sphere) of the cation and the shifts for the two anions extrapolate to the same value of the chemical shift which is indicative of the

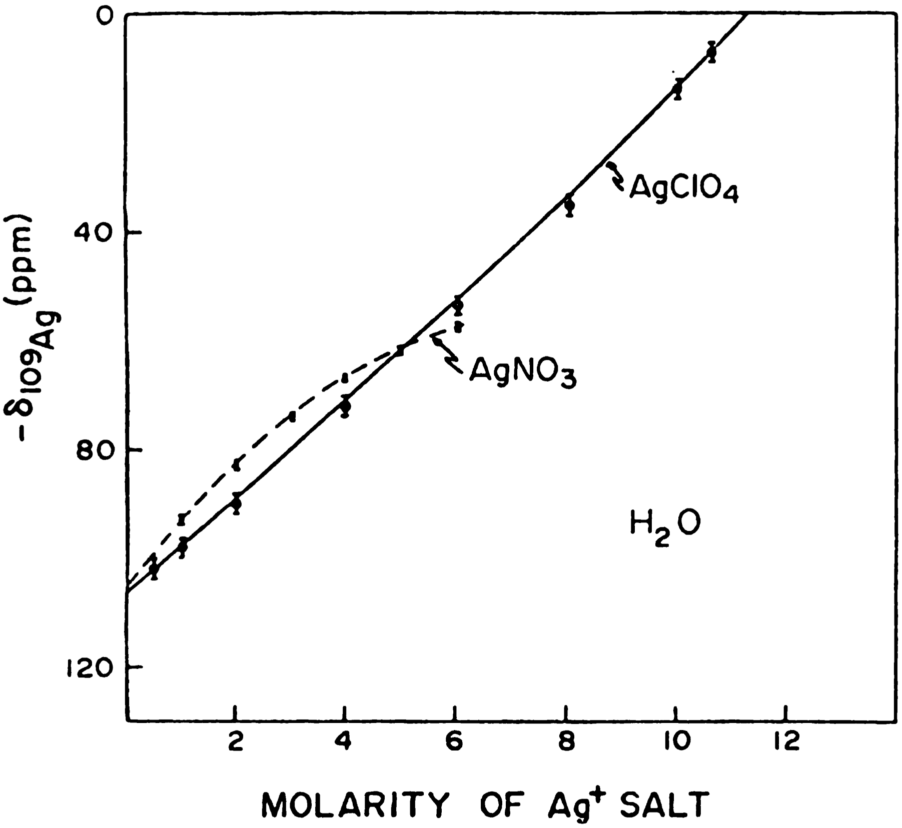


Figure 4. Silver-109 chemical shifts of silver salts in water.

chemical shift of free solvated Ag^+ ion in aqueous solutions, it is possible to assume that the upfield shift with increasing concentration is due to increasing cation-anion interaction and ion pair formation. This assumption is also in accord with the conclusion proposed by Lee and Wilmshurst from their Raman studies on aqueous silver nitrate solution.[88]

The silver-109 chemical shift was also studied in several nonaqueous solvents. The results for acetonitrile solutions of silver nitrate is presented in Table VII. The variation of the chemical shift as a function of concentration is shown in Figure 5. There again an upfield linear shift was observed with increasing concentration as was observed with silver perchlorate in aqueous solution. In this case, the ^{109}Ag chemical shift for the solvated Ag^+ ion is considerably further downfield than in the case of water (chemical shift of $\sim$-440 ppm <u>vs</u> -100 ppm) and also the variation of the chemical shift with concentration covers a much larger range in acetonitrile than in water. These data indicate that in these solutions strong interactions exist between the cation and the solvent as well as the cation and the anion. This observation is in accordance with the conclusion of Janz <u>et al</u>.[89,90] that in these solutions complexes $Ag(NCCH_3)_2^+$ and $Ag(NCCH_3)^+$ are formed and there is an equilibrium between contact ion pairs and these complexes. They arrived at this conclusion from the results of their ir, Raman, and

Table VII. Silver-109 NMR Data for $AgNO_3$ in Acetonitrile.

Conc. of $AgNO_3$, M	δppm
0.5	-429.6
1.0	-412.8
2.0	-397.2
3.0	-379.4
4.0	-362.5
5.0	-341.5
6.0	-317.0

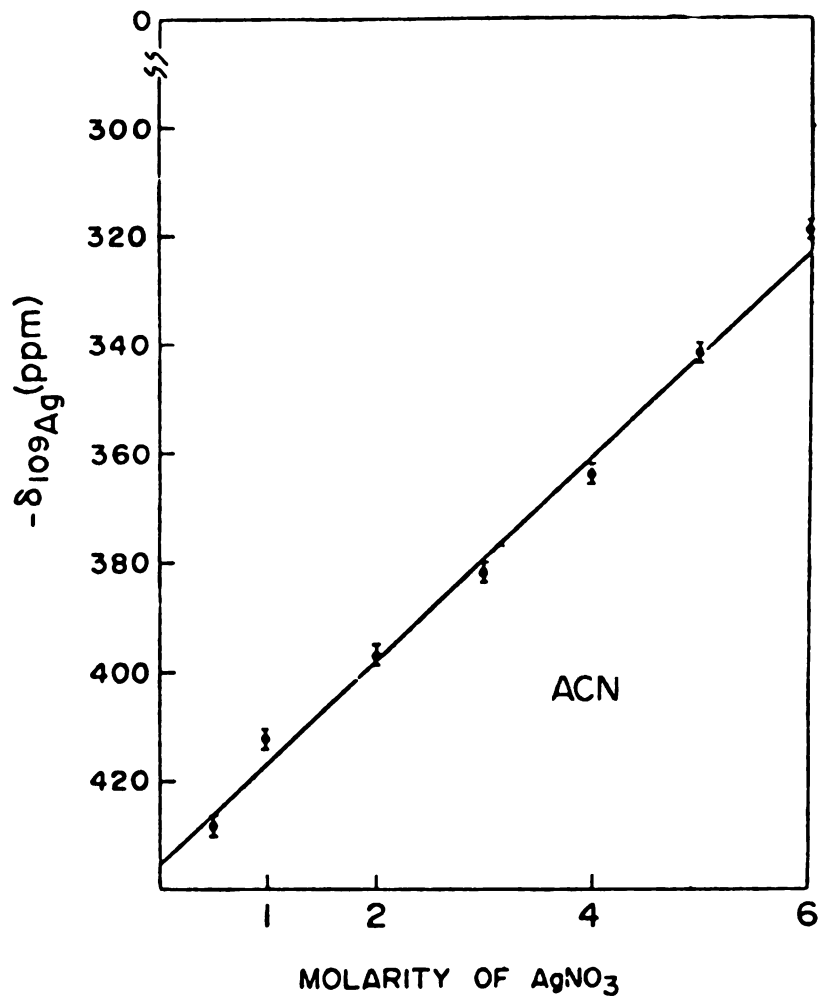


Figure 5. Silver-109 chemical shift of silver nitrate in acetonitrile.

nmr spectroscopic studies on this system.

The experiment could not be repeated with $AgClO_4$ due to low solubility of the salt in acetonitrile ($\leq$ 1 M).

Other solvents of interest, propylene carbonate, acetone, tetrahydrofuran, dimethylsulfoxide, dimethylformamide, acetonitrile, and pyridine were chosen for ^{109}Ag nmr studies since 1 M solution of $AgClO_4$ could be made for ^{109}Ag nmr studies, and the solutions were stable over a long period of time. Concentration studies were not possible because of low solubility of $AgClO_4$ ($\sim$1 M) and low level concentration, 0.5 M detection limit of ^{109}Ag for the instrument. Silver nitrate could not be tried because of low solubility of this salt in the above solvents. For concentration levels in these solvents with which experimental work was possible, ^{109}Ag chemical shifts were obtained. The results are shown in Table VIII, as are the donor numbers of the solvents used.

The data from this study indicate that the extent of low field shift is larger for solvent with higher donor number which is understandable since these solvents have higher ability to interact with Ag^+ ion and decrease the interaction of perchlorate ion with Ag^+ ion. The low field shift is largest for pyridine and acetonitrile is next lowest even though acetonitrile has the lowest donor number. This observation might be explained in terms of presence of π-bonding in these cases in addition to the σ-bonding which is present in the case of other solvents.[62,63]

Table VIII. ^{109}Ag NMR Data for 1 M $AgClO_4$ in Different Solvents

Solvent	Donor Number	δ(ppm)
PC	15.1	+ 5
AC	17.0	- 61
THF	20.0	- 41
CH_3OH	25.7	- 55
DMF	26.6	-130
DMSO	29.8	-258
CH_3CN	14.1	-529
PY	33.1	-556

The variation of ^{109}Ag chemical shift for 2M AgNO$_3$ in water-acetonitrile mixtures of varying composition was also studied as a function of solvent composition. The data are presented in Table IX. From the curvature of the plot of chemical shift vs mole fraction of acetonitrile as shown in Figure 6, it is obvious that the changes in chemical shift are large even in solvent mixtures with low mole fractions of acetonitrile. This behavior indicates that the interaction of acetonitrile with silver(I) ion is strong. The isosolvation point occurs at 0.075 mole fraction of acetonitrile which indicates a strong preferential solvation by this solvent. Similar behavior was observed in studies in which transference, conductance, and potentiometric measurements were made.[91] From the results of these studies selective solvation of Ag$^+$ ion with acetonitrile and preferential accumulation of water in the environment of the nitrate ion was concluded. It is interesting, however, that the plot is not monotonic but shows a definite and reproducible minimum at ∿0.6 mole fraction of acetonitrile. Maciel et al.[92] observed the same behavior and the minimum in the curve can be explained as follows: Upon initial addition of acetonitrile to the aqueous solution of AgNO$_3$, the silver ion interacts with the organic solvent while the nitrate ion remains hydrated, as a result the ^{109}Ag resonance shifts to lower field. At the mole fraction at which the minimum occurs,

Table IX. ^{109}Ag NMR Data for $AgNO_3$ 2 M in Water-acetonitrile Solutions.

M_{CH_3CN}/M_{H_2O}	δ(ppm)
0.000	- 82.2
0.018	-139.0
0.037	-197.2
0.079	-277.8
0.128	-330.5
0.187	-364.9
0.257	-385.6
0.341	-404.0
0.447	-414.5
0.587	-418.9
0.757	-414.3
0.970	-396.4

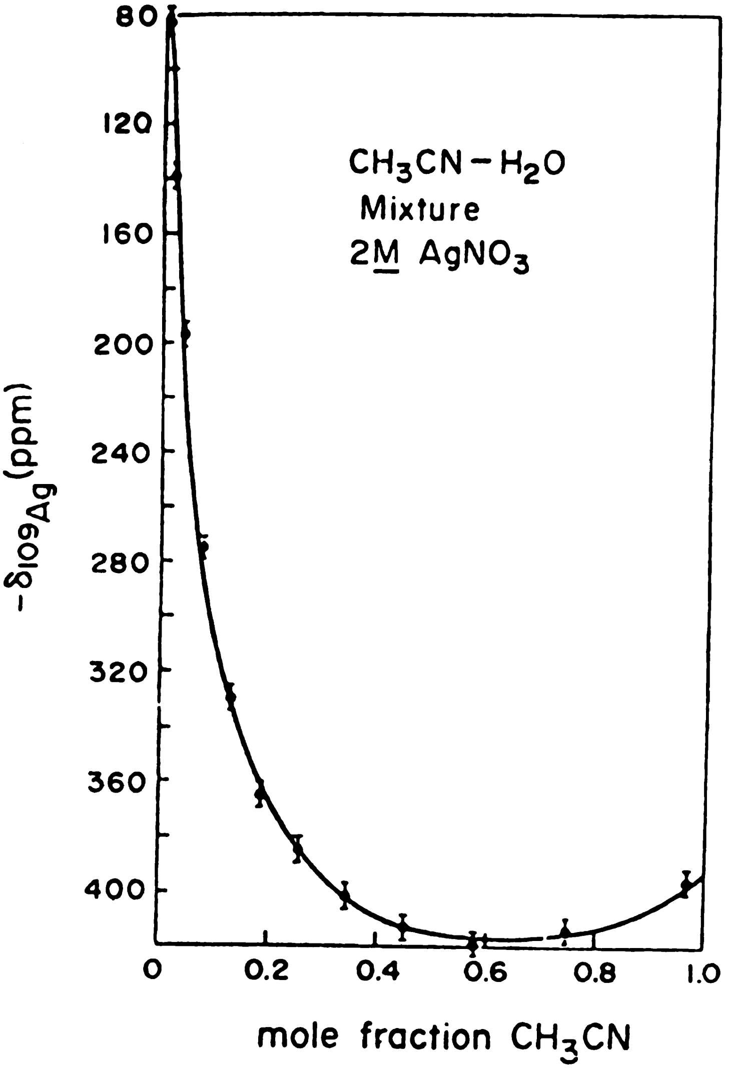


Figure 6. Variation of the chemical shifts of the silver-109 resonance as a function of solvent composition for binary solvent, water and acetonitrile.

NO_3^- is still hydrated but at higher mole ratio, the hydration sphere of NO_3^- ion is removed and since NO_3^- is poorly solvated by acetonitrile, the interaction between Ag^+ with NO_3^- increases and the shift toward higher field occurs.

In all solutions used in ^{109}Ag nmr studies, only a single nmr line was observed, because the rate of exchange of species interacting with Ag^+ ion is fast, therefore, the observed resonance signal corresponds to the population average of all the Ag-species present in the solutions.

2. A Proton NMR Study of Solutions of $AgNO_3$ in Water, Acetonitrile and Their Mixtures

The variation of $^1H(CH_3CH)$ chemical shift as a function of $AgNO_3$ mole fraction was measured in solutions of $AgNO_3$ in acetonitrile. The measurements were made with two instruments, T60 and Varian 56-60. The results from the two sets of measurements are in good agreement. The chemical shifts are referred to TMS resonance. The data are presented in Table X, and a plot of chemical shift vs mole fraction of $AgNO_3$ is shown in Figure 7. From the data, it becomes apparent that as the mole fraction of salt increases from 0.026 to 0.30 the chemical shift moved downfield by 13±3 Hz. For the same change in mole fractions, Janz[89] observed 28 Hz and Schneider[91] 10 Hz downfield shift in the ^1H chemical shift. The observed downfield

Table X. Proton-1 NMR Data for Solutions of $AgNO_3$ in Acetonitrile

Conc. M	Mole Fraction of Ag^+	Chemical Shift-Line Width[a] (by T60)		Chemical Shift-Line Width[b] (by Varian 56-60)	
0.0	0.000	0.0 Hz	1.0 Hz	0.0 Hz	1.5 Hz
0.5	0.026	3.0	1.0	2.0	2.5
1.0	0.052	4.5	1.0	4.0	2.0
2.0	0.101	7.0	1.5	7.5	2.0
3.0	0.150	9.5	1.5	9.5	2.0
4.0	0.198	13.5	1.5	14.0	2.0
5.0	0.244	15.0	1.5	15.0	2.0
6.0	0.290	15.5	1.5	18.0	2.5
7.0	0.301	16.5	2.0	18.5	2.0

[a,b] Chemical shifts were first referred to TMS and then further related to the chemical shift of pure CH_3CN (neat solvent).

