385128

THE EFFECT OF SOME ANIONS ON THE COORDINATION OF ALUMINUM III BY DIMETHYLFORMAMIDE (DMF)

USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A Thesis

Presented to

the Faculty of the Department of Chemistry

Appalachian State Teachers College

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

by

J. Harrison Burns

June , 1977

THE EFFECT OF SOME ANIONS ON THE COORDINATION OF

ALUMINUM III BY DIMETHYLFORMAMIDE (DMF)

USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

1977

by

J. Harrison Burns

Approved by:

Professor

Chairman, Advisory Committee

Dean of the Graduate School

LIST OF FIGURES

TABLE OF CONTENTS

Page

INTRODUCTION	1
Theory	2
Chemical Shifts	3
Spin-spin Coupling	4
Coordination Numbers (Direct Method)	5
Determination of Some Coordination Numbers	8
Indirect NMR Methods	2
EXPERIMENTAL	4
Materials	4
Analysis of Aluminum	4
Preparation of Samples	7
Tuning of the NMR Instrument	1
RESULTS AND DISCUSSION	5
Conclusion. \ldots 3	4
LIST OF REFERENCES	6

Figure 1.	Pure Dry DMF	6
Figure 2.	DMF containing $A\ell(C\ell O_4)_3$	6
Figure 3.	Effect of Concentration of DMF on $A\ell^{+3}$ Analysis. Al(NO ₃) ₃ solution	16
Figure 4.	Drying Apparatus	19
Figure 5.	Spectrum of DMF with water	22
Figure 6.	Spectrum showing 13 C H ₃ peaks and bound DMF. Salt is Al(ClO ₄) ₃	22
Figure 7.	Example of peaks used for calculations. Salt is Al(NO ₃) ₃	23
Figure 8.	Peaks used for calculations plus water. Salt is $A\ell(NO_3)_3$	23
Figure 9.	13 C H $_3$ showing 60 Hz peaks. Salt is Al(NO $_3$) $_3$	27
Figure 10.	Movement of spinning side bands. Salt is $Al(NO_3)_3$.	27
Figure 11.	Pure dry DMF showing new side bands	2 9
Figure 12.	$Al_2(SO_4)_3$, DMF	2 9
Figure 13.	Effect of rf field intensity on Coordination Number .	31
Figure 14.	Effect of Aluminum ⁺³ Concentration on Coordination Number. $Al(NO_3)_3$ solution	33

```
Page
```

LIST OF TABLES

Table 1.	Check on the	method of	aluminum	analysis			15

Pauli theorized in 1928¹ that nuclei spin about their axis and that certain nuclei with unbalanced nuclear charge have magnetic moments, but experimental verification had to wait several years for the necessary technology. It wasn't until 1945 that magnetic moments were detected in bulk matter independently by Purcell, Torry and Pound² and by Block, Hansen and Pachard³.

Experimentally Purcell, Torry and Pound used a "bridge method"⁴ to measure magnetic resonance. The "bridge method" utilized a single coil in a large magnetic field tuned with another coil outside the magnetic field. The sample tube was placed in the coil in the magnetic field. Resonance in the sample caused the tuned circuit to become unbalanced resulting in an absorption signal.

An induction method, commonly called the "double coil method"⁵, which utilizes a transmitted coil and a receiver coil placed at right angles to each other and at right angles to the large magnetic field, was used by Block, Hansen and Pachard. The resonance signal from a sample is separated from the transmitter signal by the geometrical arrangement of the coils.

The work to be described was done with a JEOLCO JNM-C-6OH high resolution nuclear magnetic resonance instrument which is a

INTRODUCTION

Page

double coil instrument. The frequency from the transmitter coil is 60 megahertz (Mhz) and the large magnetic field strength is 14,092 gauss.

Theory

A spinning nucleus in a large magnetic field can be compared to a gyroscope in a gravitational field. As the gyroscope precesses with a frequency that depends on the strength of the gravitational field, so the nucleus precesses with a frequency that depends on the magnitude of the large magnetic field. The frequency of precession is given by the Lamor equation⁶,

$$\gamma'_{0} = \frac{\gamma}{2\pi} H_{0}$$
(1)

Where ν_0 is the precessional frequency in Hertz, H_0 is the strength of the large magnetic field and γ is the magnetogyric ratio which is a property of the nucleus. Equation 1 shows that the frequency of precession is directly proportional to the magnetic field.

At right angles to the magnetic field H_0 , the transmitter produces an oscillating magnetic field, H_1 , at about the same energy as radio waves. When the frequency of precession of the nucleus is the same as the frequency of oscillation of H_1 , some of H_1 is absorbed by the nucleus. When energy is absorbed by the nucleus, resonance occurs and the tuned circuit becomes unbalanced. This change in the circuit can be detected as an absorption or dispersion signal. Most NMR instruments, and the instrument used for this work, have "sweep coils" that change the strength of the large magnetic field H_0 and the frequency of the transmitter remains constant. There are 2I + 1 possible orientations for a nucleus in a magnetic field.⁷ Spin quantum number, I, for a proton is 1/2, thus giving it two possible spin states, one with and the other against the H₀ field. Energy is absorbed or emitted by the proton as it "flips" from one position to another.

