COMPLEX COMPOUNDS OF 1,5-DIMETHYLTETRAZOLE AND OF THE 1-METHYL DERIVATIVES OF DIAZOLES AND TRIAZOLES

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY
DELORES MAUREEN BOWERS

1971

This is to certify that the

thesis entitled

COMPLEX COMPOUNDS OF 1,5-DIMETHYLTETRAZOLE AND OF
THE 1-METHYL DERIVATIVES OF DIAZOLES AND TRIAZOLES

presented by

DELORES MAUREEN BOWERS

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date 11/4/71

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ABSTRACT

COMPLEX COMPOUNDS OF 1,5-DIMETHYLTETRAZOLE AND OF THE 1-METHYL DERIVATIVES OF DIAZOLES AND TRIAZOLES

By

Delores Maureen Bowers

Complex compounds of 1,5-dimethyltetrazole, 1-methyl-1,2,4-triazole, 1-methyl-1,2,3-triazole, 1-methylimidazole and 1-methylpyrazole with silver(I) perchlorate were studied in nitromethane and acetonitrile solutions by proton magnetic resonance spectroscopy. The donor proton chemical shifts were measured as a function of the donor-acceptor mole ratio in order to determine the stoichiometry of the complexes formed in solution. The stoichiometry of the 1,5-dimethyltetrazole-silver(I), 1-methylpyrazole-silver(I) and 1-methylimidazole-silver(I) complexes in nitromethane solutions were found to be $[Ag(Lig)_2{}^+]$. In other cases, although evidence was obtained for the complexation reaction, the resulting complexes were quite insoluble in nitromethane. The following solid complexes were isolated for the triazole-silver(I) systems: mono(1-methyl-1,2,3-triazole)silver(I) perchlorate and mono(1-methyl-1,2,4-triazole)silver(I) perchlorate.

From the magnitudes of the proton chemical shifts for each equivalent proton on the ligand molecules measured upon

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complexation with silver ions, it appears that: 1) the 1-methylpyrazole molecule coordinates with the silver ion through the 2-nitrogen, 2) the 1-methylimidazole molecule coordinates with the silver ion through the 3-nitrogen, 3) the 1-methyl-1,2,4-triazole molecule coordinates with the silver ion through the 4-nitrogen, and 4) the 1-methyl-1,2,3-triazole probably coordinates with the silver ion through the 3-nitrogen. In the case of 1,5-dimethyltetrazole, the magnitudes of the changes in the chemical shifts of the 1-methyl and 5-methyl protons upon ligand complexation were approximately the same, therefore, coordination may occur through the 3-nitrogen or have an equal probability of occurring through 2-, 3-, and 4-nitrogen.

The relative donor abilities of the azoles were studied by sodium-23 nmr. Erlich (1) has shown that the varying abilities of non-aqueous solvents to change the electron density of the sodium ion is related to the solvent's donor ability as expressed by Gutmann's (2) donor number (D.N.). In fact, a linear relationship exists between the sodium-23 chemical shift and the donor number of ten different solvents.

Trends in the sodium ion electron density changes in mixed azole-solvent systems were studied by observing the sodium-23 resonance as a function of ligand to sodium ion mole ratios at ligand mole fractions of < 0.10. The solvents employed in this study were nitromethane (D.N. = 2.7), acetonitrile (D.N. = 14.1), acetone (D.N. = 17.0) and pyridine (D.N. = 33.1). The relative donor abilities were observed to be: 1-methy

methylpyrazole

tetrazole.

1. Erlich, R.
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2. Gutmann, V
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to be: 1-methylimidazole > 1-methyl-1,2,4-triazole > 1-methylpyrazole > 1-methyl-1,2,3-triazole > 1,5-dimethyltetrazole.

REFERENCES

1. Erlich, R. H. Doctoral Dissertation, Michigan State University, 1971.

2. Gutmann, V. Coordination Chemistry in Nonaqueous Solvents. Vienna: Springer-Verlag. 1968, and references cited therein.

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COMPLEX COMPOUNDS OF 1,5-DIMETHYLTETRAZOLE AND OF THE 1-METHYL DERIVATIVES OF DIAZOLES AND TRIAZOLES

By

Delores Maureen Bowers

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1971

The autho
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ACKNOWLEDGMENTS

The author wishes to express her appreciation to Professor A. I. Popov for his guidance and encouragement throughout the duration of this investigation, for the use of his laboratory facilities, and most of all for the friendship and the philosophy of science which he imparted.

Special thanks go to my husband, Jim, and to my good friend Ronald Erlich, for their understanding, patience, encouragement and helpful discussions.