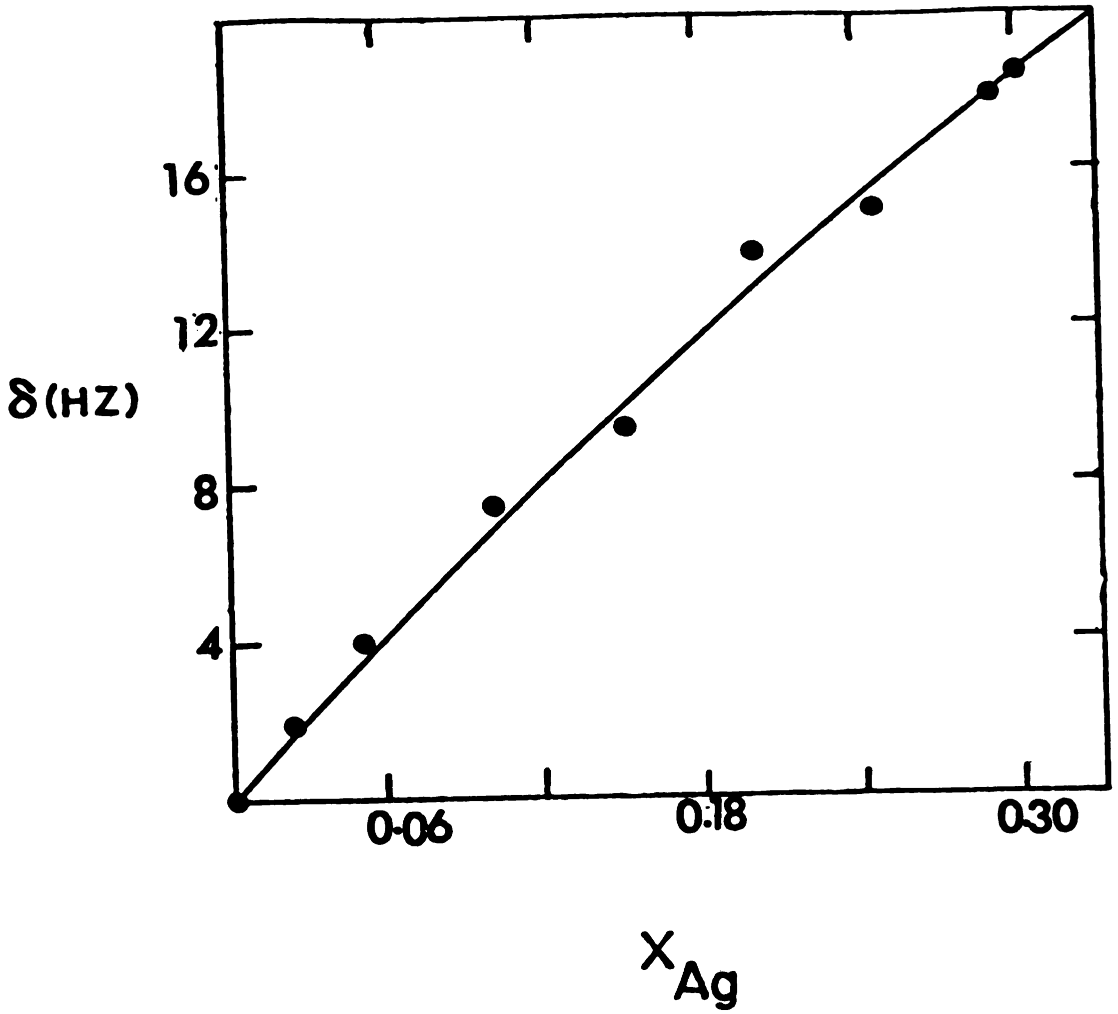


Figure 7. Proton-1 chemical shifts (CH_3CN) as a function of mole fraction of $AgNO_3$ in acetonitrile solutions of $AgNO_3$.

shift on addition of the salt to the solution indicates that as the concentration increases there is a decrease of electron density around hydrogen atoms which might be due to the complexation of more acetonitrile with Ag^+ ion. In all solutions only one resonance line was observed due to fast exchange of molecules.

The same experiment was repeated in H_2O as a solvent. The results are presented in Table XI and Figure 8. Chemical shifts are referred to DSS (page 52) resonance since TMS is not very soluble in H_2O. As the mole fraction of the salt was increased, almost no systematic change in the $^1H(H_2O)$ resonance was observed which may be due to a weaker interaction of H_2O with Ag^+ ion than with that of CH_3CN.

The variations of $^1H(CH_3CN)$ and $^1H(H_2O)$ resonances as a function of mole fraction of either solvents were also measured in solution of constant concentration of $AgNO_3$, [2 M], and different composition of the two solvents. For comparison the ^1H nmr studies were conducted in solution with different composition in the absence of Ag^+ salt. Data are presented in Table XII and XIII. The plots of chemical shift vs concentration for different cases are shown in Figures 9 and 10.

The results indicate that in the absence of Ag^+ ion, as the mole fraction of H_2O increases there is a downfield shift of $^1H(CH_3CN)$ resonance which might be due to the interaction of the hydrogen atom of H_2O with nitrogen atom of acetonitrile which causes deshielding of acetonitrile.

Table XI. Proton-1 NMR Data for Aqueous Solution of $AgNO_3$.

Concentration of Salt, M	Chemical Shift[a] Hz	Line Width Hz
5	278	4.5
4	279	3.0
2	279	2.0
1	279	1.2
0	276	1.0

[a] Chemical shifts are referred to DSS.

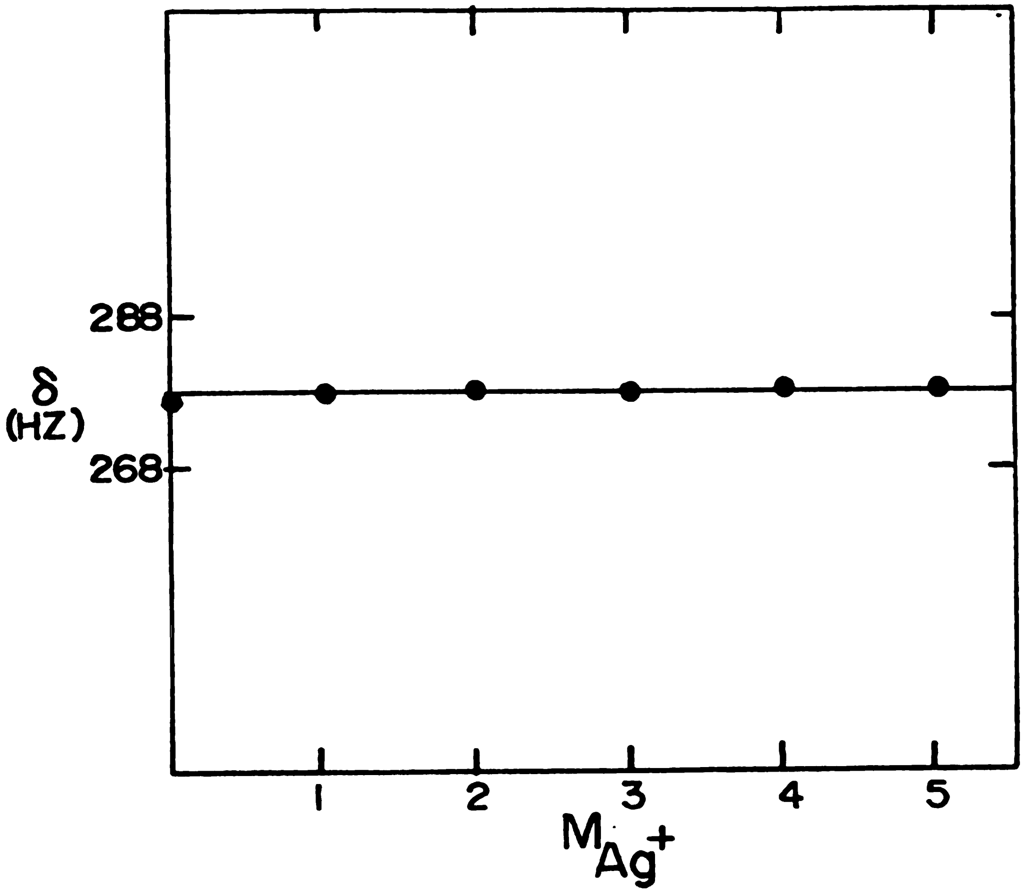


Figure 8. Proton-1 chemical shifts (^1H_2O) as a function of $AgNO_3$ concentration in water.

Table XII. Proton-1 NMR Data in Acetonitrile-water Mixtures.

X_{CH_3CN}	X_{H_2O}	Chemical Shift (Hz) $^1H(CH_3CN)$	Chemical Shift (Hz) $^1H(H_2O)$
0.000	1.000	---	290
0.018	0.982	138	290
0.079	0.921	131	274
0.257	0.743	122	246
0.450	0.550	121	229
0.580	0.420	120	211
0.756	0.244	117	198
0.870	0.130	118	177
1.000	0.000	117	---

Table XIII. Proton-1 NMR Data of Solutions of $AgNO_3$ in Acetonitrile-Water Mixtures.

X_{CH_3CN}	X_{H_2O}	Chemical Shift (Hz) $^1H(CH_3CN)$	Chemical Shift (Hz) $^1H(H_2O)$
0.000	1.000	---	290
0.018	0.982	141	286
0.079	0.921	137	284
0.257	0.743	128	254
0.450	0.550	128	236
0.580	0.420	127	222
0.756	0.244	126	219
0.870	0.130	125	217
1.000	0.000	125	---

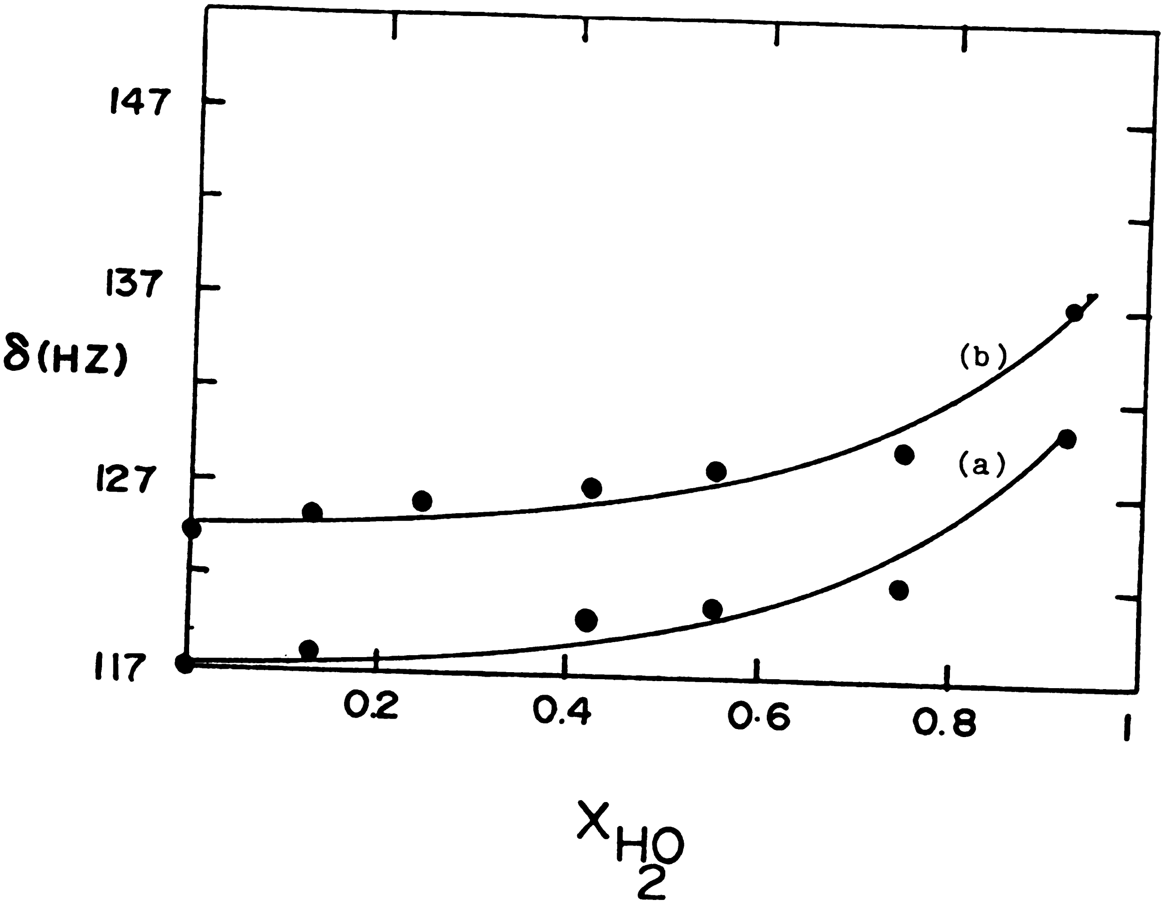


Figure 9. Proton-1 chemical shifts (CH_3CN) as a function of water mole fraction in water-acetonitrile mixtures (a) in the absence and (b) presence of the $AgNO_3$.

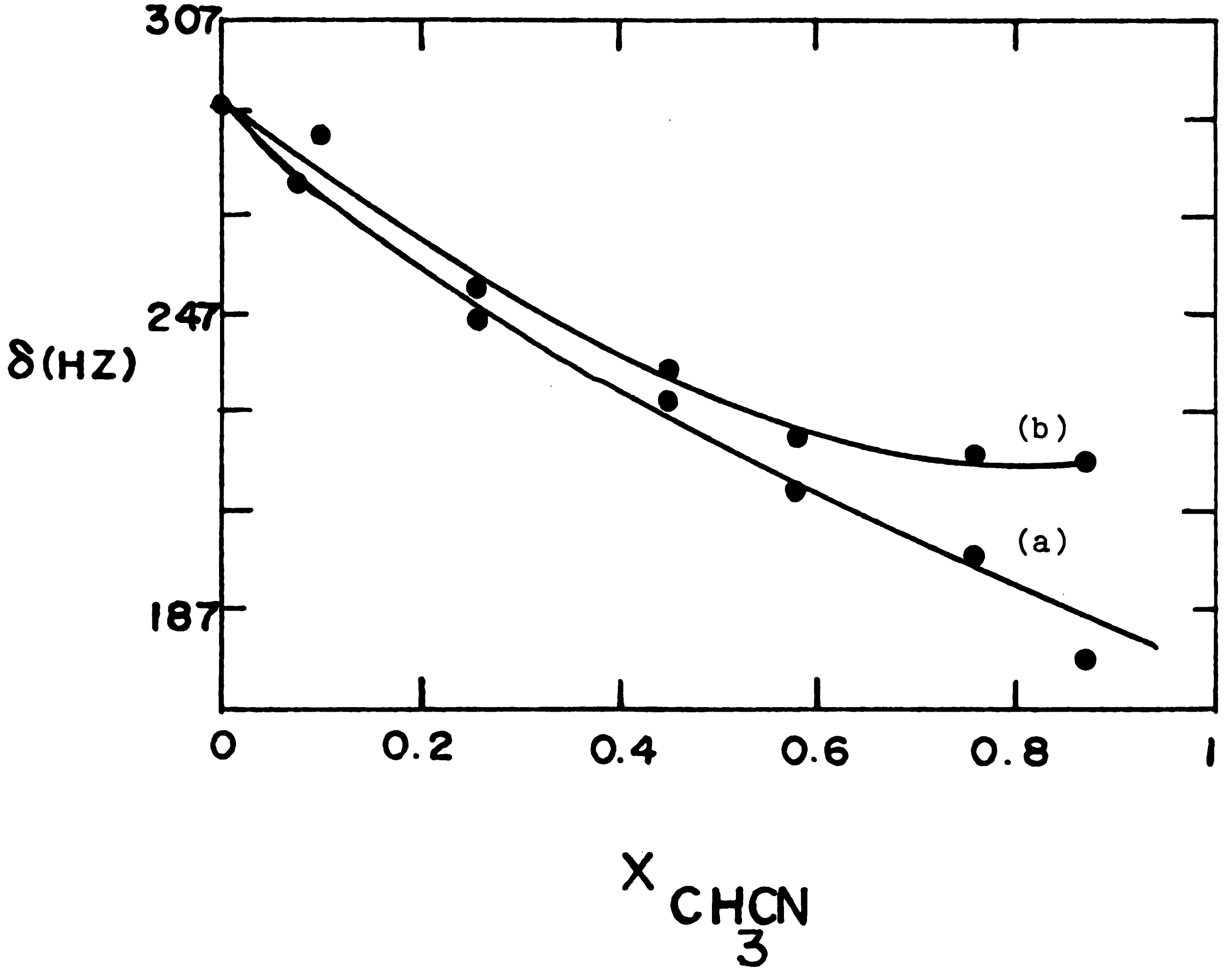


Figure 10. Proton-1 chemical shifts (H_2O) as a function of acetonitrile mole fraction in acetonitrile-water mixtures (a) in the absence and (b) presence of the $AgNO_3$.