The intensity of an absorption signal is proportional to the concentration of absorbing nuclei if the peak is not saturated (if enough nuclei remain in the lower spin state to absorb more energy if it were available).

Chemical Shifts

If a spectrum was recorded of different NMR active nuclei, such as 1 H and 13 C, in the same large magnetic field, signals in quite different areas of the spectrum, separated by thousands of hertz, would be observed. Also, if a spectrum was recorded of a compound that contains hydrogens that are chemically different, different signals would be observed but with a separation of only a few hertz. Both types of separation are called chemical shifts.

An example of chemical shift is the two signals observed in a spectrum of methanol. The downfield (lower field strength) signal would be due to the hydrogen of the hydroxyl group and the upfield signal would be due to the three hydrogens of the methyl group. The difference in position of the two signals is due to small differences in the magnetic fields around the protons. The reason that the protons

"feel" two different magnetic fields is because there are different electronic configurations about the two types of protons. The electrons usually shield the protons from the external magnetic field. Signals from less shielded protons are shifted downfield.

The relationship between the screening constant, σ , and the magnetic field, H_N , experienced by a given nucleus, N, is shown by the equation:⁸

$$H_{N} = H_{0} (1 - \sigma).$$
 (2)

Equation 2 shows that nuclei that are highly shielded (have a large screening constant, σ) will require a higher applied field, H₀, for resonance to occur.

Chemical shift, S, is given by the equation:⁹

$$S = \sigma - \sigma_r \tag{3}$$

Where σ_r is the screening constant for the reference signal. The reference commonly used is tetramethylsilane (TMS). Most organic compounds have negative chemical shifts when TMS is used as the reference.

Spin-Spin Coupling

Each signal that represents a chemically different type of hydrogen is at times split into a set of smaller signals. This splitting results from spin-spin coupling between nonequivalent nuclei. The NMR signal from one type of nuclei is affected by the magnetic field generated by neighboring nuclei. Spin-spin coupling occurs through the electrons associated with the nuclei being observed. The coupling constant, J, is independent of Ho and its magnitude is usually measured in hertz.

The splitting patterns of signals are related to the number of neighboring nuclei, position of nuclei, and the ways they arrange themselves in the large magnetic field.¹⁰ Decoupling, the elimination of the splitting of a signal, can take place if the nuclei causing the splitting are irradiated at their absorbing frequency, $\sqrt{2}$, while recording the spectrum in the usual way.¹¹

Coordination Numbers (direct method)

To determine a coordination number by the direct method, the ligands coordinated with the metal ion must produce a signal separate from that signal produced by the ligands not coordinated with the metal ion. In the work to be described, the solvent dimethylformamide, $HCON(CH_3)_2$ (DMF), is also the ligand being studied. A spectrum of DMF is shown in figure 1. The smaller of the three main peaks, furthest downfield, is due to the single formyl hydrogen, and the two larger peaks are from the methyl groups. The four small peaks, two on either side, nearest the large methyl signals are spinning sidebands.



Figure 1. Pure dry DMF.



Figure 2. DMF containing $A \ell (C \ell O_4)_3$.

The four outer small peaks, two on either side, are due to spin-spin coupling of the methyl protons bound to carbon-13 nuclei 12 , 13 . Since $1.108\%^{14}$ of the carbon in the sample is carbon-13, the signal produced by these four peaks is 1.108% of the total signal produced by the methyl groups.

Upon adding $A\ell(C\ell O_4)_3$ to the DMF, two more small peaks appear to the left, downfield, between the spinning sidebands and the large methyl peaks (figure 2). The two signals are produced by the DMF bound to the aluminum III ions. The concentration of the bound DMF can be found by comparing the area of the bound DMF peak with the area of the peak produced by spin-spin coupling with carbon-13.

(concentration of bound DMF) _	(
(area of bound signal)	
or	
(concentration of bound DMF) = (DMF solvent concentration)	(

Half of .01108 is used in the equation because the area of only one carbon-13 coupled peak was used. In this work the area of one downfield carbon-13 coupled peak and the area of the corresponding downfield bound methyl peak were used in the calculations; the upfield bound methyl signal overlapped the bulk signal, causing integration of this peak to be very uncertain.

6

DMF solvent concentration)(.01108) (area of¹³C coupled DMF)

$\frac{(.01108)}{2} \times \frac{(area of bound signal)}{(area of {}^{13}C coupled DMF)}$

The coordination number, n, is found by dividing the bound solvent concentration by the metal ion concentration.

 $n = \frac{(DMF \text{ solvent } x (.01108)}{2} x \frac{(area \text{ of bound signal})}{(area \text{ of } {}^{13}\text{C coupled DMF})}$ (ion concentration)

Since the bound DMF lowers the bulk DMF concentration, the following correction was made to find the actual DMF concentration.

(actual DMF solvent _ (initial DMF solvent - n (ion concentration) concentration) concentration)

Successive approximations were made until there was no change in n.