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1. A comparative

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LIST OF FIGURES (Cont.)

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Figure

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Figure

LIST OF FIGURES IN APPENDIX II. (Cont.)

ABB

PMT

1,5-DiMeTz

1-Me-1,2,4-Trz

1-Me-1,2,3-Trz

1-MeIz

1-MePz

DMSO

Py

DMF

S

A

D

Lig

D.N.

ABBREVIATIONS USED IN TEXT

PMT	=	Pentamethylenetetrazole
1,5-DiMeTz	=	1,5-Dimethyltetrazole
1-Me-1,2,4-Trz	=	1-Methyl-1,2,4-triazole
1-Me-1,2,3-Trz	=	1-Methyl-1,2,3-triazole
1-MeIz	=	1-Methylimidazole
1-MePz	=	1-Methylpyrazole
DMSO	=	Dimethylsulfoxide
Py	=	Pyridine
DMF	=	Dimethylformamide
S	=	Solvent molecule
A	=	Acceptor molecule
D	=	Donor molecule
Lig	=	Ligand
D.N.	=	Gutmann's Donor Number

Numerous hetero

interesting physiolo

numerous 1,5-disubst

for their stimulati

system (1,2) which,

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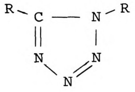
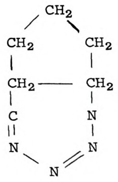
I. INTRODUCTION

Numerous heterocyclic nitrogen compounds possess interesting physiological properties. In particular numerous 1,5-disubstituted tetrazoles (I) are known for



(I)

for their stimulating action on the central nervous system (1,2) which, in certain cases, is strong enough to cause convulsions. Pentamethylenetetrazole (often abbreviated as PMT) (II) is a well known convulsant which has



(II)

been used in shock therapy and also as an agent for the evaluation of the a

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evaluation of the activity of experimental anti-convulsant drugs.

It seems reasonable to assume that the physiological activity of the tetrazoles and other heterocyclic nitrogen compounds is related to their physicochemical properties. On the basis of this assumption a detailed investigation of the physicochemical properties of tetrazoles has been initiated in this laboratory. Since electron donor (or complexing) abilities of tetrazoles may be important for its physiological activity, particular attention was paid to the study of tetrazole complexes. Previous work on these complexes is summarized in the historical section.

It was of interest to us to extend those studies to other nitrogen heterocycles containing two or three nitrogen atoms. The object of the investigation, therefore, was to compare the complexing abilities of a number of nitrogen ring compounds and, if possible, to determine the structure of the complexes in solution. Nuclear magnetic resonance spectroscopy was selected as the primary investigative technique.

Azoles are an

five-membered ring

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Prefixes for azoles

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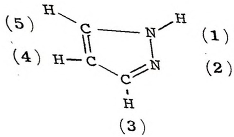
II. HISTORICAL

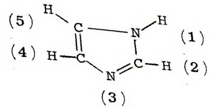
A. Azole Nomenclature

Azoles are an interesting class of polyheteroatomic five-membered ring compounds which contain nitrogen. Azole rings contain one imino nitrogen (-$\overset{|}{N}$-) and at least one tertiary nitrogen (=N-). The ring is further characterized by the presence of two double bonds and three single bonds. Prefixes for azoles describe the number of nitrogen atoms in the ring; therefore, diazole, triazole, tetrazole, and pentazole indicate two, three, four, and five nitrogens respectively. Azole structures are shown in Figure 1. Diazole exhibits two structural isomers, 1,2-diazole or pyrazole (Fig. 1a) and 1,3-diazole or imidazole (Fig. 1b). Ring system numbering begins with the imino nitrogen (usually in the 1- or 2-position) and proceeds around the ring in such a way that all the other nitrogens receive the lowest possible number. The presence of the imino proton and the π-electron system causes some of the azoles to assume two tautomeric forms which are not distinguishable in the parent azoles but which appear when the ring becomes monosubstituted. For example, the triazoles give two ring isomers which can exist as two valence tautomers

DIAZOLES

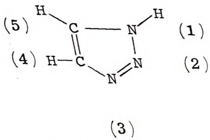


1,2-diazole or pyrazole
(Fig. 1a)

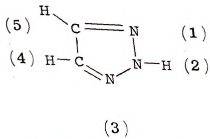


1,3-diazole or imidazole
(Fig. 1b)

TRIAZOLES

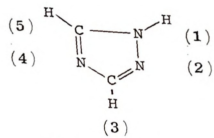


1,2,3-1H-triazole
(Fig. 1c)