When the $AgNO_3$ is present, the same phenomenon is taking place but in addition there is also a downfield shift caused by interaction of Ag^+ ion with the nitrogen atoms. For $^1H(H_2O)$ in the absence of the salt there is an upfield shift of $^1H(H_2O)$ resonance when the mole fraction of acetonitrile is increased. This shielding of proton might be due to interaction of hydrogen atom with nitrogen atom of acetonitrile. This shielding is less when the salt is present in the mixture which indicate due to complexation of acetonitrile with Ag^+ ion, less acetonitrile molecules are present to interact with H_2O. At high mole fraction of acetonitrile all water molecules contribute in the interaction with acetonitrile and the $^1H(H_2O)$ chemical shift remains constant. Schneider[91] has done similar studies in these systems. He explained the downfield shift of $^1H(CH_3CN)$ resonance to the formation of $[Ag(CH_3CN)_2]^+$, complex and the upfield shift of $^1H(H_2O)$ resonance on the addition of acetonitrile to the ruptures of the hydrogen bonds between water molecules. This effect was not as great when the silver salt was present.

3. A Carbon-13 NMR Study of Solutions of $AgNO_3$ in CH_3CN and CH_3CN-H_2O Mixtures

The variation of the ^{13}C chemical shift as a function of $AgNO_3$ concentration in acetonitrile solutions was measured. The results are presented in Table XIV. The

Table XIV. Carbon-13 Data of Solutions of $AgNO_3$ in Acetonitrile

Conc. of $AgNO_3$, M	Chemical Shift ($-^{13}CN$) ppm	Chemical Shift ($-^{13}CH_3$) ppm
0.0	117.89	1.34
0.1	117.97	1.38
0.2	118.06	1.40
0.5	118.27	1.47
0.7	118.42	1.52
1.0	118.64	1.57
2.0	119.30	1.79
3.0	119.91	1.97
4.0	120.45	2.06
5.0	121.01	2.25
6.0	121.49	2.34
7.0	121.80	2.49

plot of chemical shift vs concentration is shown in Figure 11. For both carbon atoms: $-{}^{13}CH_3$ and ${}^{13}CN$ a downfield shift was observed as the concentration of salt was increased. The extent of shift was more for the $-{}^{13}CN$ than the $-CH_3$. These results are not unexpected since acetonitrile is known to interact with the Ag^+ ion through the nitrogen atoms.

The ${}^{13}C$ chemical shifts were also measured for solutions of $AgNO_3$ in acetonitrile-water mixtures. The results are presented in Table XV. The variation of chemical shift vs mole fraction of water for both acetonitrile carbons is shown in Figure 12. The data indicate that as the mole fraction of water is increased a low field shift of both carbons is observed. The extent of shift is larger for $-{}^{13}CN$ than $-{}^{13}CH_3$. This low field shift was also observed for protons in acetonitrile and as it was explained it is due to interaction of water with acetonitrile through nitrogen atoms.

If one compares the results from three different techniques: ${}^{1}H$, ${}^{13}C$, ${}^{109}Ag$ nmr, it is obvious that the ${}^{109}Ag$ has the largest chemical shift range. a) For the concentration range of 1 to 6 M for solutions of $AgNO_3$ in acetonitrile, the change in the chemical shift of: ${}^{1}H(-CH_3)$ is $\sim$0.2 ppm, ${}^{13}C(-CH_3)$ is $\sim$0.77 ppm, ${}^{13}C(-CH_3)$ is $\sim$0.77 ppm, ${}^{13}C(-CN)$ is $\sim$2.85 ppm and for ${}^{109}Ag(AgNO_3)$ is $\sim$96 ppm. b) For the concentration range of 1 to 5 M of $AgNO_3$ in aqueous solutions, the change in the chemical shift

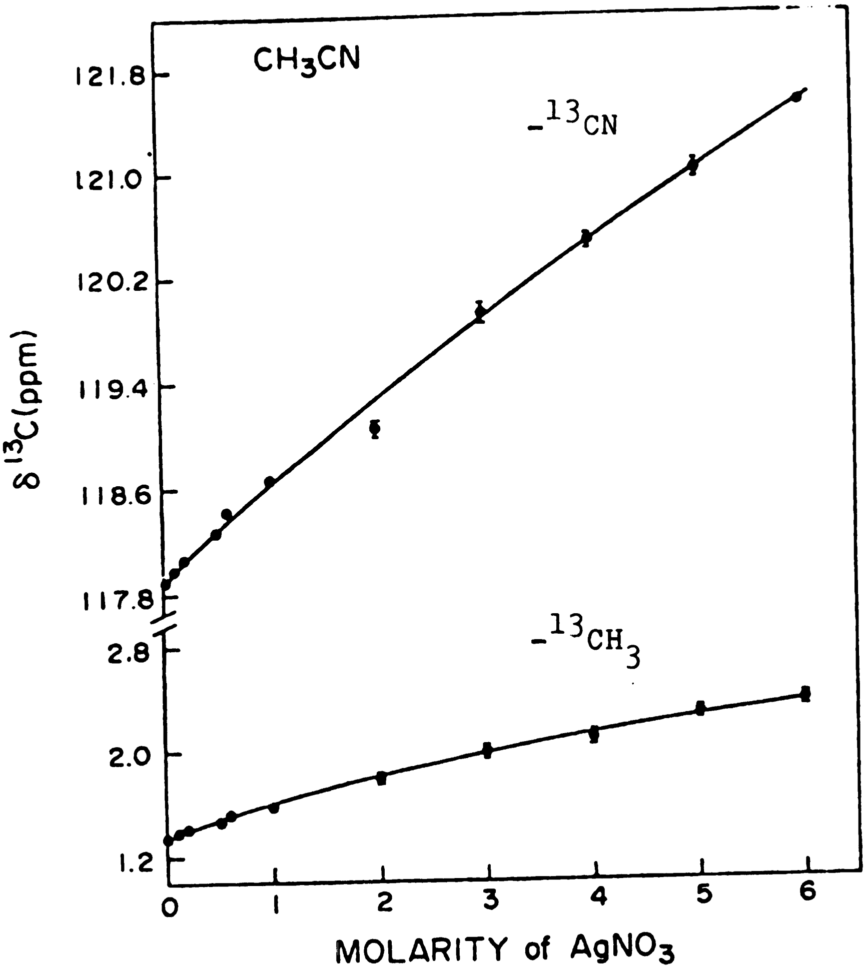


Figure 11. Carbon-13 chemical shifts as a function of silver nitrate concentration.

Table XV. Carbon-13 Data of Solutions of $AgNO_3$ in Acetonitrile-water Mixtures.

X_{H_2O}	X_{CH_3CN}	Chemical Shift $-^{13}CN$	Chemical Shift $-^{13}CH_3$
0.000	1.000	119.28	1.81
0.130	0.870	119.48	1.84
0.244	0.756	119.70	1.87
0.420	0.580	120.08	1.96
0.550	0.450	120.33	2.03
0.743	0.257	120.83	2.16
0.921	0.079	121.45	2.35
0.982	0.018	121.67	2.39

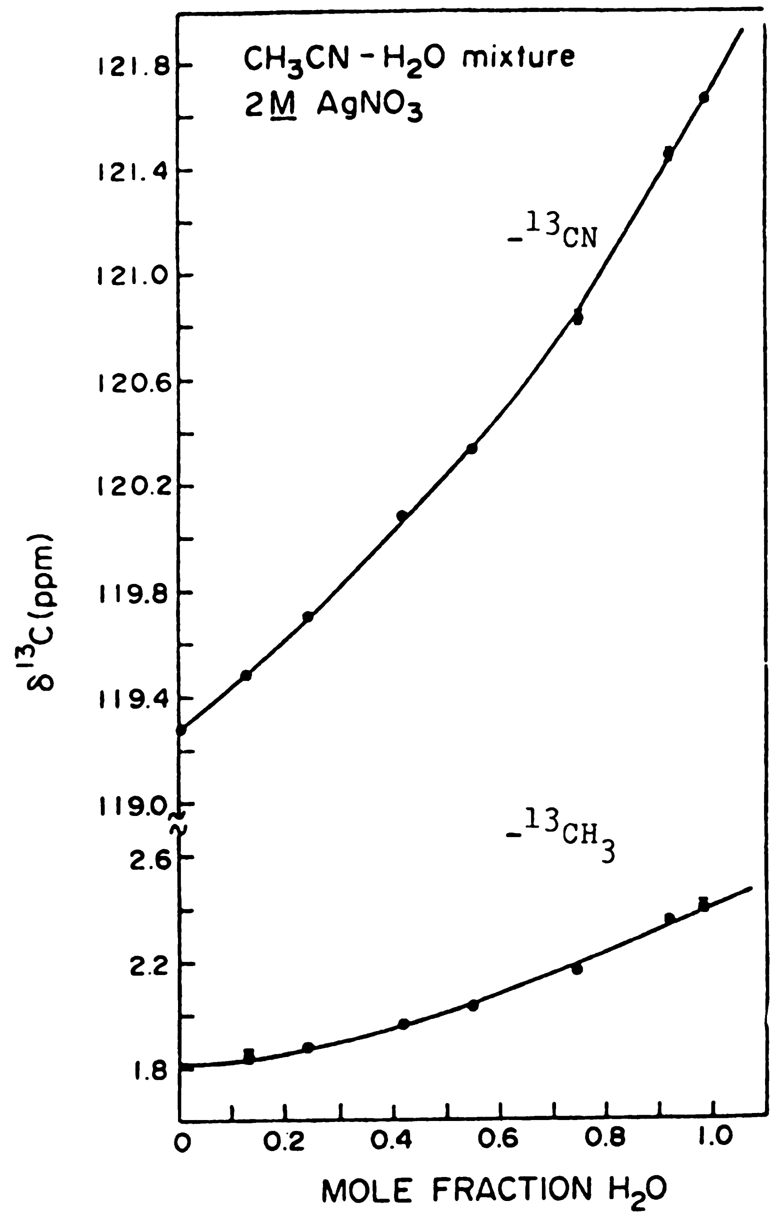


Figure 12. Carbon-13 chemical shift as a function of water mole fraction in mixtures of water-acetonitrile.

of: $^{1}H(H_2O)$ is ∿0.0 ppm and $^{109}Ag(AgNO_3)$ is ∿30 ppm.
c) For solutions of $AgNO_3$ in a mixture of acetonitrile-water, the change of the chemical shift for mole fraction change of acetonitrile from 0 to 1 are for: $^{1}H(-CH_3)$ ∿0.26 ppm, for $^{13}C(-CH_3)$ 0.58 ppm, for $^{13}C(-CN)$ ∿2.39 ppm and for $^{109}Ag(AgNO_3)$ ∿300 ppm..

B. NMR Studies of Ag(I) Complexes in Solution

1. A ^{109}Ag nmr Study of the Complexation Reaction of Ag^+ Ion with Benzene and Toluene

Silver-109 nmr spectra were obtained in a series of solutions of 1 M $AgClO_4$ with varying mole ratios of ligand to the metal ion in different solvents. Benzene and toluene were used as the ligands. Complexation reactions were studied in propylene carbonate, dimethylformamide, dimethyl sulfoxide, acetone, methanol and pyridine solutions. These solvents were preferred because they dissolve Ag^+ salts, they are miscible with benzene and toluene, dissolve the doping agent, and the solutions in these solvents are stable.

The data are presented in Tables XVI and XVII and plots of chemical shift as a function of mole ratio of ligand to metal are shown in Figures 13-19.

The data indicate that as the mole ratio of ligand to metal ion increases in the solutions, the ^{109}Ag resonance

Table XVI. ^{109}Ag Chemical Shift as a Function of Benzene/ $AgClO_4$ Mole Ratio in Various Solvents.

PC		AC	
$[\mathrm{Bz}]/[\mathrm{Ag}^+]$[a]	δppm	$[\mathrm{Bz}]/[\mathrm{Ag}^+]$[b]	δppm
0	+ 5.2	0	- 61.3
1/10	- 7.0	1/10	- 59.5
1/7	- 8.5	1/1	- 91.4
1/3	- 40.2	2/1[c]	-129.4
1/2	- 57.2	3/1	-165.3
1/1.5	- 78.7	5/1	-218.2
1/1	-127.5	7/1	-282.2
2/1	-205.5	8/1	-303.3
3/1	-262.5	9/1	-341.1
4/1	-289.5	10/1	-369.1
5/1	-323.2		
6/1	-340.2		
7/1	-352.4		
8/1	-366.5		
9/1	-375.3		
10/1	-389.1		

Table XVI. Continued.

THF		CH_3OH[d]	
$[Bz]/[Ag^+]$	δppm	$[Bz]/[Ag^+]$	δppm
0	- 14.9	0	- 55.1
1/2	- 31.5	1/10	- 65.6
1/1	- 79.6	1/2	- 97.1
2/1	-113.7	1/1	-146.5
3/1	-152.2	2/1[e]	-188.9
4/1	-191.5	3/1	-244.9
5/1	-233.6	4.22/1	-283.4
7/1	-277.7	5/1	-300.0
8/1	-311.3	7/1	-335.0
9/1	-344.6		
DMSO[f]		DMF[g]	
0	-257.5	0	-130.3
1/2	-256.2	1/2	-136.4
1/1	-256.4	1/1	-143.0
2/1	-255.4	2/1	-154.8
3/1	-251.2	3/1	-178.4
4/1	-249.2	4/1	-195.0
		5/1	-200.3
		6/1	-211.6

Table XVI. Continued.

	PY[h]
[Bz]/[Ag$^+$]	ppm
0	-556.2
1/2	-554.5
1/1	-554.5
2/1	-551.8
3/1	-547.5
4/1	-543.1

[a,b] At mole ratios higher than 10/1, both salt and doping agent were not soluble enough.

[c] Signal could be seen only after 5 h scanning, while for the rest of the samples 1 h was enough.

[d] Above mole ratio of 7, two phases were formed in the solution which might indicate the mixability of benzene in CH_3OH is limited, so chemical shift of ^{109}Ag in these solutions was not measured.

[e] Signal could be seen after 5 h scanning, while for the rest of the samples 1-2 h was enough.

[f] Above mole ratio of 4/1 = Bz/Ag$^+$, the benzene and DMSO were not mixable.

[g] Decomposition took place in all the solutions after a while so the experiments should be done fast in these solutions.

[h] At L/M = 4/1 solution seems to be saturated, so higher mole ratio was not examined.

Table XVII. ^{109}Ag Chemical Shifts and Line Width as a Function of Toluene/AgClO$_4$ Mole Ratio in Different Solvents

PC[a]		AC	
[Tol]/[Ag$^+$]	δppm	[Tol]/[Ag$^+$]	δppm
1/2	-77.0	1/10	-57.7
1/2	-146.0	1/2	-57.7
2/1	-232.6	1/1	-93.6
3/1	-292.1	2/1	-132.9
4/1	-315.7	3/1	-179.3
5/1	-336.2	4/1	-215.1
6/1	-349.8	5/1	-245.0
0	5.0	6/1	-268.5
		7/1	-305.2
CH$_3$OH[b]		THF[c]	
0	-55.5	0/1	-15
1/10	-70.0	1/2	-41
1/2	-117.2	1/1	-78
1/1	-132.0	2/1	-130
2/1	-200.3	3/1	-174
3/1	-257.1	4/1	-214
4/1	-288.5	5/1	-248
5/1	-307.8	6/1	-282
6/1	-325.3		

Table VII. Continued.