Determination of Some Coordination Numbers

The usefulness of NMR as a direct method to determine coordination numbers was shown in 1960 by Jackson, Lemons and Taube 15 using AlCl₂, Al(ClO₄)₃ and water systems. In these systems at ambient temperature using ¹⁷O NMR, two peaks were observed, but the peak due to the bound water overlapped the bulk water peak. The two peaks were separated by the addition of the paramagnetic ion Co(II). Jackson, Lemons and Taube estimated the coordination number of water to aluminum (III) to be about six. A low signal to noise ratio made the determination of the exact coordination number unreliable.

Swineheart and Taube¹⁶ reasoned that methanol coordinated similarly to water and since it is a more massive molecule the exchange rate between bulk and bound solvent should be slower. In 1962 a Mg(ClO_4)₂, methanol system was cooled down to -76^oC and an NMR spectrum showing two peaks, one for the bound and one for the bulk solvent, was obtained. Swinehart and Taube were able to determine a coordination number of 5.7 \pm 0.2 for the Mg⁺²- methanol complex. In 1963 Connick and Fiat¹⁷ were able to use 17 ONMR to find coordination numbers for aluminum and beryllium by using water enriched to 11.48% ¹⁷O. This enrichment technique gave a much better signal to noise ratio than the attempt by Jackson, Lemons and Taube. Coordination numbers found for aluminum was 6.07, 5.95, 5.85 and 5.82 with an average of 5.92.

In 1965 Thomas and Reynolds¹⁸ found that aluminum perchlorate in dimethylsulfoxide (DMSO) gave a bound and bulk signal at room temperature using PMR spectroscopy. They were also the first to use methyl peaks spin-spin coupled to carbon-13 as an internal standard. Coordination numbers with an average of 5.91 \pm 0.33 were reported¹⁹ but a recalculation of published data gave a coordination number of 5.67. Better methods of drying the solutions by Olander, Marianelli and Larson²⁰ gave a coordination number of 6.0 ± 0.2 . In 1966 Fratiello, Schuster and Miller²¹ reported separate

resonance signals for bulk and bound solvent at ambient temperature

for SbCl₅, DMF systems using PMR spectroscopy. They also reported separate signals for bound and bulk solvent in aluminum chloride-DMF systems. 22

In 1967 Movius and Matwiyoff²³ did a detailed study of $A\ell(C\ell O_4)_3$, DMF systems using proton and 27 AlNMR. They found a coordination number of $6.03 \pm .03$ for the Al⁺³-DMF complex.

Fratiello and Schuster²⁴ reported that if the aluminum was in the form of the chloride, bromide or iodide salt, it formed a coordination complex with DMF and with the coordination number equal to approximately 6. The salts were purified by sublimation and the solutions were prepared in a vacuum.

Movius and Matwiyoff²⁵ did a study of anhydrous DMF solutions of aluminum perchlorate and aluminum halides. For the preparations of the aluminum halides, solvent systems, they first made anhydrous Al(DMF)₆ X₃ and then added it to anhydrous DMF. Coordination numbers of six were reported in all cases and the following chemical shifts were observed:

	Free methyl		Coordinated methyl		Free formyl	Coordinated formyl	
	a	b	a'	b'	C	c'	
$Al(ClO_4)_3$	83	93	102	112	398	415	
ALCL3	83	93	103	118	399	448	
AlBr ₃	83	93	104	119	399	440	
All 3	83	93	105	118	399	430	

Chemical shift is in Hz relative to cyclohexane.

Movius and Matwiyoff designated the upfield methyl peak as a, the downfield methyl peak as b and the formyl peak as c. At room temperature the DMF molecule is in a planar form and has the structure²⁶

The following work has been done involving different aluminum salts but in aqueous medium using 27 AL 19 F and 31 P NMR. In 1968 Eppecleim and Lutz²⁷, working with $Al_2(SO_4)_3$, water systems using 27 AlNMR, found a peak next to the larger Al(H₂O)₆ peak which they attributed to $A\ell(H_2O)_5(HSO_4)^{+2}$. Further work done by Akitt²⁸ led him to believe the peak was due to the $A\ell(H_2O_5(SO_4)^+)$ complex. Additions of sulfuric acid gave rise to a third peak. In 1959 Connick and Poulsen²⁹ used ¹⁹F NMR to show that $A\ell F_3$ in H_2O existed as $A\ell F_2^{+1}$ complexes. Eight years later Yamazaki and Takeuchi³⁰ did a low temperature study in which they found a third peak that they attributed to $A\ell F_3$. A fourth peak was found by Matwiyoff and Wageman³¹ which they attributed to $A\ell F_4^{-1}$. They also did a PMR study on AlF3, $\rm H_2O$ systems at -25 $^{\rm O}C$. Studies of the bound and bulk

signal showed that the complexes are best represented by the formulas:

 $A\ell(H_2O)_5F^{+2}$, $A\ell(H_2O)_4F_2^{+1}$ and $A\ell(H_2O)_3F_3$. A hydration number for the $A\ell F_4^{-1}$ complex could not be determined.