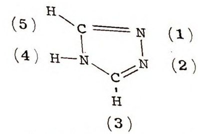


1,2,3-2H-triazole
(Fig. 1d)

1,2,3-triazole or v-triazole



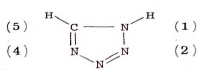
1,2,4-1H-triazole
(Fig. 1e)

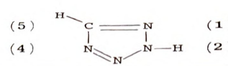


1,2,4-4H-triazole
(Fig. 1f)

1,2,4-triazole or s-triazole

TETRAZOLES





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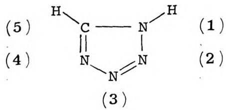
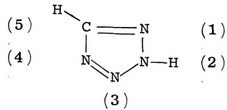
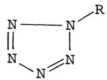


1,2,3,4-1H-tetrazole
(Fig. 1g)



1,2,3,4-2H-tetrazole
(Fig. 1h)

PENTAZOLES



1,2,3,4,5-pentazole
(Fig. 1i)

Figure 1. A comparative view of the azole structures.

(Fig. 1c - 1f). Th

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(Fig. 1c - 1f). The IUPAC nomenclature distinguishes between the possible tautomeric forms by listing the position of the nitrogens on the ring, the position of the imino proton, and then the base name as follows: 1,2,3-1H-triazole (Fig. 1c), 1,2,3-2H-triazole (Fig. 1d), 1,2,4-1H-triazole (Fig. 1e), and 1,2,4-4H-triazole (Fig. 1f). There are also two tautomeric forms for the tetrazole: 1,2,3,4-1H-tetrazole (Fig. 1g) and 1,2,3,4-2H-tetrazole (Fig. 1h). Although the IUPAC nomenclature is normally employed for the triazoles and tetrazoles, the names pyrazole and imidazole are commonly employed for the diazoles.

B. Parent Compounds

The term azole first appears in the literature in the mid 1850s and reappears as more members of the series were discovered. By the end of the century all six of the azole ring structures had been mentioned. Scientists most involved in this work were German, Italian, and Swedish; all interested in organic synthesis. They prepared and characterized derivatives of the parent azoles which, in turn, led to the synthesis and description of the parent azoles.

Diazoles

In 1858, Debus (3) discovered a compound with the empirical formula $C_3N_2H_4$ when he allowed glyoxal and ammonia to react. The compound became known as glyoxaline; this term is occasionally used today. Structural assignment of the two double b

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of the two double bonds and three single bonds with protons at the 1-, 2-, 4-, and 5-positions on the ring is credited to Japp in 1882 (4). This compound was renamed "iminazole" (the British equivalent, imidazole, which is most commonly used today) by the German chemist Hantzsch in 1888 (5). Hantzsch also developed and classified azoles as five-membered polyheteroatomic ring systems containing at least one tertiary nitrogen.

The imidazole nucleus is probably the most widely studied of all the azole rings, because of its natural occurence in biological systems (6). Not only does the imidazole ring appear as part of the amino acid histidine, but it also plays a significant role in medicine as part of the histamine drug family.

In 1885, Knorr (7) introduced the name "pyrazole" to designate the 1,2-diazole nucleus. He derived the name after a comparison with pyrrole, the five-membered double-unsaturated ring with one imino nitrogen and four carbon atoms. The difference in the basic ring structure is the replacement of a methine group (=CH-) next to the imino nitrogen with a tertiary nitrogen (=N-). Knorr also synthesized and characterized many members of the pyrazole family, but Buchner (8) and Balbiano (9) were credited with preparing the parent compound, $C_3N_2H_4$.

Until recently (10) the pyrazole moiety was not known to occur in biological systems. This fact is very surprising since the structural isomer, imidazole, occurs frequently.

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Kost and Grandberg (11) have reviewed the frequency of occurence of the pyrazole moiety and its chemical applicability. They found that initially it was used in the dye and drug industry. More recently the use of pyrazole derivatives in medicine has become more wide spread, specifically because of their new-found bacteriostatic, bacteriocidal, and fungicidal activity. Also pronounced sedative action on the central nervous system (12,13) has been demonstrated for the aryl- and alkyl-pyrazoles.

Triazoles

In 1860 both Zinin (14) and Hofmann (15) synthesized several compounds which were shown to be derivatives of 1,2,3-triazole. The structure of the unsaturated ring was not proposed until 1886 when Pechmann (16) prepared and characterized the simple monocyclic triazole ring. In 1910, Dimroth and Fester (17) also synthesized the 1,2,3-triazole compound by condensation of hydrazoic acid and acetylene at 100^o.