DMSO[d]		DMF	
$[\mathrm{Tol}]/[\mathrm{Ag}^+]$[d]	δppm	$[\mathrm{Tol}]/[\mathrm{Ag}^+]$[e]	δppm
0	-257.5	0	-130.3
1/2	-256.0	1/2	-137.0
1/1	-255.8	1/1	-144.0
2/1	-253.6	2/1	-160.9
3/1	-251.8	3/1	-175.4
		4/1	-186.7
		5/1	-204.2

PY	
$[\mathrm{Tol}]/[\mathrm{Ag}^+]$[f]	δppm
0	-556.2
1/2	-552.7
1/1	-552.7
2/1	-548.4

---

[a] At above mole ratio of 6/1 the solubility is not enough (at L/M = 7, solution is not clear), it might be due to low solubility of $AgClO_4$ in toluene.

[b] At mole ratio above 6/1 two phases were formed because of the low mixability of the toluene with CH_3OH.

[c] At mole ratio above 6/1 solution seems saturated.

[d] At mole ratio L/M = 3/1, the toluene and DMSO are not mixable.

[e] At mole ratio of 6/1, two phases were formed.

[f] The solution was saturated at $[\mathrm{Tol}]/[\mathrm{Ag}^+] = 2/1$ and above that precipitation took place.

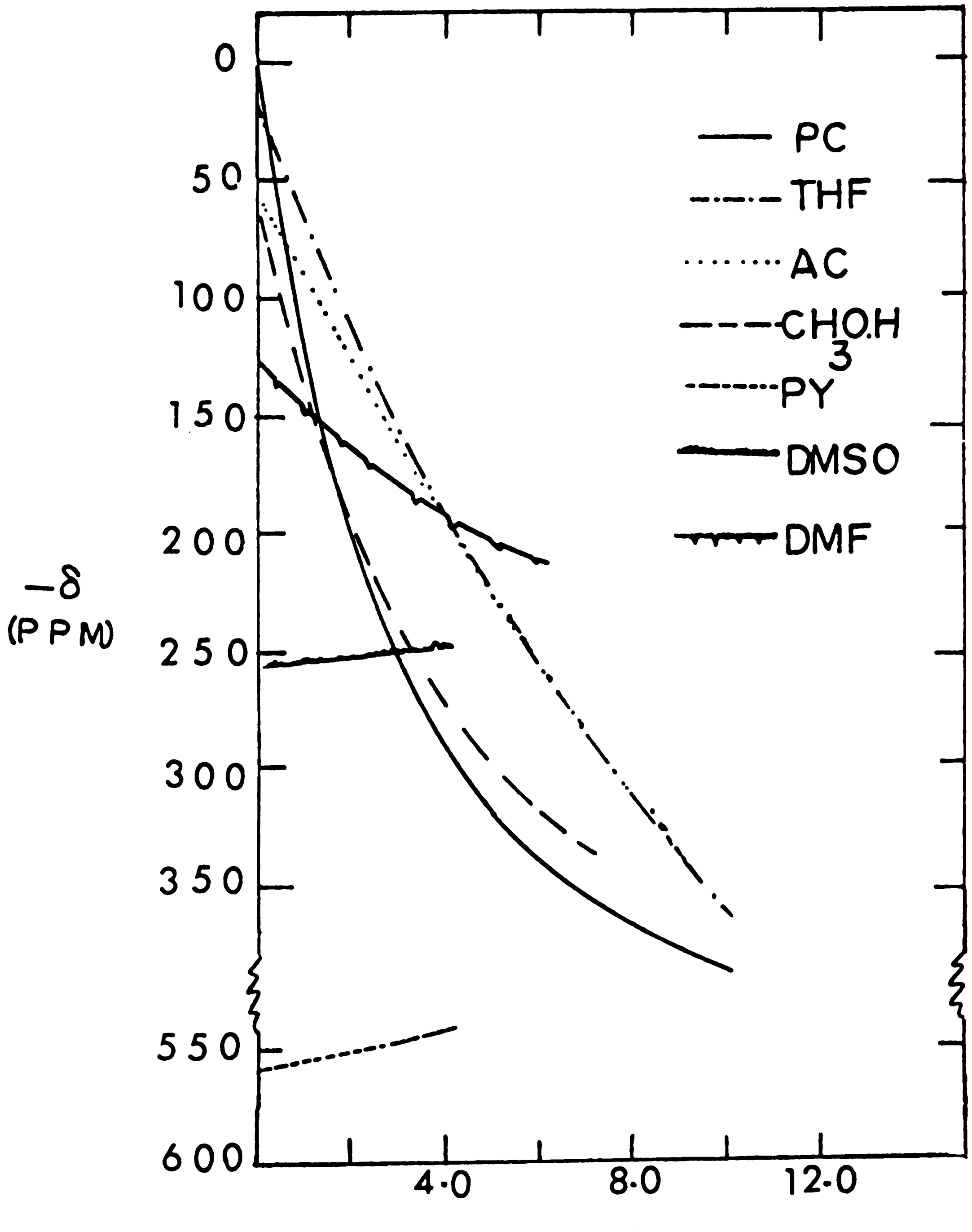


Figure 13. Chemical shifts of ^{109}Ag as a function of benzene/$AgClO_4$ molar ratios in various solvents. (In this plot experimental points are not displayed to prevent crowding. The same plots are shown in the following figures in more detail.)

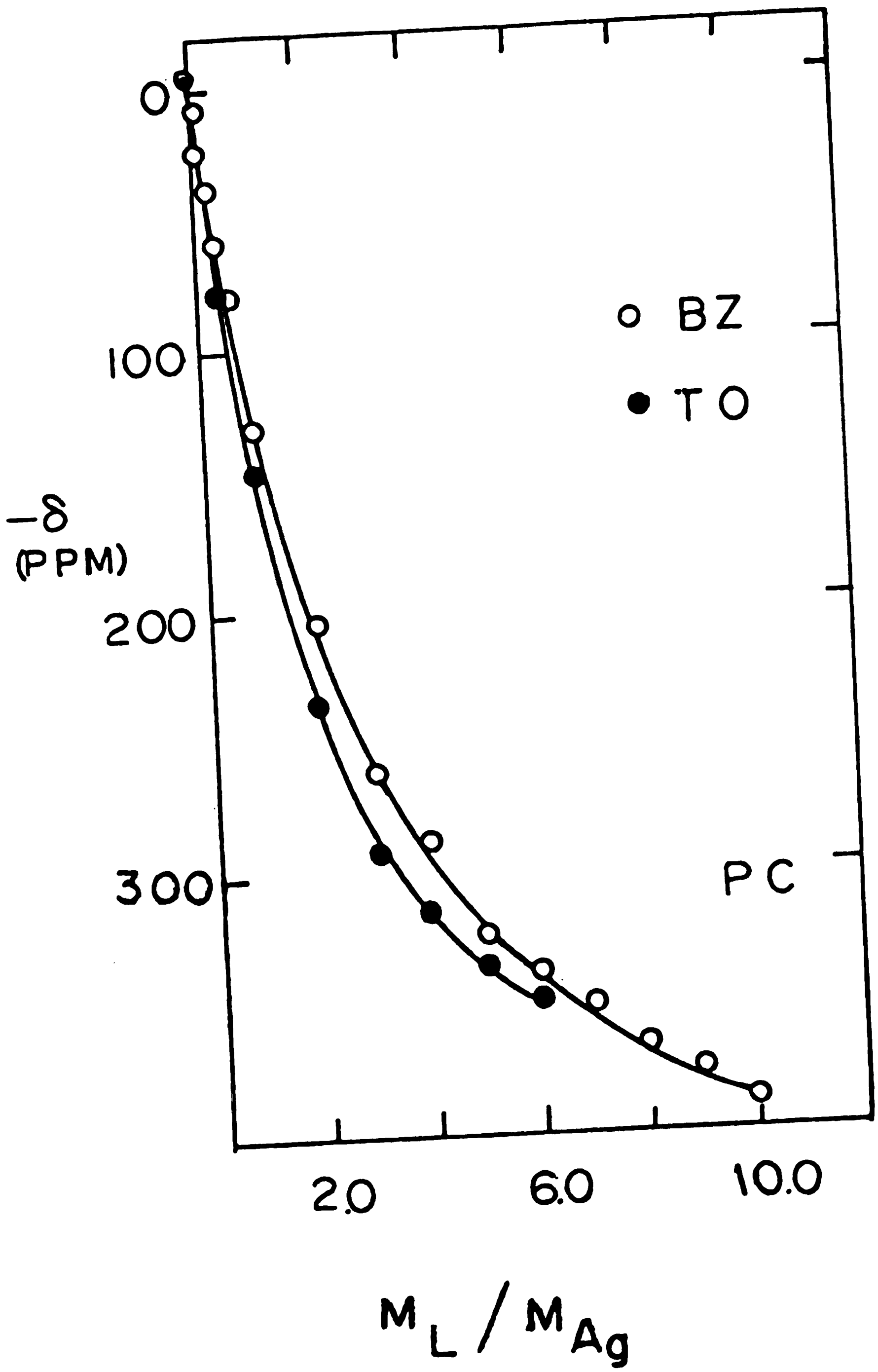


Figure 14. Chemical shifts of ^{109}Ag as a function of ligand/ $AgClO_4$ molar ratio in propylene carbonate. (Ligand either benzene or toluene) (In this figure and following figures with the same point sizes the error range is less than the point sizes used.)

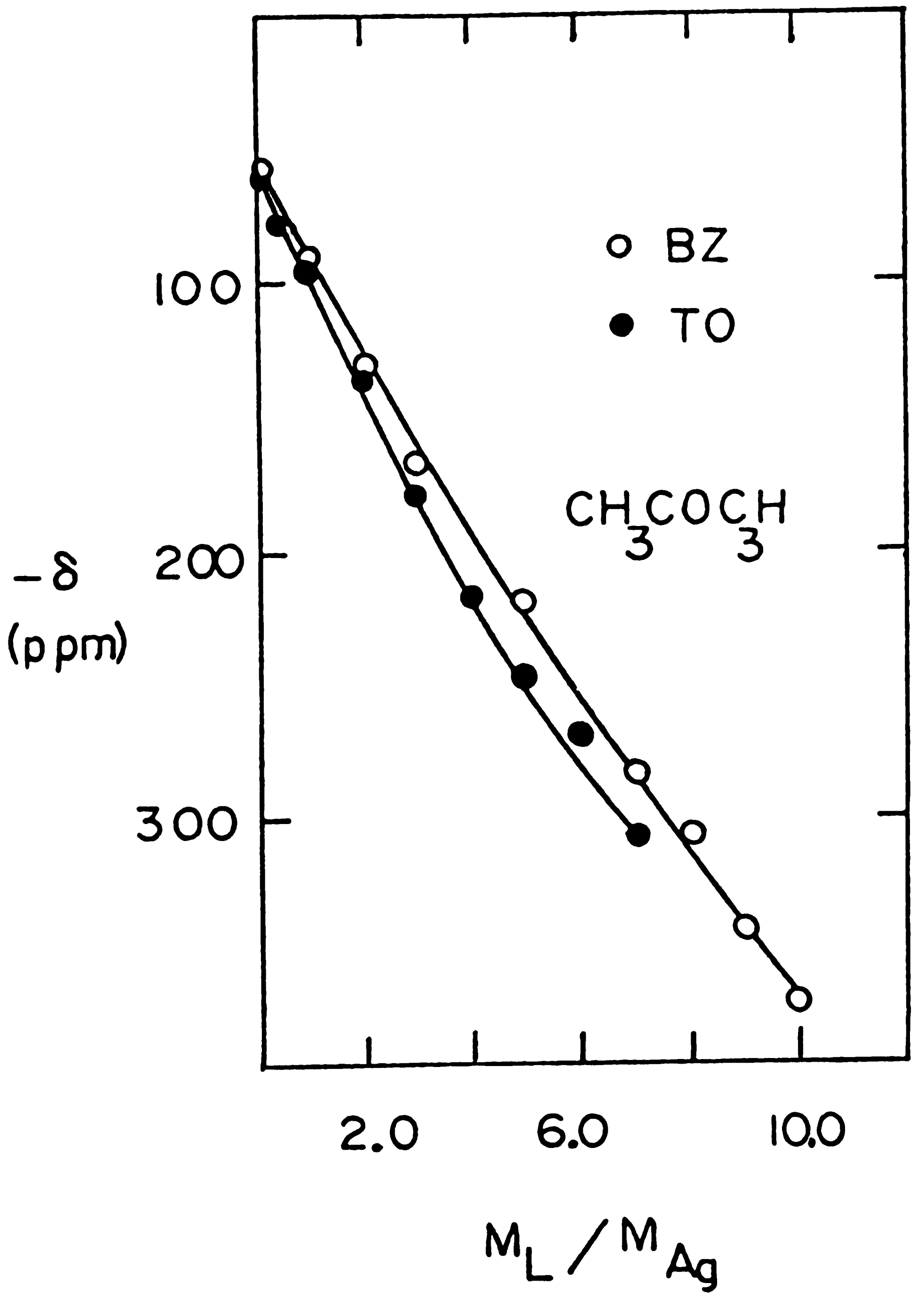


Figure 15. Chemical shifts of ^{109}Ag as a function of ligand/ $AgClO_4$ molar ratio in acetone. (Ligand is either benzene or toluene.)

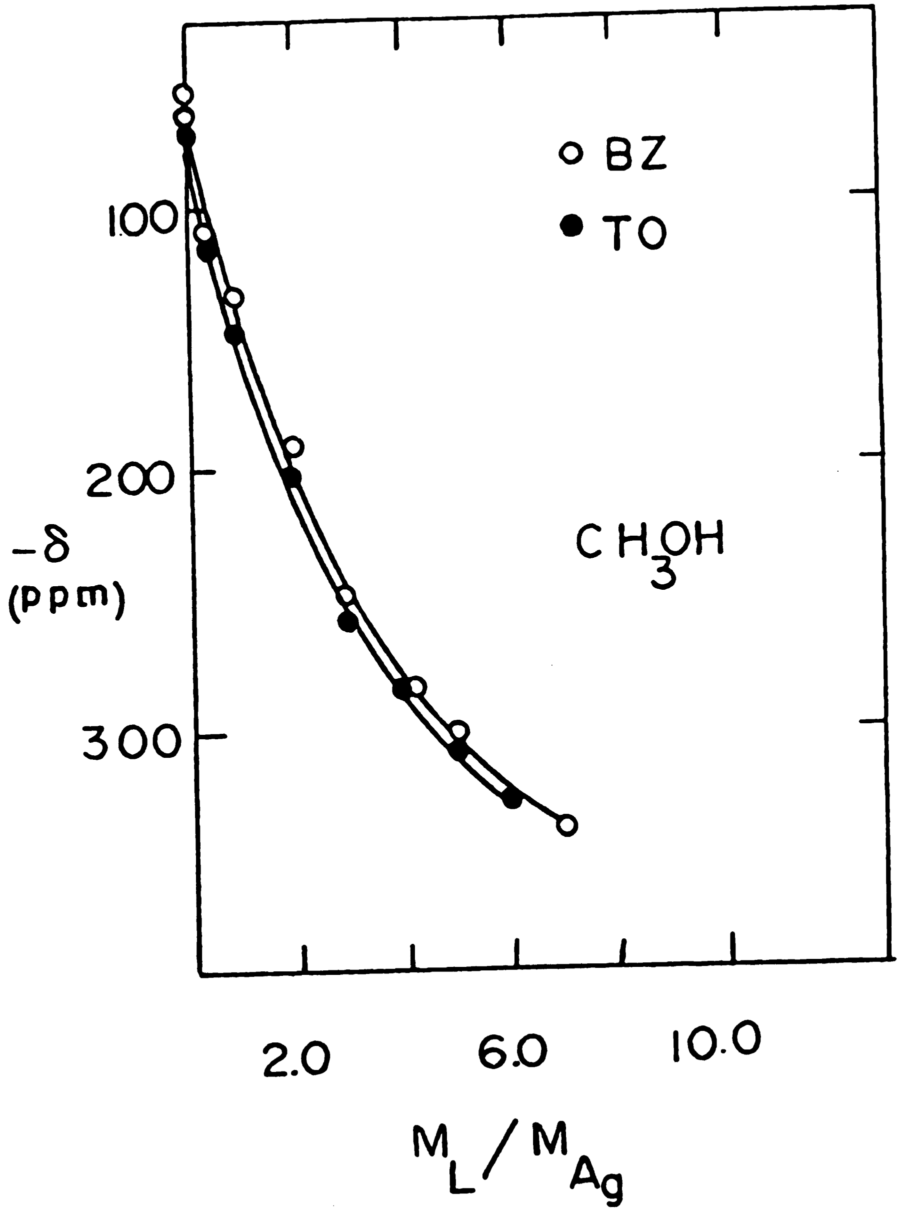


Figure 16. Silver-109 chemical shifts as a function of ligand/$AgClO_4$ molar ratio in methanol. (Ligand is either benzene or toluene.)