An²⁷Al and ³¹P study of AlPO4, H₂O systems done by Akitt³² showed that the aluminum III complexes with the phosphoric acid. With concentrations of .4 moles of acid to .1 mole of aluminum III, all of the $A\ell^{+3}$ was tied up with the acid. At these concentrations the $Al(H_2O)_6^{+3}$ peak in the ²⁷AlNMR spectrum completely disappeared. At concentrations on the order of 9.5 to 1 (phosphoric acid to aluminum), the aluminum complex had a molar ratio of 1 to 3. By changing the concentration of phosphoric acid to aluminum salt, Akitt was able to observe different Al^{+3} , phosphoric acid complexes.

Indirect NMR Methods

There are other methods using NMR which give coordination numbers indirectly. One method developed by Malinowski and Knapp³³ can be used when there is no signal separation between bulk and bound solvent. It involves the shift of the proton signal with temperature change and the concentration change of the salt. The shift of the proton signal, S corr. sol. (corrected solution for differences in volume magnetic susceptibility) is given by the equation:

$$S$$
 corr. sol. = $\chi_N S_N + \chi_s S_s$ (4)

S $_{\rm N}$ is the chemical shift of pure water or solvent relative to ethane or other internal standard, and $\mathcal{S}_{\rm s}$ is the chemical shift of

the hydrated form. $\chi_{
m N}$ is the mole fraction of the solvent not coordinated. X_s is the mole fraction that is coordinated. The moles of salt is given by m. Letting χ_N = (55.55 -mn)/55.55, χ_s = mn/55.55, and solving for the coordination number n, the following equation is obtained when the solvent is water:

n =
$$\frac{(55.55)}{m}$$
 [(Scorr.sol. - S_N)/(S_s - S_N)] (5)

ordination number of NaC&water systems. Using the same technique on $Al(NO_3)_3$ -water systems, they obtained a value of 13.4 ± 0.9 for the coordination number³⁴. Malinowski and Knapp suggested that their value could be due to a secondary layer of water molecules about the $A\ell^{+3}$ ion or hydration of the nitrate ion. Akitt³⁵ suggested that their value of S_s is in error and if corrected gives a value for n of about six. Aqueous solutions of ${\rm A}\ell({\rm NO}_3)_3$ have been studied by Matwiyoff, Darby and Movius³⁶ at low temperatures. A coordination number of 6.01 ±.02 in 2.1 molar solutions was found using NMR.

An empirical method was developed by Swift and Sayre³⁷ in which line widths of bound solvent peaks of ions of known hydration number are compared with line widths of bound solvent peaks of ions of unknown hydration number. This empirical method gave hydration numbers of several ions such as H^+ (0.1), NH_4^+ (0), Mg^{+2} (3.9), Ca^{+2} (4.5), $\operatorname{Sr}^{+2}(5.0)$, $\operatorname{Ba}^{+2}(5.7)$, $\operatorname{Zn}^{+2}(3.9)$, $\operatorname{Cd}^{+2}(4.6)$, $\operatorname{Hg}^{+2}(4.9)$ and $Pb^{+2}(5,7)$ with an uncertainty of ± 0.3 in each.

Malinowski and Knapp obtained values of about four for the co-

EXPERIMENTAL

Materials

Reagent Grade Chemicals were used in all cases. Electrolyticlly purified cooper metal, aluminum wire, sodium a cetate, aluminum sulfate, ethylenediaminetetraacetic (EDTA) and DMF were obtained from Fisher. Aluminum nitrate, anhydrous aluminum chloride, acetic acid, hydrochloric acid, ammonium hydroxide, phosphoric acid were obtained from Mallinckrodt. Hydrated aluminum chloride was obtained from Allied Chemicals. Aluminum perchlorate was obtained from City Chemical Corporation. Baker 7-(4-sulfo-1-naphthylazo)-8 hydroxyquinoline-5 sulfonic acid, [4-HOSO₂C₁₀H₆-1-N-N-7-C₆H (8-OH-5-SO₃H)N:CHCH:CH], F.W. 459. 47 (SNAZOX) was used to prepare the indicator solution.

Analysis of Aluminum

To determine the effect of the anion on the Al^{+3} , DMF systems, the aluminum ion concentration must be known. It is difficult, however, to determine the concentration of Al^{+3} directly. EDTA complexes very well with Al^{+3} in a one to one ratio but a suitable indicator for a direction titration is not available. Copper (II) ion forms a colorless complex with EDTA but forms a colored complex with the indicator SNAZOX³⁸. A known amount of EDTA greater than the moles of $A\ell^{+3}$ is added to an aluminum unknown at a pH of about 2. The pH is then adjusted to 4.6, and the excess EDTA is back titrated with a standard Cu^{+2} solution. Near the end point the pH is kept at 4.6 by using acetic acid or ammonium hydroxide. The end point comes when the uncomplexed SNAZOX complexes with the excess Cu^{+2} ion giving a yellow color. In checking the technique using a known $A\ell C \ell_3$ standard a difference of 0.2% was found (Table 1).

Table 1. Chec	ek on the	method
Weight of alum	inum	Volum
.3142g		
Volume Cu ⁺²	Volume	$A\ell^{+3}$
5.57ml	.950	ml
5.58 ml	.950	ml
5.56 ml	.950	ml
$[Cu^{+2}] = .01002$	М	% di
[EDTA]=.01000	М	

Two drops of SNAZOX indicator was added in each analysis.