Little is known of the chemical nature of the 1,2,3-triazole and its derivatives, or of their biological activity.

The name "triazole" was first given to the equivalent $C_2N_3H_3$ ring by Bladin (18), when he discovered several substituted 1,2,4-triazole derivatives. His description of the ring system was not correct (19,20), but he still receives the credit for its discovery.

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All known 1,2,4-triazoles have been obtained synthetically (21); this ring moiety has not been detected in natural systems. Certain types of 1,2,4-triazoles, usually members of the fused ring systems, are capable of inhibiting fog formation on photographic emulsions. Some 1,2,4-triazoles are useful as herbicides and stimulants. The most widely studied herbicide is Amizol (3-amino-1,2,4-triazole). The most widely studied stimulant is Azoman (4-cyclohexyl-3-ethyl-1,2,4-triazole), which is about ten times more powerful than Metrazol (pentamethylenetetrazole) as a stimulant (22).

Tetrazole

Because of Bladin's interest in the synthesis of triazoles, it is not surprising that in 1885 he expanded his work to include investigations of five-membered ring systems containing four nitrogen atoms (23). He proposed that these new ring derivatives be called tetrazoles (24). By 1892 he had isolated the parent 1,2,3,4-tetrazole compound (25).

Chemical investigations of tetrazoles have shown that they are nucleophilic reagents whose characteristics vary with the position and type of substitution. This, in turn, is believed to be the reason for the pharmacological variance in the substituted tetrazoles studied by Gross and Featherstone (1) and Stone (2). These scientists have shown that substituted te

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nts, depending on the position and type of substitution.

Pentazoles

Ugi (26) has reviewed the history of pentazole; he has
ted that as early as 1893 Noelting and Michel (27) pro-
ed, but did not isolate or characterize, the first
tazole derivative. All known derivatives are unstable
room temperature and decompose explosively except for
p-dimethylaminophenylpentazole (28) which, according to
authors, is stable for several hours. Because of pent-
le's explosive nature, few chemical and physical proper-
s have been reported, and no chemical applications have
n proposed or tested.

C. General Properties

Since each of the parent azole compounds contains one
o hydrogen and a tertiary nitrogen giving the molecule
polarity, it is not surprising that these compounds
highly associated through hydrogen bonding. This as-
ation can be demonstrated by comparing the boiling
ts of the azoles (b.p. > 187^{o}) with that of 1,3-cyclo-
adiene (b.p. 40.8^{o}), a double unsaturated five-membered
containing only carbon atoms (Table I). These parent
es are amphoteric. They can act as acids and lose
imino proton to stronger bases, or they may act as
by accepting a proton from stronger acids. Values of

pK_a and $pK_{a'}$ for the

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pK$_a$ and pK$_{a'}$ for the various azoles are given in Table I.

Recently Hansen et al. (29) studied the acidic and basic nature of the azoles (with the exception of pentazole) in water. They found that a linear relationship exists between the pK$_a$ and the number of nitrogen atoms in the unsaturated heterocyclic ring. However, the protonation constant, pK$_{a'}$, of these compounds is not a linear function of the number of nitrogens in the ring. Instead, the order of basicity, both from calorimetric experiments and from pH titrations, was observed to be: imidazole >> pyrazole $\cong$ 1,2,4-triazole > 1,2,3-triazole $\geq$ 1,2,3,4-tetrazole. The last two members, 1,2,3-triazole and 1,2,3,4-tetrazole, showed no pronounced signs of protonation by perchloric acid.

Barlin and Batterham (30) investigated a series of imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, and 1,2,3,4-tetrazole compounds by proton magnetic resonance and discussed the spectra of the neutral molecules, the cations, and the anions. The neutral molecules were studied in deuterochloroform, the cations were studied in trifluoroacetic acid, and the anions were studied in 2 N sodium deuteroxide. Some of the 1-methyl derivatives were also investigated. A comparison of their spectra in deuterochloroform and trifluoroacetic acid indicated that the imidazole and 1,2,4-triazole attain cation stabilization through an amidinium type resonance (Fig. 2). After protonation of the 1-methylimidazole in the 3-position, the

Table I. Physical and chemical properties of azoles and their methyl derivatives.