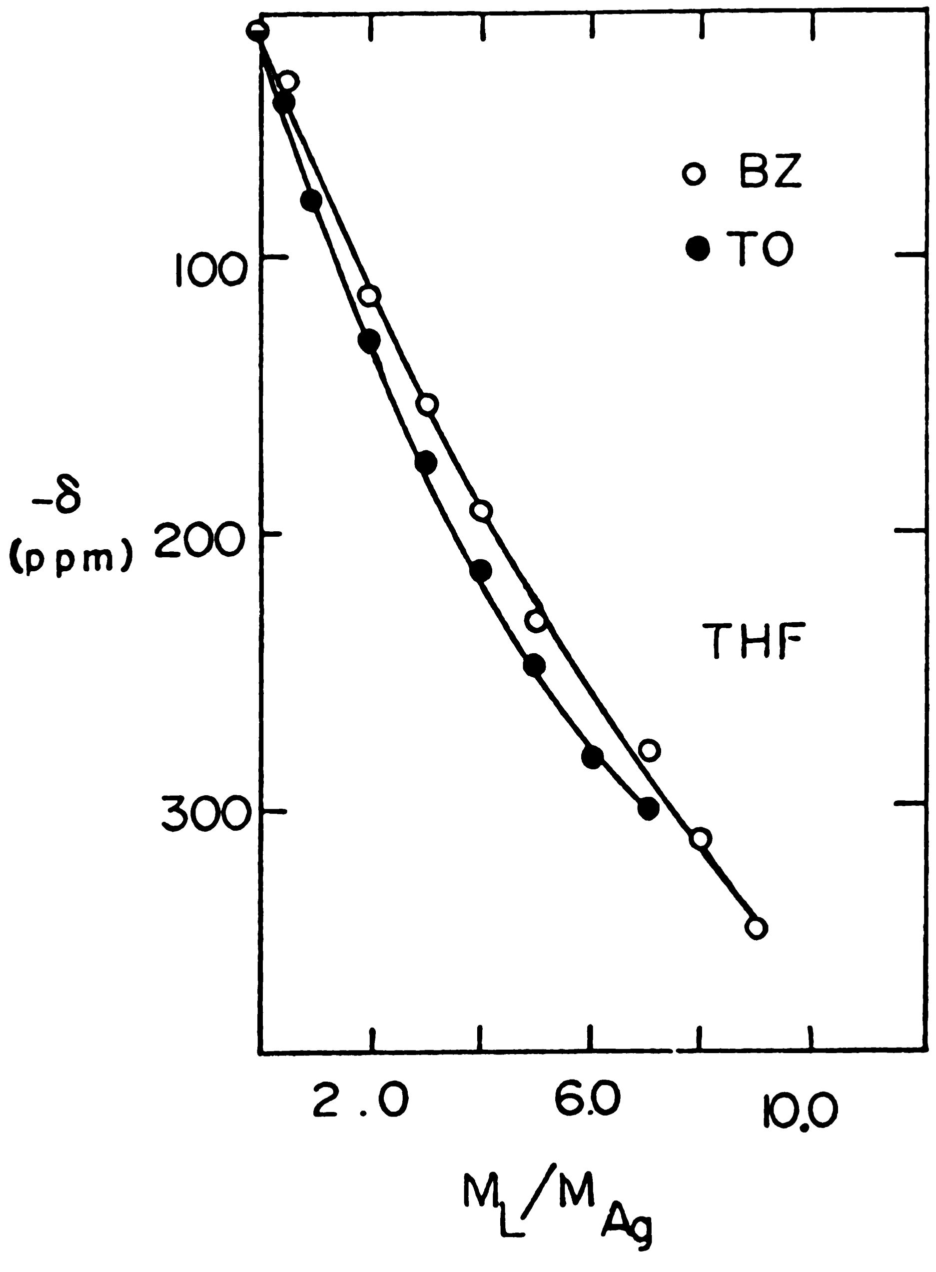


Figure 17. Silver-109 chemical shifts as a function of ligand/$AgClO_4$ molar ratio in tetrahydrofuran. (Ligand is either benzene or toluene.)

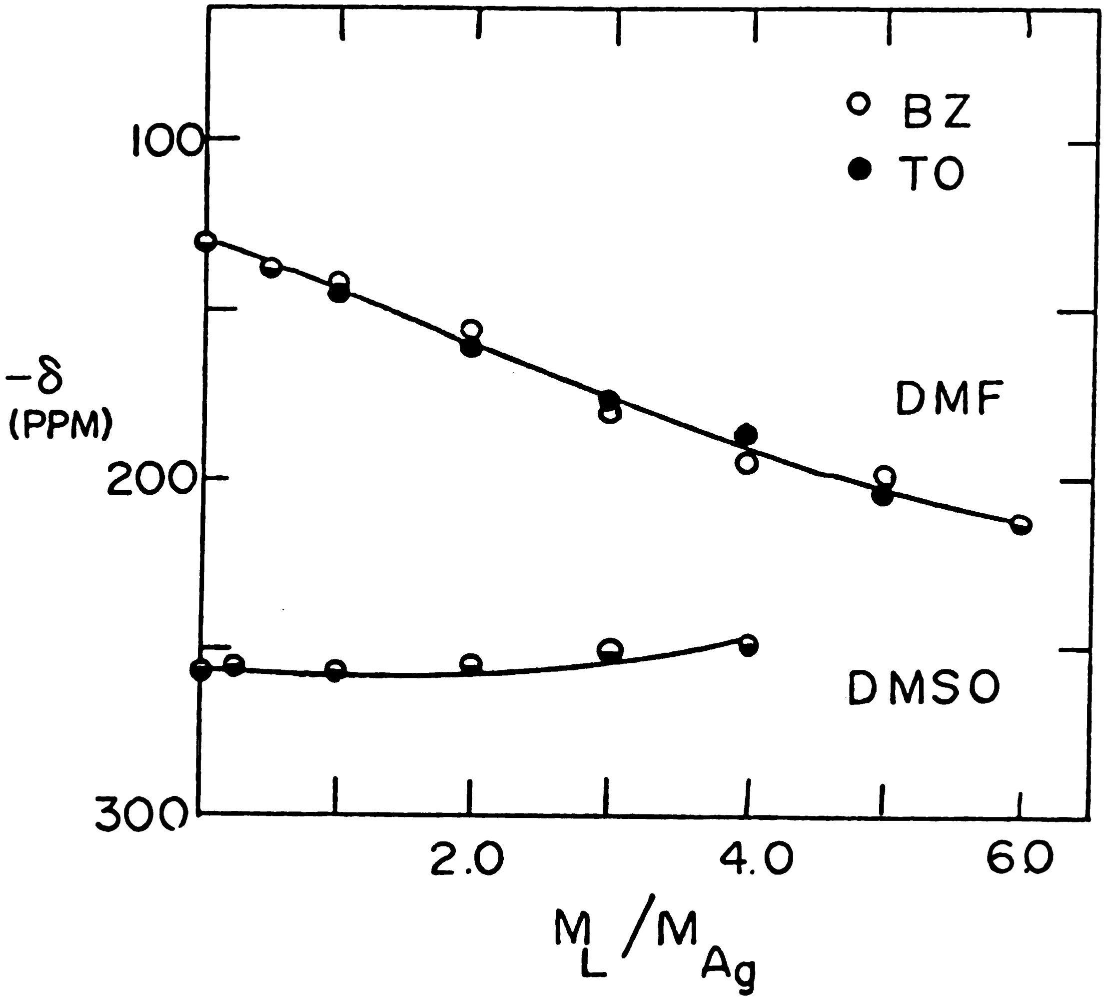


Figure 18. Silver-109 chemical shifts as a function of ligand/$AgClO_4$ molar ratio in dimethylformamide and dimethylsulfoxide. (Ligand is either benzene or toluene.)

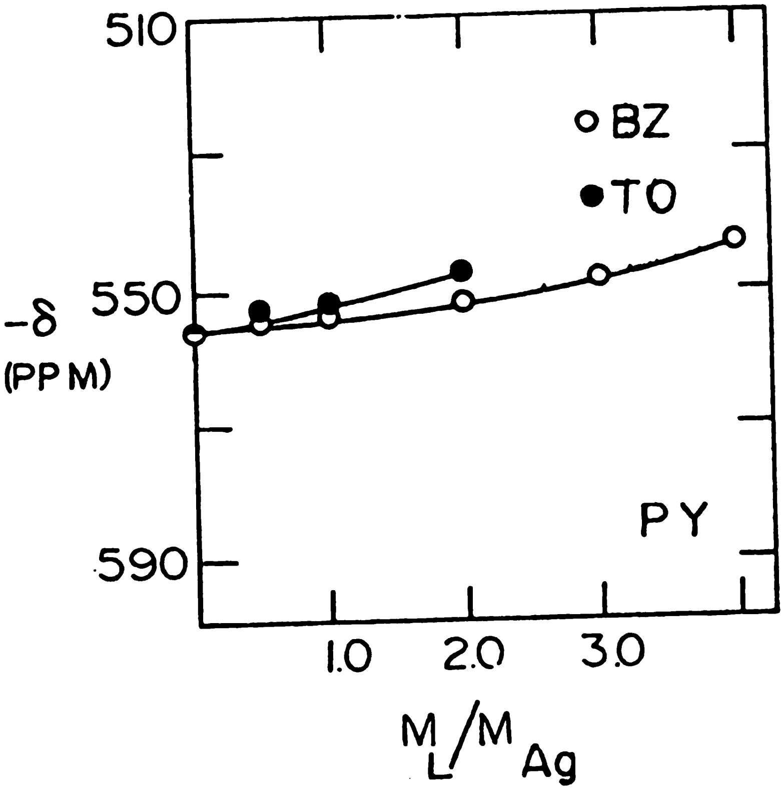


Figure 19. Silver-109 chemical shifts as a function of ligand/AgClO$_4$ molar ratios in pyridine. (Ligand is either benzene or toluene.)

shifts down field. Maciel et al.[75] also observed a similar behavior when thiourea or tetramethyl thiourea were added as ligands to solutions of Ag^+ ion in DMSO. They related this downfield shift to the deshielding of ^{109}Ag as a result of complexation of Ag^+ ion with these ligands. However, the extent of the shift to lower field due to the interaction of Ag^+ ion with ligand is different in different solvents (Figure 13) which indicates that the solvent plays an important role in these complexation processes. In the case of solvents with low or moderate donor number such as PC, THF, AC and CH_3OH the shift to lower field is larger. For solvents with higher solvation ability such as DMF and DMSO, the extent of shift is less. In pyridine, which is known to form a stronger complex with Ag^+ ion, the change in the chemical shift is very small.

From the comparison of the results for the two ligands (benzene and toluene) one notices that the downfield shift is more pronounced for the toluene than benzene, in propylene carbonate, acetone, methanol, and tetrahydrofuran. In these solvents the complexation of Ag^+ seems to be stronger with toluene than benzene, from the curvature of the plots of chemical shifts vs the mole ratio of ligand to metal ion (Figures 13-17). The same conclusion was reached from solubility measurements[42], a larger stability constant was found for toluene than benzene and the stronger interaction Ag^+ ion with toluene was related to the inductive effect of $-CH_3$ group in the ring. This difference in stability is leveled off in dimethylformamide and dimethylsolfoxide which are better solvating agents than former solvents.

2. A ^{109}Ag nmr Study on Complexation Reaction of Ag^{+} Ion with Pyridine.

Silver-109 nmr spectra were obtained in a series of 1 M $AgClO_4$ solutions with varying mole ratios of pyridine to metal ion in different solvents such as propylene carbonate, dimethylformamide, dimethyl sulfoxide, acetone, and methanol. The recorded values of the chemical shifts for each solvent case are shown in Table XIX and the plots of chemical shift vs molar ratio of pyridine to metal ion are presented in Figure 20 and also in detail in Figures 22-27. The data indicate that the ^{109}Ag resonance shifts downfield with increasing concentration of pyridine which is due to the interaction of Ag^{+} ion with pyridine. In all solvents used, the chemical shifts approach the same value at higher mole ratio of ligand which shows that the chemical shift is independent of solvent used and the Ag^{+} ion is all complexed by pyridine. In the case of acetonitrile as a solvent a pronounced break is observed in the plot of chemical shift vs mole ratio of pyridine to metal ion at mole ratio of 2:1 which can be an indication of the stoichiometry of the complex which is a known Ag^{+}-pyridine complex species.

Table XVIII. Silver-109 chemical shifts as a function of temperature. A for regular reference solution, B for reference solution in dewar type tube, (reference solution is saturated aqueous solution of $AgClO_4$ ∿12.5 M doped with Fe^{+3}.)

A		B	
Temperature, °C[a]	δppm	Temperature, °C	δppm
-106	0.0	-31	-3.5
- 88	0.0	-23	-3.0
- 73	-0.9	-13	-1.5
- 55	0.0	- 3	-0.8
- 36	0.0	12	0.9
- 16	0.0	20	0.0
19	0.0	36	0.8
37	0.0	41	1.0
61	0.0	49	0.8
87	0.8	51	0.9
91	0.8	53	1.0
116	0.8	66	1.5
		71	3.0
		80	2.0
		84	3.5
		93	1.7
		96	3.5

[a] Below -31°C solution froze.

Table XIX. Silver-109 Chemical Shifts as a Function of Pyridine/$AgClO_4$ Molar Ratio in Different Solvents at Different Temperatures.

		PC			
55°		28°		-48°	
$[PY]/[Ag^+]$	δppm	$[PY]/[Ag^+]$	δppm	$[PY]/[Ag^+]$	δppm
12.38	-538.7	0.00	12.2	0.00	- 1.0
		0.99	-178.4	0.99	-191.5
		1.98	-360.3	1.98	-377.8
		3.99	-480.1	3.99	-542.3
		5.99	-525.6	5.99	-586.8
		8.99	-547.5	8.99	-593.8
		12.38	-553.0	12.38	-595.6

		Acetone			
28°		-22°		-36°	
0.00	-56.8	0.00	- 70.0	0.00	- 71.7
0.99	-212.5	0.99	-223.0	5.99	-572.9
2.97	-428.5	2.97	-453.0	8.99	-586.9
4.00	-474.0	4.00	-516.0	12.38	-589.5
5.99	-517.7	5.99	-560.6		
8.99	-542.2	8.99	-577.2		
12.38	-554.5	12.38	-582.4		

Table XIX. Continued.

DMSO			
28°		3°	
[PY]/[Ag$^+$]	δppm	[PY]/[Ag$^+$]	δppm
0.00	-258.0	0.00	-265.9
0.99	-341.0	0.99	-347.2
2.50	-430.3	2.97	-452.1
3.99	-468.8	5.99	-519.4
5.99	-503.7	8.99	-551.8
7.92	-524.7	12.38	-567.6
8.99	-535.2		
9.90	-542.2		
12.38	-555.0		
DMF			
28°		-44°	
0.00	-130.3	0.00	-132.0
0.99	-272.0	0.99	-285.1
1.98	-393.5	1.98	-413.6
3.99	-477.5	3.99	-539.8
7.40	-527.3	5.99	-571.9
9.90	-544.5	7.40	-592.5
12.38	-554.5	12.38	-593.9

Table XIX. Continued.