The aluminum analysis was also checked to determine the effect of DMF and none was found (figure 3). There was an error of $\pm .0001$ M in the determination of $A\ell^{+3}$ concentration which could be due to experimental error when DMF was present. When the actual determinations of aluminum were made the amount of DMF was less than 14%.

 od of aluminum analysis

 ne of $A\ell C\ell_3$ solution
 $[A\ell^{+3}]$

 250.0 ml
 .04658 M

 Volume EDTA
 Average $[A\ell^{+3}]$

 10.00 ml
 .0465 ±.0001 M

 10.00
 .0465 ±.0001 M

ifference in weighted and analyzed [Al⁺³] 0.2%



Figure 3. Effect of Concentration of DMF on Al^{+3} Analysis. Al(NO₃)₃ solution.

EDTA was weighed out directly and used as a standard. Electrolytically purified copper metal was weighed out, dissolved in nitric acid, diluted to a known volume and then standardized with EDTA. The acetate buffer was made by adding 69 grams of sodium acetate and 5.7 ml of glacial acetic acid to water and diluting to 500 ml.³⁹ The exact pH of 4.6 was reached by adding more acetic acid and monitoring the pH with a pH meter.

SNAZOX indicator was prepared by saturating DMF with SNAZOX powder.

The aluminum standard was made by dissolving a weighed aluminum wire in HC ℓ and diluting to volume.

Preparation of Samples

The aluminum salts were purified when possible. $Al(ClO_4)_3$ and $Al_2(SO_4)_3$ were recrystallized twice from a saturated water solution. Reagent grade $Al(NO_3)_3$ was used without purification. Aluminum orthophosphate⁴⁰ was prepared by dissolving aluminum in phosphoric acid. The solution was diluted with distilled water and filtered to remove any undissolved aluminum. The filtrate was neutralized with NH₄OH and the precipitate which resulted was washed with distilled water. Both anhydrous and hydrated aluminum chloride were used to prepare the aluminum chloride, DMF solutions. In preparing the samples the salt was weighed to give an approximate concentration and then added to purified DMF. Anhydrous aluminum chloride was weighed in a glove bag.

Since DMF decomposes at its normal boiling point, it was purified by vacuum distillation. The first and last 10% portions were discarded.

Drying the potentially explosive sample of $A\ell(C\ell O_4)_3$ in DMF was accomplished by a method similar to that of Arthur, Haynes and Varga 41 . The solution was refluxed through Davidson molecular sieve (the molecular sieve selectively takes water out of the solution), pore size 3A and 5 - 12 mesh beads. The solution was refluxed at about 40 - 50° C under a reduced pressure of about 2 cm of mercury. The sample was heated by means of an electric heating mantel and stirred by a magnetic stirrer (Figure 4). The solvent vapors passed through the side tube of the Soxhlet extractor and were condensed by the water-cooled condenser. The condensate passed through the molecular sieve and returned to the drying flask by means of the siphon tube. A glass wool screen kept the beads of molecular sieve from the siphon tube. The liquid nitrogencooled trap was used to protect the pump from volatile compounds as the solutions were being dried. The pressure was maintained by adjusting both the dry nitrogen flow into the system and the pumping rate.

Two methods were used to determine water in the samples. The first method was Karl Fisher titrations⁴². Stabilized Karl Fisher



Figure 4. Drying Apparatus.

reagent was used in conjunction with a Corning Model 10 pH meter equipped with platinum electrodes. The end point was determined by two methods, visual and potentiometric. Solutions were titrated in a wax sealed beaker. The limits of detection of water were about .016 $mg/m1 \pm .002$. At the end point one drop would turn the solution from yellow to brown and also there was a sharp change in the -mv scale readings.

The second method used was NMR spectroscopy. By adding a small amount of water to a solution the position of the water peak was determined. See figure 5. The single sharp peak downfield from the two large methyl peaks is the water peak. Also the water peak can be seen in figure 8.

Calculation of the water concentration is similar to that of the coordination number. The concentration of the internal standard, the carbon-13 methyl group, is obtained by multiplying the concentration of the DMF by 1/2 the carbon-13 concentration.

$$[{}^{13}CH_3] = (12.92 \text{ M}) (.00554)$$
 (6)

To obtain the concentration in moles of hydrogen, equation 6 is multiplied by 3.

$$[H] = (12.92 \text{ M}) (.00554) (3) \tag{7}$$

The concentration of hydrogen in the water signal is given by

equation 8.

[H] = (12.92 M) (.00554) (3) x
$$\frac{(\text{area of water peak})}{(\text{area of }^{13}\text{CH}_3 \text{ peak})}$$
 (8)
To obtain the water concentration, equation 8 is divided by 2.
[H₂O]=(12.92M)(.00554) $\frac{(3)}{(2)}$ x $\frac{(\text{area of water peak})}{(\text{area of }^{13}\text{CH}_3 \text{ peak}}$ (9)
In the sample that produced the spectrum seen in figure 9, the intration of water was found to be .20 mg/ml. Limits of detect

[H] = (12.92 M) (.00554) (3) x
$$\frac{(\text{area of water peak})}{(\text{area of } ^{13}\text{CH}_3 \text{ peak})}$$
 (8)
To obtain the water concentration, equation 8 is divided by 2.
[H₂O]=(12.92M)(.00554) $\frac{(3)}{(2)}$ x $\frac{(\text{area of water peak})}{(\text{area of } ^{13}\text{CH}_3 \text{ peak}}$ (9)
In the sample that produced the spectrum seen in figure 9, the entration of water was found to be .20 mg/ml. Limits of detect

conce tion of water were determined to be less than 0.10 mg/ml. In dried samples the portion of the spectrum where water would appear was completely flat (Figure 7-8).

Tuning of the NMR Instrument

The NMR instrument was tuned using a sealed sample of ethylbenzene which contained a small amount of tetramethylsilane (TMS). The instrument was adjusted to give maximum peak height and resolution of the methyl group. Ringing was maximized using the TMS peak. Spinning of the sample tube was started at this time so the sample was in a more uniform magnetic field. After the instrument was tuned, the ethylbenzene sample was replaced by the DMF solutions. The tuning of the instrument was checked occasionally during the recording of the spectra. To obtain the spectrum of the bound DMF and the carbon-13



Windmont mann Wington Man minist

methyl peak that were used for area measurements, the sweep width was reduced by a factor of ten and the signal was amplified for maximum signal to noise ratio. The relative areas under the peaks were obtained by planimeter measurements of no less than 5 spectra. The integrator on the NMR instrument was not used because of the noise at high amplification and the proximity of the bulk signal.

Lower temperature operation was accomplished with the NMR instrument by using accessories which utilize liquid nitrogen for cooling.

RESULTS AND DISCUSSION

The first portion of the research was to evaluate the JEOLCO C-60H Nuclear Magnetic Resonance instrument at Appalachian State University. This was done by determining the coordination number of a known system. The $A \not(DMF)_n (C \not O_4)_3$ complex used for this purpose has been studied by several workers and the value of n was found to be six. 43, 44

JEOLCO instrument at ASU, reagent grade DMF and $A\ell(C\ell O_4)_3$ were used without purification and low coordination numbers, on the order of 2.6, were measured. After purification of DMF and $Al(ClO_4)_3$ low coordination numbers (3 - 4) were still obtained. In work done by Olander, Larson and Marianelli⁴⁵, it was shown that small amounts of water in $DMSO-Al(ClO_4)_3$ systems did not greatly affect the coordination number. It was found that in mole ratios, [DMSO] to $[H_2O]$ of 67, n was essentially six. It was erroneously assumed that small amounts of water in solution of DMF and $A\ell(C\ell O_4)_3$ would not affect the coordination number. In the spectrum shown in figure 9, the water peak is visible slightly downfield from the downfield bound peak of DMF. For this sample the mole ratio, [DMSO] to [H₂O], was calculated to be about 800 and gave a coordination number of 5.3. Assuming that all the water visible was coordinated with the aluminum, a total coordination number of 5.9 for

In the first attempt to determine a coordination number using the

both DMF and water was calculated. After drying the samples until no water peak showed on the spectra (24 hours), a coordination number of 5.9 ± 0.2 was found. Figure 7 is an example of bound DMF in a dry $Al(ClO_4)_3$, DMF solution. Since the sum of water and bound DMF gave a coordination number of 5.9 or almost 6, similar experiments could be used to determine the coordination number for water - Al^{+3} complexes at low concentrations of water at room temperature. A technique which could be useful to determine if all the water were bound to the aluminum would be to vary the concentration of water and observe any shift in the water peak. As long as all water is complexed the signal will be stationary. If uncoordinated water is present, the signal will shift.⁴⁶

Another problem that was encountered can be seen in figures 9 and 10. Both ${}^{13}C$ methyl peaks should be the same size but the upfield peak is larger than the other. It was discovered later in the research that the larger ¹³C methyl peak is actually two peaks. It was also determined that the extraneous peak was one of four peaks that are symmetrical to the two large bulk solvent peaks (two on either side, having a separation of 120 Hz or 60 Hz from the corresponding large bulk DMF peak). Since the peaks are symmetrical, they probably are not due to any impurity. Spin-spin coupling between the proton and nitrogen-15 was proposed but Becker⁴⁷ gives J for the N-CH₃ bond at only 1 - 3 Hz. No mention of these symmetrical peaks has been found in the literature.



Also, peaks with the same separation were found at times in the ethylbenzene spectra. Since the frequency of the extraneous peaks had a separation from the corresponding bulk peak of 60 Hz, the possibility exists that they are related to the AC line current and are particular to the NMR instrument. Only the ¹³C methyl peak without the extraneous peak could be used as an internal standard.

A minor problem was the identification of the spinning side bands. This was accomplished by changing the spinning speed of the sample as seen in figure 10. They also had to be positioned so as not to hide any other peak such as a small water peak.