THF			
28°		22°	
$[PY]/[Ag^+]$	δppm	$[PY]/[Ag^+]$	δppm
0.000	- 7.8	0.000	- 8.8
0.247	- 80.5	0.495	-101.4
0.495	-116.7	3.998	-481.0
3.466	-459.3	5.990	-519.5
3.998	-477.5	8.987	-547.5
5.990	-514.3	12.380	-556.3
7.920	-533.5		
9.900	-546.6		
12.380	-553.0		
CH_3CN			
28°		21°	
0.00	-529.1	0.00	-535.2
0.99	-505.6	0.99	-509.9
0.99	-504.6	1.98	-488.0
1.98	-485.4	3.99	-514.2
2.97	-496.7	6.93	-537.8
3.99	-510.2	9.90	-550.1
6.93	-532.6	9.90	-549.2
6.93	-533.5	12.38	-556.2
9.90	-546.6		
12.38	-553.6		

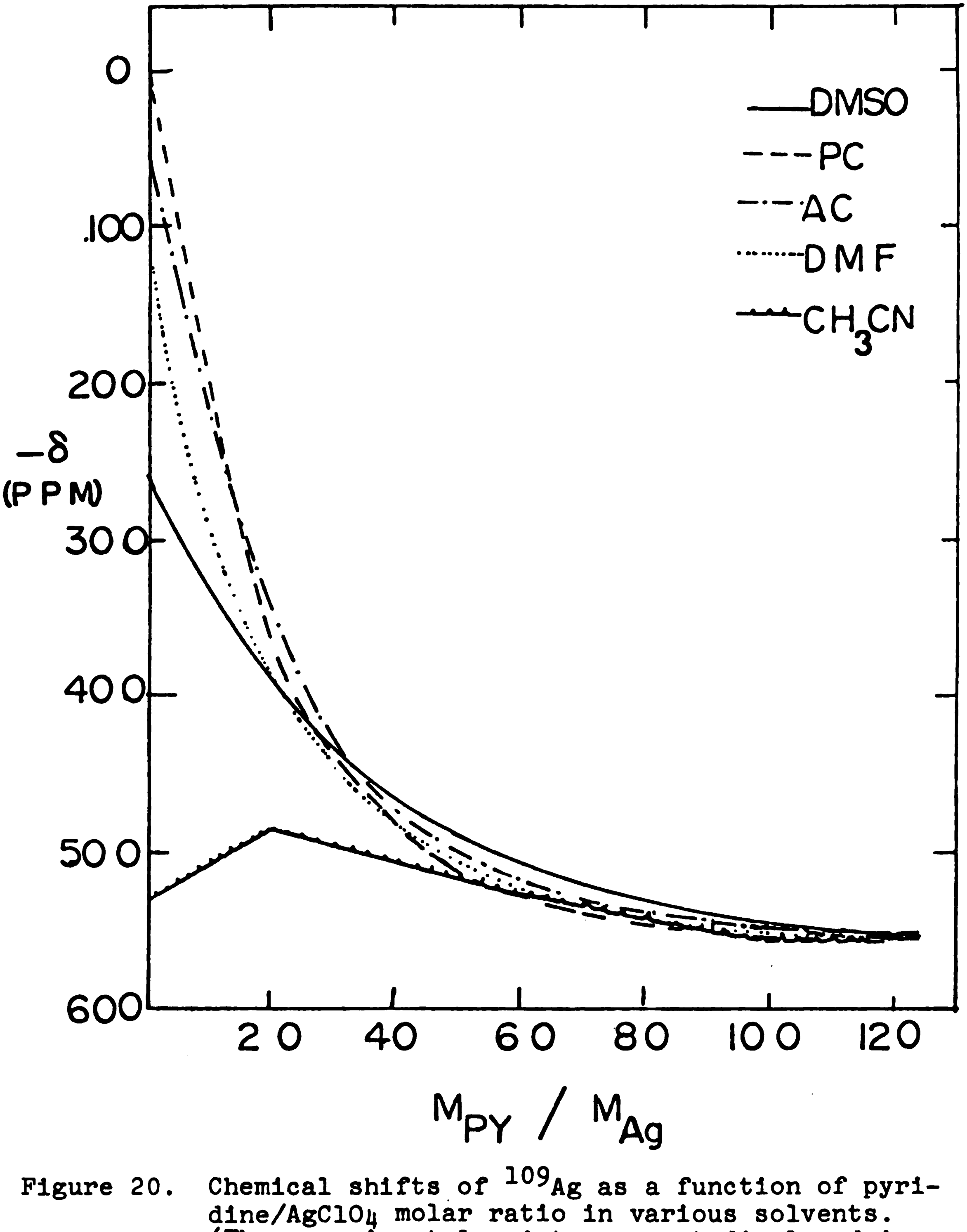


Figure 20. Chemical shifts of ^{109}Ag as a function of pyridine/$AgClO_4$ molar ratio in various solvents. (The experimental points are not displayed in this plot to prevent crowding, but the same plots are shown in following figures in more detail.)

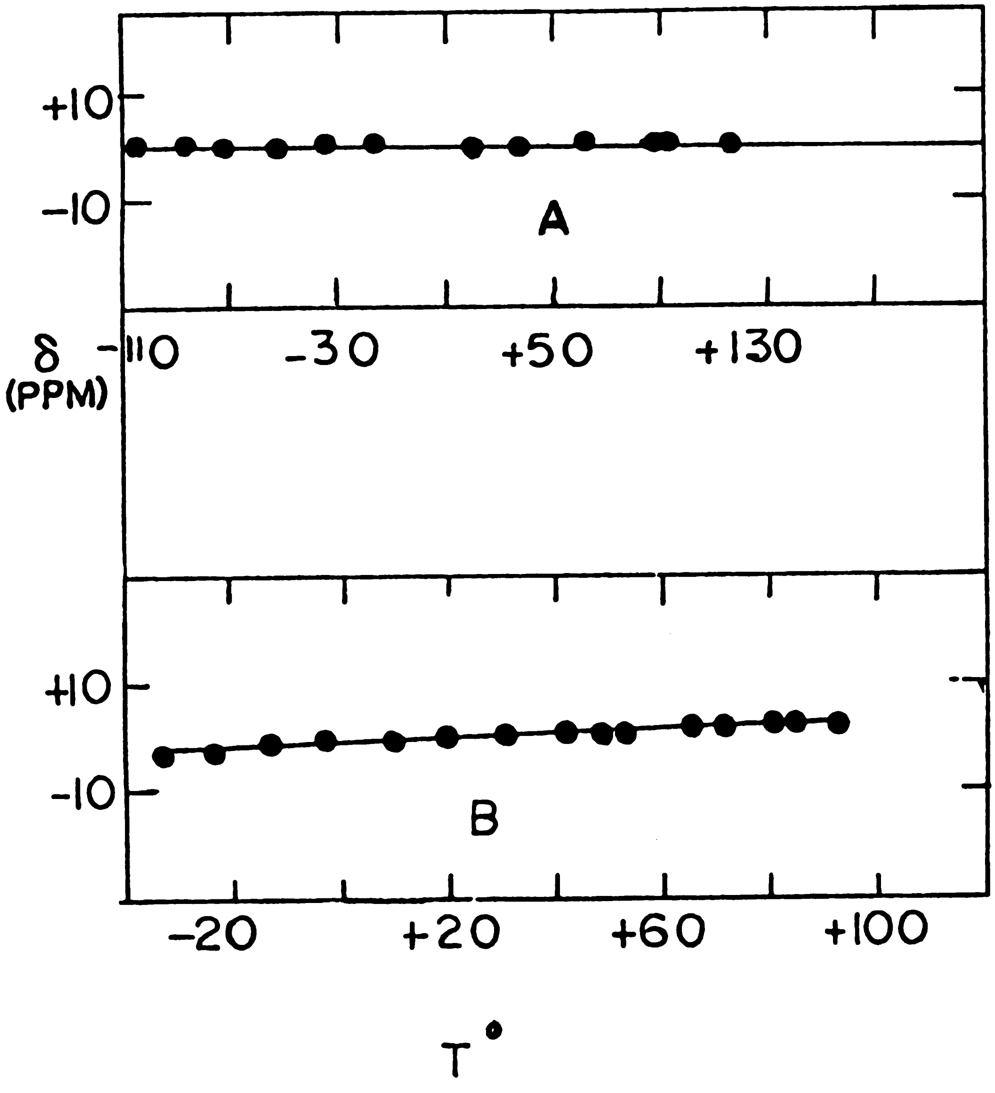


Figure 21. Silver-109 chemical shifts as a function of temperature: A) for reference solution in dewar type tube, B) for reference solution in regular nmr tube.

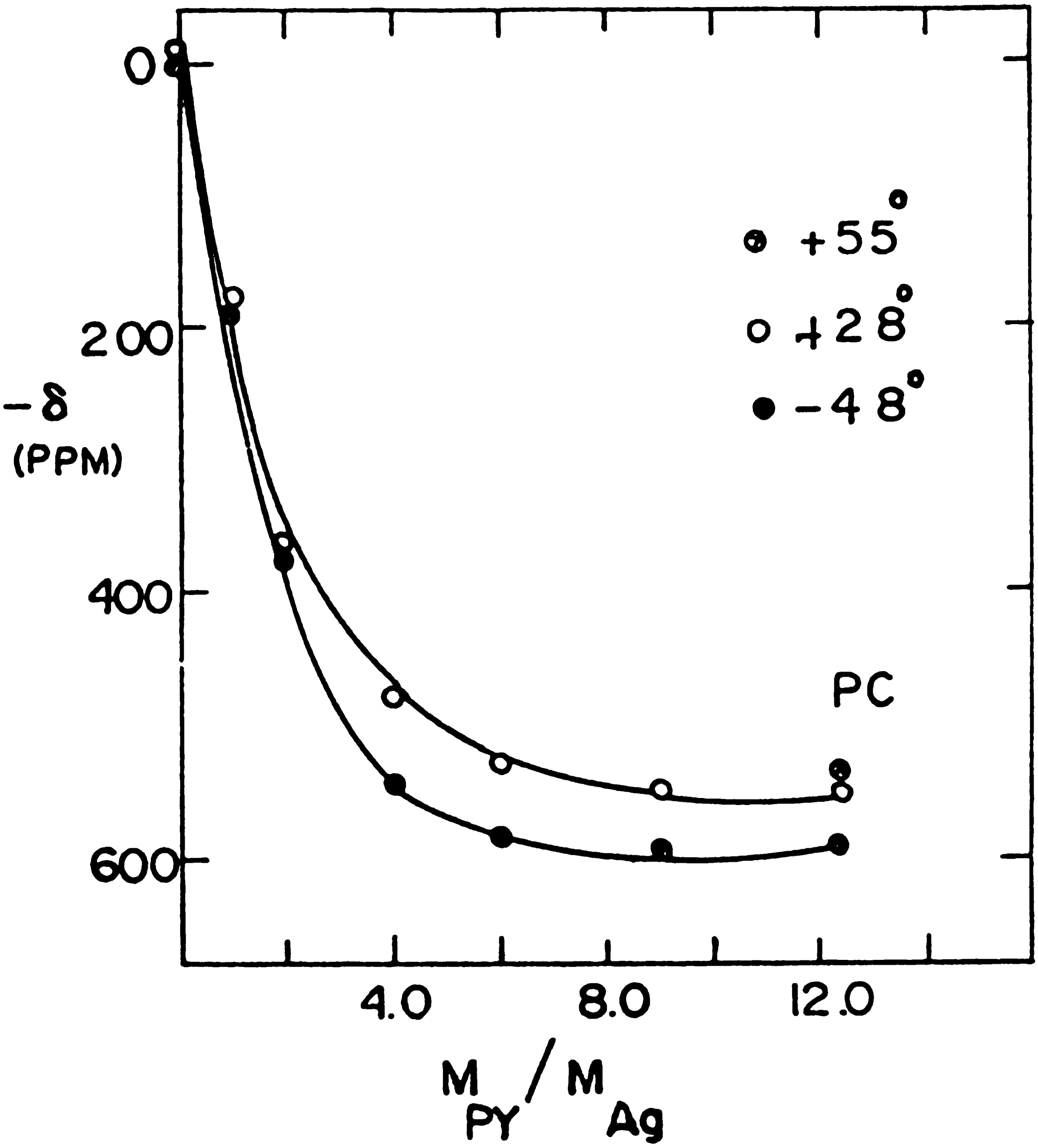


Figure 22. Chemical shifts of ^{109}Ag vs pyridine/$AgClO_4$ molar ratio in propylene carbonate at different temperatures.

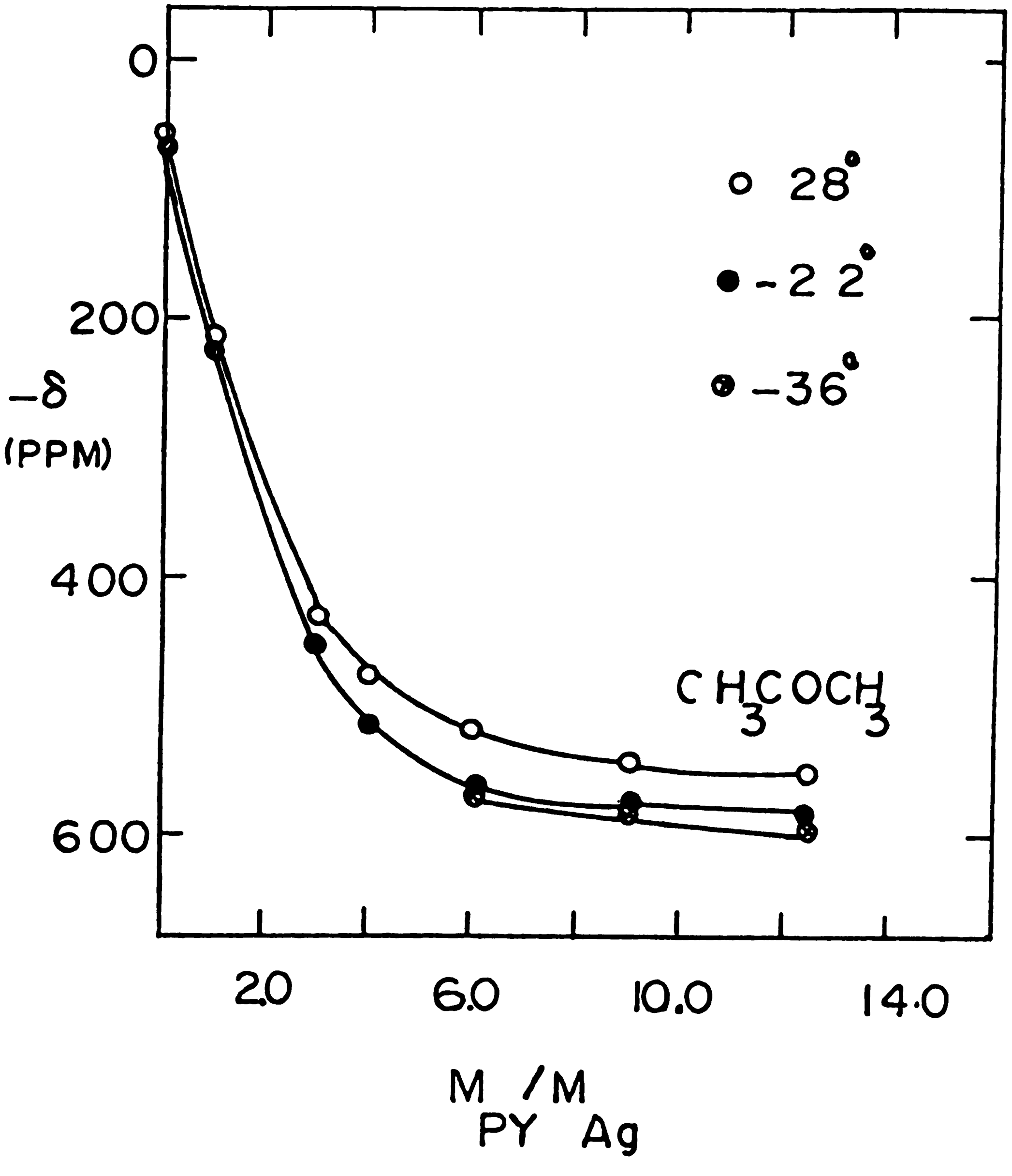


Figure 23. Silver-109 chemical shift as a function of pyridine/AgClO$_4$ molar ratio in acetone at different temperatures.