Another form of side bands was observed (figures 11 and 12). They appear as two symmetrical peaks, one on either side of the two bulk signals. They grow smaller but do not change position and the other side bands grow larger and move outward as the spin speed is increased (figure 11). This form of side band was first noticed in an $Al_2(SO_4)_3$, DMF solution as seen in the lower spectrum (figure 12). Problems with the spinning mechanism may have caused this type of side band.

Problems of instability of the power supply were also encountered at times. The instability presented itself as a large increase in background noise and the NMR instrument was impossible to tune. It was corrected at times by turning the power supply off and then on again.



Figure 12. $Al_2(SO_4)_3$ DMF.

It was found that the transmitter signal intensity had an effect on the coordination number (figure 13). The sample used to obtain figure 13 had an $A_{\ell}(NO_3)_3$ concentration of $.01949 \pm .00004$ and the average ratio of bound DMF to carbon-13 methyl peak of $1.6 \pm .1$ at 50 decibels (db). This gave a coordination number of $6.0 \pm .4$. At 46 db signal intensity, the coordination number goes up. (As the number of decibels goes down, the transmitter signal intensity increases.) The increase in the coordination number is probably due to saturation (decreased signal area) of the smaller peak. At 36 db the coordination number is down again probably due to equal saturation of the carbon-13 methyl peak and bound DMF. A frequency of 50 db was used for collecting data.

T The second portion of the research was to determine the effect of the anion on the coordination number. The $A l^{+3}$ ion in the presence of the perchlorate anion formed a coordination compound with DMF with a coordination number of 5.9 ± .2.

The next anion studied was the chloride ion. Anhydrous aluminum chloride reacted violently with DMF. An attempt to dry a hydrated aluminum chloride, DMF sample yielded a white precipitate in the DMF. A NMR spectrum of these solutions showed no $A\ell^{+3}$ -DMF complex. The white precipitate dissolved in dilute acid and was assumed to be aluminum hydroxide. In the refluxing of the solution during the drying process, HC ℓ was probably lost according to the equation:

 $A \ell^{+3} + 3 C1^{-} + 3H_2O \implies A \ell(OH)_3 \downarrow + 3HC1 \uparrow$





The third aluminum salt attempted was $A \ell (NO_3)_3$. The drying technique worked very well and it was found that the aluminum ion formed a complex with the DMF in the presence of the nitrate ion.

The coordination number remained fairly constant over the range of concentrations tested as seen in figure 14 and the average was found to be 5.7 ± 0.4 . The difference between n = 5.7 and n = 6 could be explained by experimental error, a small amount of water in the sample (not visible as a separate peak) or it could be that the NO₃⁻ ion is spending some time in the coordination sphere. Since no excess HNO₃ was added, a certain amount of hydrolysis could have occurred. ⁴⁸

Movius and Matwiyoff⁴⁹ found that the position of the bound peak depended on the halide ion (see page 10). The bound peaks for the $A \overset{*3}{\ell}$ -DMF complex, when the nitrate salt was used, were in the same position as when the perchlorate salt was used.

Solutions of $A \ell_2(SO_4)_3$, DMF were made and dried. At room temperature there was no indication that the aluminum ion formed a complex with DMF in the presence of the sulfate ion. The temperature was lowered to -50°C and still there was no indication of bound DMF (Figure 12).

Workers researching $Al_2(SO_4)_3$, H_2O systems have shown⁵⁰ that not all of the Al^{+3} is in the form of $Al(H_2O)_6^{+3}$ complex. Using





 27 Al NMR, a second weak signal was found upfield from the 27 Al(H₂O) $_6^{+3}$ signal which was attributed to the ${}^{27}A\ell(H_2O)_5(SO_4)^{+1}$ ion. The cation in question in the DMF system might be totally $A\ell(SO_4)^{+1}$, which may not cause a noticeable shift of bound DMF in the proton NMR spectrum.

A solution of $AlPO_4$, DMF was attempted but aluminum phosphate was found to be insoluble in neutral DMF. The neutral solution was acidified by the addition of phosphoric acid and the aluminum phosphate dissolved; however, no bound DMF appeared in the NMR spectrum. Akitt, Greenwood and Lester⁵¹, investigating Al^{+3} , PO_4^{-3} and H_2O systems, found that as the PO_4^{-3} ion is increased, the ${}^{27}A\ell(H_2O)_6^{+3}$ peak decreases. Both ²⁷Al and ³¹P NMR were used. The paper did not state the anion in the case of the initial aluminum salt. Similar aluminumphosphate complexes would be expected to form in DMF.

Conclusion

By the use of $Al(ClO_4)_3$ salt in DMF, it was determined that the JEOLCO JNM-C-60 NMR instrument was sufficiently stable and sensitive to determine coordination numbers.

It was also determined that the drying method using the Soxhlet extractor would not work when the chloride ion was used. The chloride ion was apparently lost as hydrogen chloride gas during the refluxing of the solution. Very small amounts of water do affect the coordination of $A\ell^{+3}$ and DMF. A coordination number of 5.3 was obtained when the

molar ratio of [DMF] to $[H_2O]$ was 800 as compared to a coordination number of $5.9 \pm .2$ of a dried sample.

Aluminum forms a complex with DMF in the presence of the nitrate or perchlorate ion. In the case of the nitrate ion the coordination number was determined to be 5.7 \pm 0.4. The aluminum did not form a complex with DMF, visible to the NMR, when sulfate or phosphate was present.