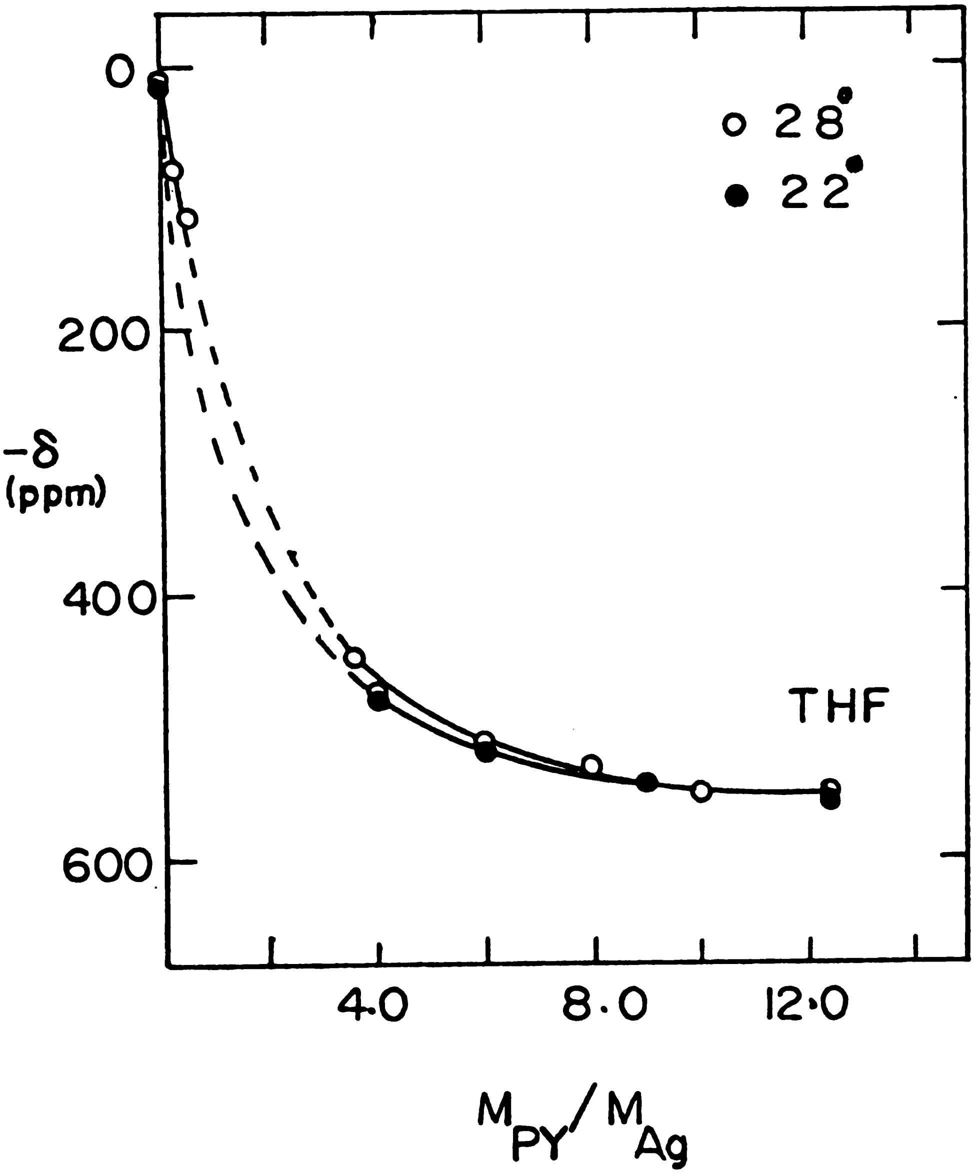


Figure 24. Silver-109 chemical shift as a function of pyridine/$AgClO_4$ molar ratio in tetrahydrofuran at different temperatures.

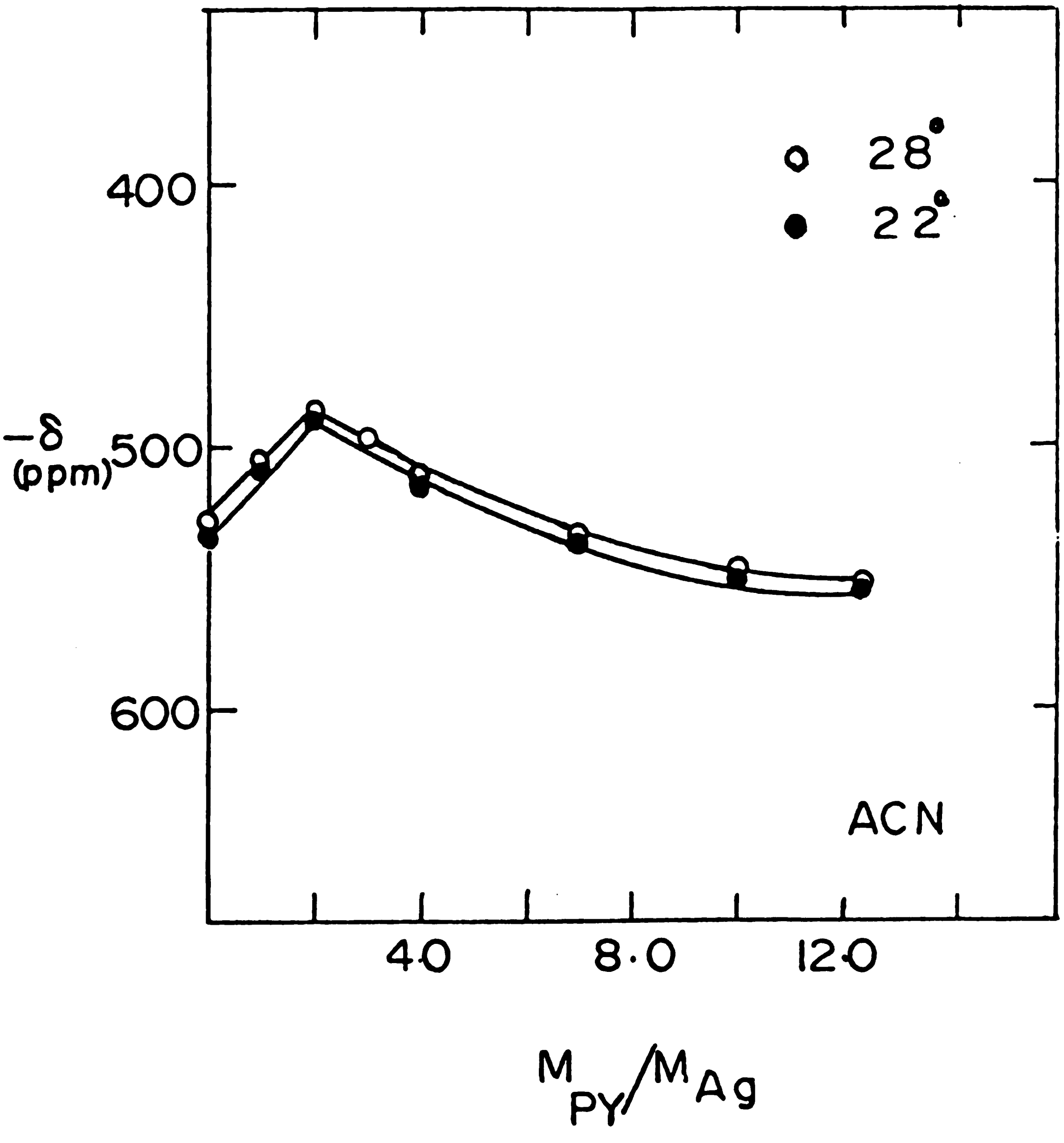


Figure 25. Chemical shifts of ^{109}Ag as a function of pyridine/$AgClO_4$ molar ratio in acetonitrile at different temperatures.

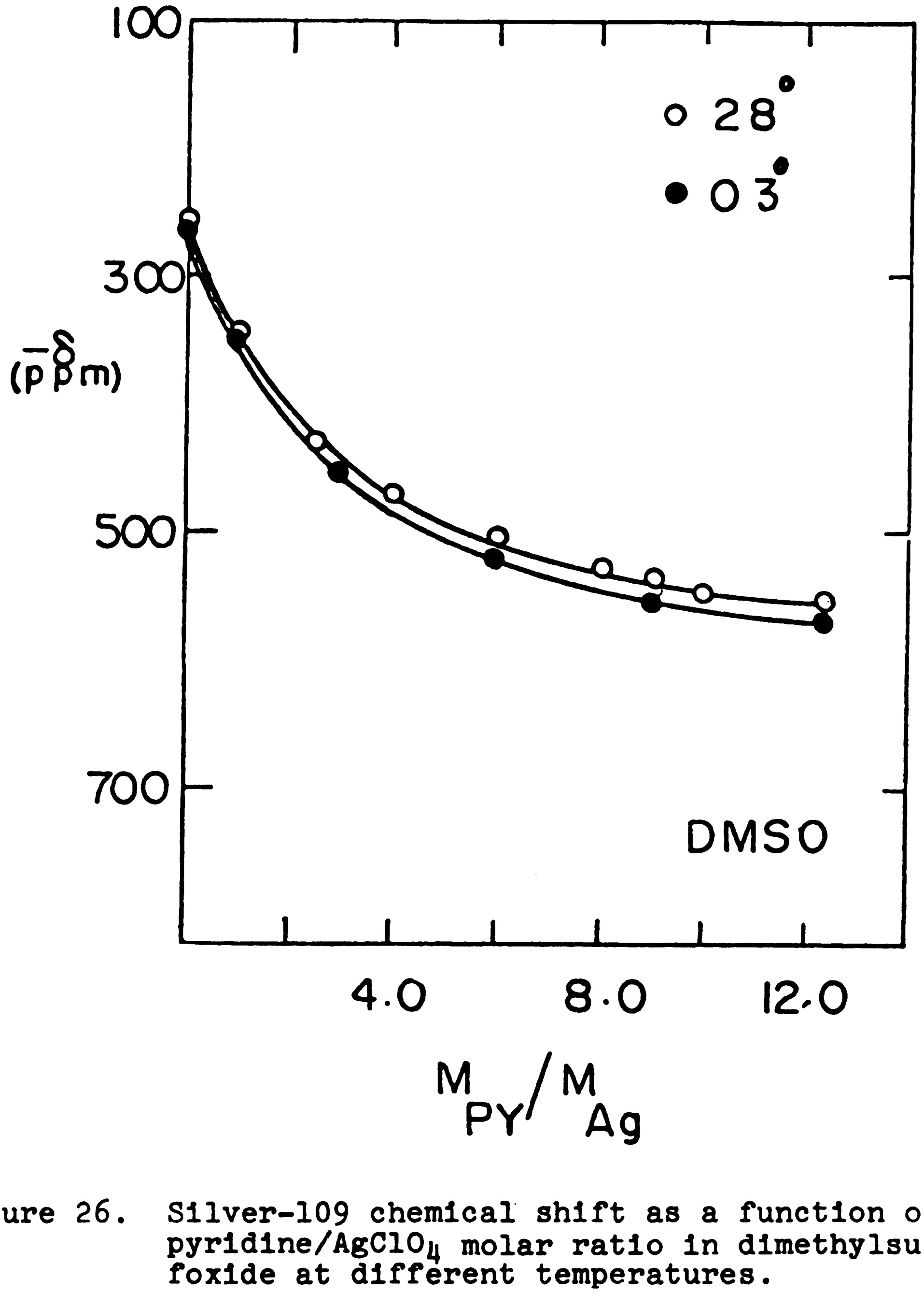


Figure 26. Silver-109 chemical shift as a function of pyridine/$AgClO_4$ molar ratio in dimethylsulfoxide at different temperatures.

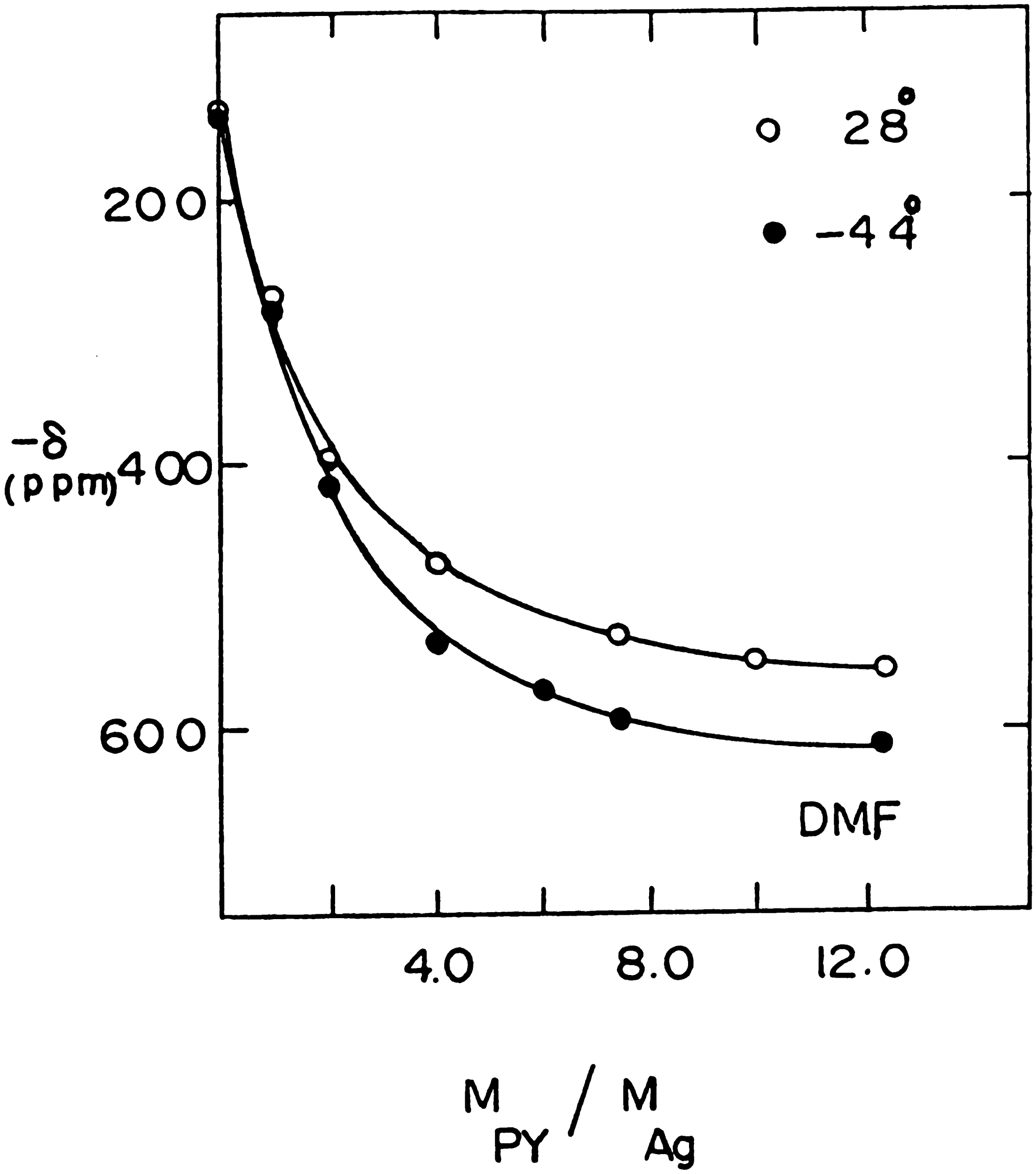


Figure 27. Chemical shifts of ^{109} vs pyridine/$AgClO_4$ molar ratio in dimethylformamide at different temperatures.

The influence of temperature on the ^{109}Ag chemical shift was studied. The measurements were made using an insulated reference solution (in a dewar type tube). This arrangement allowed the determination of true temperature effects on the ^{109}Ag chemical shifts. It is seen from Table XVIII and Figure 21 that the chemical shift of the insulated reference solution is much less temperature-dependent than the chemical shift of the uninsulated sample.

The results of silver-109 nmr studies on the 1 M $AgClO_4$ solution with varying molar ratios of pyridine in different solvents and temperatures are presented in Table XIX. The plots of chemical shift vs the molar ratio of ligand to metal ion for each solvent case are shown in Figures 22-27.

The results indicate that in all solvents tried, the shift to lower field is larger at lower temperature and the effect of temperature is more on the Ag^+ complexed with pyridine than on the solvated Ag^+ ion. In addition, the approach of the chemical shift to the limiting value is more pronounced (the steeper slope) at lower temperature which might be due to a greater stability of the complex at lower temperatures. This observation is in agreement with the results of calorimetric studies on this system (page 40). From this measurement, a negative enthalpy for the reaction was calculated.[59,60]

3. Complexation Reaction of Ag^+ Ion with Substituted Pyridine Derivatives

Since a linear relationship between the logarithms of formation constants and the basicities of the ligands in complexation of Ag^+ ion with substituted pyridine has been found,[63] it seemed interesting to find out how ^{109}Ag nmr reflects this phenomenon. Silver-109 nmr spectra were studied in 1 M $AgClO_4$ solutions with substituted pyridine compound such as 2-cyanopyridine, 4-cyanopyridine, 2,5-dichloropyridine, 2,5-dibromopyridine, and 2,6-dichloropyridine. Complexation of 2-cyanopyridine was studied in dimethyl sulfoxide, dimethylformamide and pyridine. The other solvents of interest could not be tried because of low solubility of this ligand. The chemical shift was measured as a function of 2CNPy to metal ion molar ratio in these solvents. A limited number of molar ratios could be tried because of either the low solubility of the ligand or precipitation of the complex at higher molar ratio of ligand to metal ion. Results are presented in Table XX and the plot of chemical shift vs molar ratios of ligand to metal is shown in Figure 28. From the data it is clear that the extent of downfield shift for this ligand in DMF and DMSO is less than in pyridine for the same molar ratio range. In pyridine, little change in the chemical shift of ^{109}Ag-resonance was observed on the addition of 2CNPy. For other mentioned substituted pyridines, ^{109}Ag nmr spectra were run in a series of 1 M $AgClO_4$ solutions with a ligand to metal

Table XX. ^{109}Ag Chemical Shifts and Line Widths as a Function of 2CNPy/AgClO$_4$ Molar Ratio in Different Solvents

DMSO[a]		DMF[b]		PY[c]	
[2CNPy]/[Ag$^+$]	δppm	[2CNPy]/[Ag$^+$]	δppm	[2CNPy]/[Ag$^+$]	δppm
1/2	-268.5	0.41	-172.2	1/2	-552.7
1/1	-277.2	0.50	-181.0	1/1	-553.1
2/1	-295.0	0.83	-209.8	2/1	-549.6
		1.00	-221.3		

[a,c] Above L/M = 2/1, precipitation took place.

[b] At L/M = 2/1 molar ratio, precipitation took place.

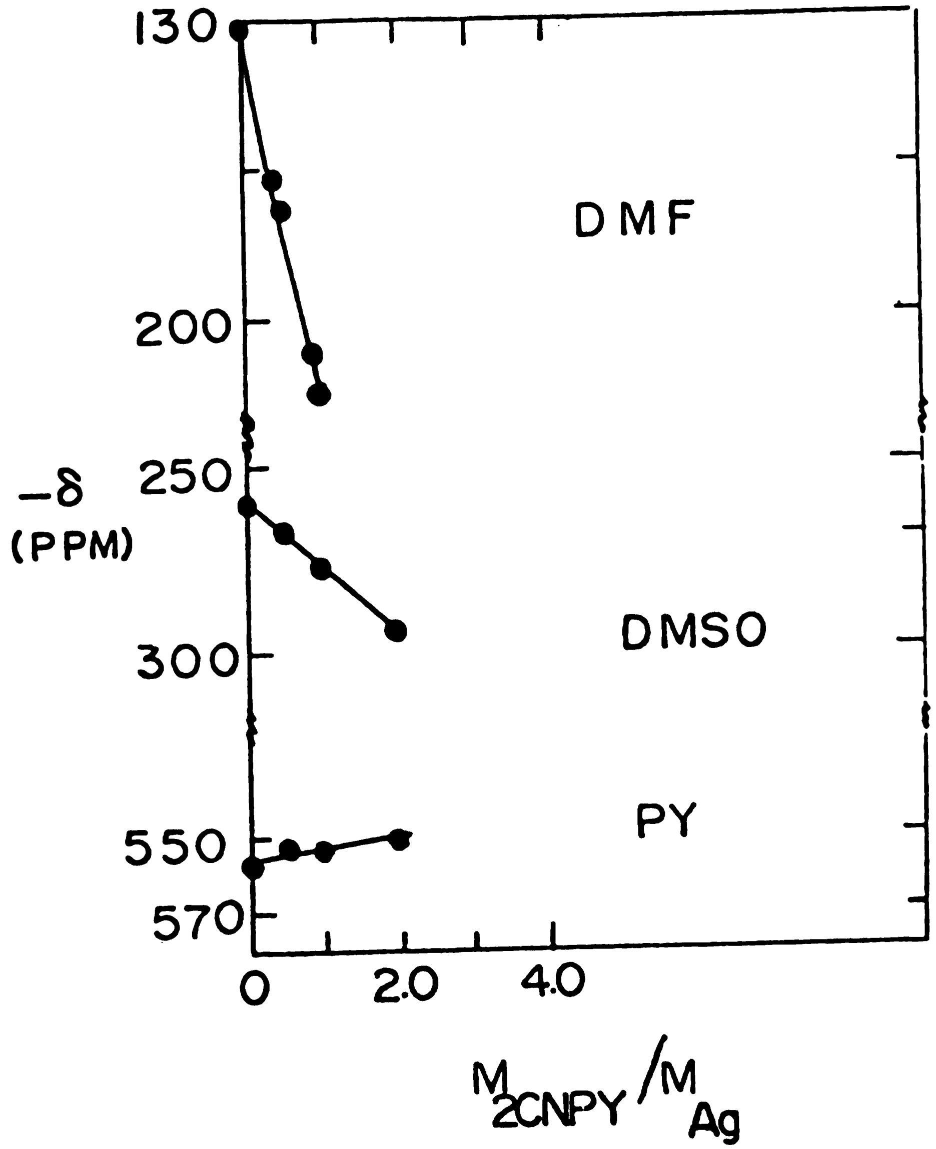


Figure 28. Silver-109 chemical shift as a function of 2-cyanopyridine/$AgClO_4$ molar ratio in various solvents.

molar ratio of 1/2 in DMSO. At higher molar ratio of ligand to metal ion, precipitation took place. For the 2,5-dichloropyridine study, tetrahydrofuran was also used as a solvent. Other substituted pyridines were not soluble in this solvent.

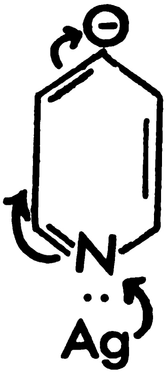
The results are presented in Table XXI. The data for Py and 2CNPy as ligands are also presented for the sake of comparison. The results indicate that the downfield shift of ^{109}Ag resonance upon complexation is considerably greater for pyridine than for the substituted pyridines. However, for these compounds, a decrease of reactivity toward the Ag^+ ion is expected due to withdrawing properties of substituents on the ring. As mentioned earlier, a linear relationship between the logarithm of the complexity constant and the basicity of a series of substituted pyridine has been obtained.[63,64] Therefore, it is possible to conclude that the higher downfield shift for the pyridine complex is due to a stronger interaction of this ligand with Ag^+.

The data for 2-cyanopyridine and 4-cyanopyridine indicate that the downfield shift for Ag^+ ion is greater when it interacts with 4CNPy than 2-cyanopyridine. In this case the higher reactivity of 4-cyanopyridine has been explained[62] on the basis of increased π-bonding as a result of structures like the following which involves multiple bonding of the silver ion to the ligand which makes

Table XXI. Silver-109 Chemical Shifts of $AgClO_4$ + Ligand in THF and DMSO.

L/M	Solvent	δ(ppm)	Ligand:1
1/2	DMSO	-258.8	2-5DiClPy
1/2	DMSO	-257.1	2-6DiClPy
1/2	DMSO	-284.2	4CNPy
1/2	DMSO	-261.5	2-5DiBrPy
1/2	DMSO	-268.5	2CNPy
1/2	DMSO	-308.0	Py
1/2	THF	-116.7	Py
1/2	THF	- 79.2	2-5DiClPy

this complex more stable than the one formed with 2-cyanopyridine.



4. Carbon-13 nmr Studies of Complexation of Ag^+ Ion with Benzene and Pyridine

Carbon-13 nmr spectra were run on a series of solutions of $AgClO_4$ with either pyridine or benzene as ligands in different solvents such as THF, DMSO, and PC. These solutions contained constant concentration of ligand (PY: 0.247 M, Bz: 0.249 M) and different molar ratios of metal to ligand such as 0/1 and 4/1 were tried to find out how the carbon resonance of the ligand's carbons respond to this change. The results are presented in Tables XXII and XXIII. As the data indicate, there is a change in the chemical shift of pyridine's carbon atoms as $AgClO_4$ is introduced into the solution. The change is most for the γ-carbon and least for the β-carbon. The same trend was observed in protonation of pyridine. For benzene no

Table XXII. ^{13}C Chemical Shift as a Function of Ag^+/Bz Molar Ratio in Different Solvents.

Sample	δ(ppm)	$\Delta\delta$[a]	Ag^+/Bz
Bz + Ag^+ in DMSO	129.91	+0.1±0.01	4.0
Bz in DMSO	129.81		0.0
Bz + Ag^+ in PC	128.43	-0.9±0.15	4.0
Bz in PC	129.34		0.0
Bz + Ag^+ in THF	128.73	-0.13±0.14	4.0
Bz in THF	128.86		0.0
Bz	128.60		

[a]: $\Delta\delta$ = [δ(sample solution with salt) - δ(sample solution without salt)] ± change of chemical shift for reference solvent peak in these two solutions.

Table XXIII. ^{13}C Chemical Shift as a Function of Ag^+/Py Mole Ratio in Different Solvents.

Sample	$\delta(ppm)_\alpha$	$\delta(ppm)_\gamma$	$\delta(ppm)_\beta$	$\Delta\delta_\alpha$[a]	$\Delta\delta_\gamma$[b]	$\Delta\delta_\beta$[c]	Ag^+/Py
Py + Ag^+ in PC	152.89	140.43	126.51	2.13±0.06	3.43±0.06	1.67±0.06	4.0
Py in PC	150.76	137.00	124.84				0.0
Py + Ag^+ in THF	152.87	139.89	126.18	2.28±0.11	3.91±0.11	2.11±0.11	4.0
Py in THF	150.59	135.98	124.07				0.0
Py + Ag^+ in DMSO	152.78	140.17	126.79	1.75±0.02	2.67±0.02	1.49±0.02	4.0
Py in DMSO	151.03	137.50	125.30				0.0
Py	150.38	136.04	124.09				

[a,b,c] $\Delta\delta$ = [δ(sample solution with salt) - δ(sample solution without salt)] ± the change in the chemical shift of reference peak.

change is observed within the experimental error.

For the case of benzene just one ^{13}C-resonance was observed which might be due to fast exchange of Ag^+-bonded carbons in the ring. In a report of an x-ray investigation, it was concluded that Ag^+ interacts unsymmetrically with benzene being closer to two of the carbons of benzene. It seemed interesting to carry out ^{13}C nmr studies on this system at lower temperatures where the exchange might slow down. The experiment was done for a 1.44 M $AgClO_4$ solution with benzene at 8.7/1 molar ratio of Ag^+ to benzene at -47°C in THF. This solvent was tried because of its low melting point (-109°C). No splitting of the carbon-resonance took place which indicates that the rate of exchange is fast compared to the nmr time scale, or the ^{13}C nmr is not sensitive enough to detect small changes taking place in the chemical environment of the ^{13}C nucleus.

It thus appears again that ^{109}Ag nmr is a more sensitive technique than the ^{13}C nmr for studies of complexation reactions and, in particular, for weak interactions.

Conclusions

Exploratory study of the ^{109}Ag nmr showed that this technique has a good possibility of becoming a very useful probe of the reactions of the silver ion in solutions. The low sensitivity of the ^{109}Ag signal, however, made it impossible to work at concentrations below 0.5 M and since the solubilities of silver salts in nonaqueous solvents are rather limited, the upper limit of silver salt concentration seldom was larger than 1.0 M. This narrow (and high) operational concentration range precluded quantitative studies of the silver complexes such as have been carried out previously in this laboratory with ^{7}Li, ^{23}Na and ^{133}Cs nmr.

Recent acquisition of Bruker-180 multinuclear spectrometer with a high field superconducting solenoid should enlarge considerably the scope of ^{109}Ag nmr research. Unfortunately, it arrived too late to be of use in this study. Nevertheless the comparison of the sensitivities of the DA-60 and Bruker-180 spectrometers shown in Figure 29, vividly illustrates the much superior performance of the latter instrument.

Of course, the progress in the nmr instrumentation is bound to continue and spectrometers with ultra high fields undoubtedly will become available in the future (albeit at a price!). With such spectrometers it should be possible to study very dilute solutions of silver salts and complexes in solutions and the application of ^{109}Ag nmr to chemical problems should increase manyfold.

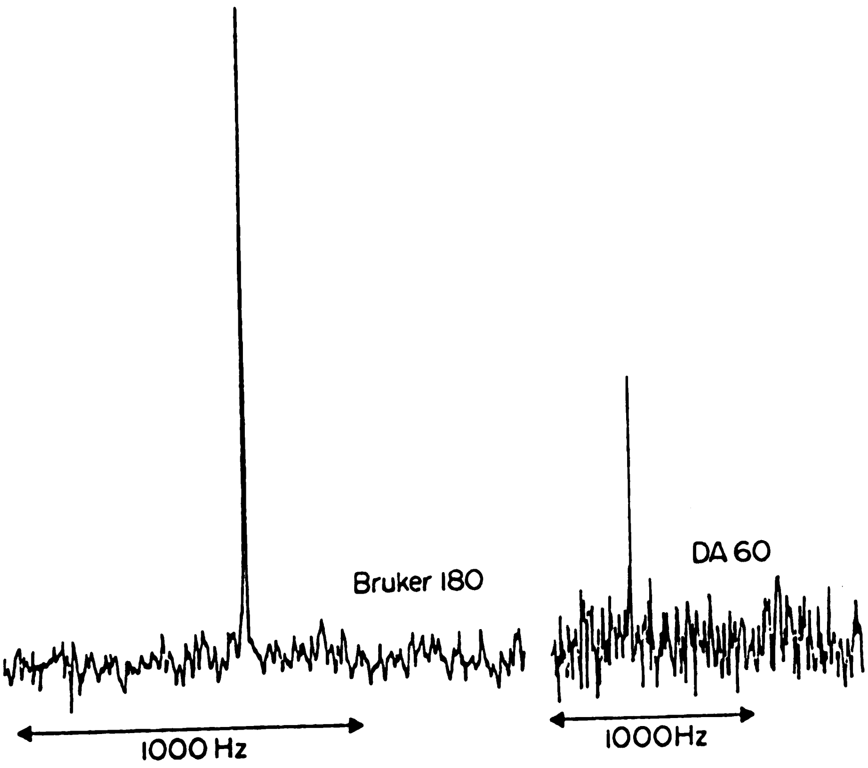


Figure 29. Silver-109 nmr resonances of aqueous solution of 1 M $AgClO_4$ doped with 1/50 M Fe^{+3} by DA60 and Bruker 180 instruments (1000 scans).

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