The anion also affects the formation of a A_{ℓ}^{+3} -DMF complex.

LIST OF REFERENCES

- Pople, J.A., W.G. Schneider and H.J. Bernstein, High-Resolution 1. Nuclear Magnetic Resonance, McGraw-Hill Book Co., Inc., New York, 1959, p. 3.
- 2. Ibid., p. 3.
- 3. Ibid.
- Ibid., p. 52. 4.
- Ibid. 5.
- Becker, Edwin D., High Resolution NMR Theory and Chemical 6. Applications, Academic Press, New York and London, 1969, p. 15.
- 7. Ibid., p. 19.
- 8. Pople, Schneider and Bernstein, op. cit., p. 8.
- 9. Ibid., p. 88.
- Becker, op. cit., p. 86. 10.
- Pople, Schneider and Bernstein, op. cit., p. 227. 11.
- Thomas, S., and W.L. Reynolds, J. Chem. Phys. 44 (8): 3148-9 12. (1966).
- 13. Becker, op. cit., p. 99.
- Thomas and Reynolds, op. cit., p. 3148. 14.
- Jackson, Jasper A., Joe F. Lemons and Henry Taube, J. Chem. 15. Phys. 32 (2): 553-5 (1960).
- Swinehart, J.H. and H. Taube, J. Chem. Phys. 37 (7): 1579-80 16. (1962).

- 17. Connick, Robert E. and Daniel N. Fiat, J. Chem. Phys. 39(5): 1349-51 (1963).
- 18. Thomas and Reynolds, op. cit., pp. 3148-9.
- 19. Ibid., p. 3148.
- 20. 41 (8): 1097-99 (1969).
- 21. Fratiello, Anthony, Ronald Schuster and Don Paul Miller, Mol. Phys. 11 (6): 597-8 (1966).
- Fratiello, Anthony, Don Paul Miller and Ronald Schuster, Mol. 22. Phys. 12 (2): 111-16 (1967).
- 23. Movius, W.G. and N.A. Matwiyoff, Inorg. Chem. 6 (4): 47-9 (1967).
- 24. Fratiello, Anthony and Ronald Schuster, J. Phy. Chem. 71 : 1948-50 (1967).
- 25. Movius, W.G. and N.A. Matwiyoff, J. Phys. Chem. 72 (8): 3063-6 (1968).
- 26. Ibid., p. 3064.
- 27.Akitt, J.W., Ann. Rep. NMR (Nucl. Magn. Resonance) Spectrosc. 5A, 465-556 (1972).
- 28. Ibid., p. 483.
- Connick, Robert E. and Richard E. Poulson, J. Phys. Chem. 29. 63 (4): 568 (1959).
- 30. Akitt, op. cit., p. 484.
- 31. Matwiyoff, N.A. and W.E. Wageman, Inorg. Chem. 9 (5): 1031-36 (1970).
- 32. 2450-7 (1971) p.-2451.

Olander, D.P., R.S. Marianelli and R.C. Larson, Anal. Chem.

Akitt, J.W., N.N. Greenwood and G.D. Lester, J.Chem. Soc. (A)

- 33. Malinowski, Edmund R. and Paul S. Knapp, J. Chem. Phys. 45 (11): 4274-9 (1968).
- Malinowski, Edmund R. and Paul S. Knapp, J. Chem. Phys. 34. 48 (11): 4989-91 (1968).
- 35. Akitt, op. cit., p. 475.
- 36. Matwiyoff, N.A., P.E. Darby and W. G. Movius, Inorg. Chem. 7 (10): 2173-4 (1968).
- 37. Swift, T.J., and W.G. Sayre, J. Chem. Phys. 44 (9): 3567-74(1966)
- 38. Guerrin, Georgette, Mary V. Sheldon and Charles N. Reilley, Chem. Anal. 49: 36-7 (1960).
- 39. Ibid., p. 37.
- 40. CRC Handbook of Chemistry and Physics 50th edition. Cleveland, Ohio: The Chemical Rubber Co., 1969-70, p. B-84.
- Arthur, Paul, W.M. Haynes and L.P. Varga, Anal. Chem. 38: 41. 1630 (1966).
- 42. Pietrzyk, Donald J. and Clyde W. Frank, Analytical Chemistry An Introduction. New York and London: Academic Press, 1974, p. 384.
- 43. Olander, Donald P., Doctoral Thesis, Lincoln, Nebr.: (1969) p. 60.
- 44. Movius and Matwiyoff, Inorg. Chem. 6 (4): 848 (1967).
- 45. Olander, D.P., R.S. Marianelli and R.C. Larson, op. cit., p. 1099.
- Malinowski and Knapp, op. cit., p. 4990. 46.
- Becker, op. cit., p. 99. 47.
- Swift and Sayre, op. cit., p. 3569. 48.
- 49. Movius and Matwiyoff, J. Phys. Chem. 72 (8): 3064 (1968).

50. Akitt, op. cit., p. 483.

51. Akitt, Greenwood and Lester, op. cit., p. 2451.