Compound	Empirical Formula	m.p.	b.p.	pK_a Proton Lost	pK_a Proton Gained	ρ (debyes)
1,3-cyclopentadiene	C_5H_6		40.8			
pyrazole	$C_3H_4N_2$	69–70	187–188	14.0[b]	2.53[a]	1.57
[illegible]	[illegible]	88–90	256	14.2[b]	6.95[a]	3.84

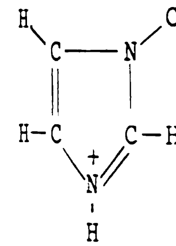
Compound	Empirical Formula	m.p.	b.p.	pK_a Proton Lost	pK_a' Proton Gained	ρ (debyes)
1,3-cyclopentadiene	C_5H_6		40.8			
pyrazole	$C_3H_4N_2$	69-70	187-188	14.0[b]	2.53[a]	1.57
imidazole	$C_3H_4N_2$	88-90	256	14.2[b]	6.95[a]	3.84
1,2,3-1H-triazole	$C_2H_3N_3$	23	240/740mm	9.42[b]	1.17[b]	1.77
1,2,4-1H-triazole	$C_2H_3N_3$	121	260	10.1[c]	2.55[a],2.30[b]	3.17
1,2,3,4-1H-tetrazole	$C_1H_2N_4$	155	sublimes	4.93[d]		5.11
1-methylpyrazole	$C_4H_6N_2$		127			
1-methylimidazole	$C_4H_6N_2$	-6	198-199		7.33[b]	
1-methyl-1,2,3-triazole	$C_3H_5N_3$	15	228		1.25[b]	
1-methyl-1,2,4-triazole	$C_3H_5N_3$	20	178			
1,5-dimethyltetrazole	$C_2H_6N_4$	71-72	sublimes			

[a] Kofmann, K., "Imidazole and Its Drivatives," from The Chemistry of Heterocyclic Compounds, ed. by Weissberger, A., Interscience Publishers, Inc., New York, 1953, Chapter I.

[b] Palmer, M. H., The Structure and Reactions of Heterocyclic Compounds, St. Martin's Press, New York, 1967, Chapter 14.

[c] Hansen, L.D., Baca, E. J. and Scheiner, P., J. Heterocyclic Chem., 7, 991 (1970).

[d] Olivera-Mandala', E., Gass. Chim. Ital., 44, 175 (1914).



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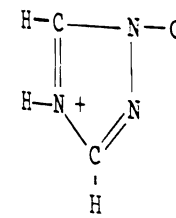

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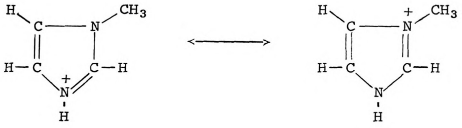
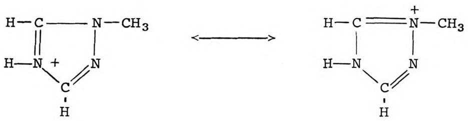


1-methylimidazolium cation



1-methyl-1,2,4-triazolium cation

Figure 2. Amidinium type resonances of the protonated 1-methylimidazole and 1-methyl-1,2,4-triazole.

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for 1-methyl-1,2,
for the 5-proton
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2-proton magnetic resonance shifts downfield by 1.26 ppm, while those of the 1-, 4-, and 5-protons shift only 0.42, 0.52, and 0.64 ppm respectively. The 2-position was affected much more because of the full positive charge associated with that position by the amidinium type resonance, while the other positions felt only a fraction of the effect of the large charge density. A similar relationship was demonstrated for the 1-methyl-1,2,4-triazole, where the protonation occurred at the 4-position producing an amidinium resonance about the 5-position. The localization of the charge density is noted from the magnitude of the downfield shifts of 1.41, 0.81, and 0.34 ppm for the 5-proton, 3-proton, and the 1-methyl protons respectively. The 1-methyl-1,2,3-triazole and the 1-methyl-1,2,3,4-tetrazole proton chemical shifts were also given, but no assignments of possible cation stabilization or specific site of interaction were made. The downfield shifts for the 1-methyl-1,2,3-triazole were 0.79, 1.29, and 0.37 ppm for the 4-proton, 5-proton, and the 1-methyl protons respectively; for 1-methyl-1,2,3,4-tetrazole, they were 0.90 and 0.27 ppm for the 5-proton and 1-methyl protons. Data for the pyrazole system were not given, but the authors did include pyrazole in their summary of data for chemical shift values for azoles in fourteen different solvents.

Pugmire and Grant (31) have also studied the cationic and anionic forms of the parent azoles by using carbon-13 nmr. They applied extended Hückel and self-consistent-field molecular wavefun

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molecular wavefunctions to both the σ- and π-electrons to explain the observed shifts of the carbon-13 resonance in relation to the charge densities and bond orders of the protonated and dissociated forms of the nitrogen heterocycles. Lynch (32) performed a similar experiment and reported a linear relationship between the carbon-13 chemical shifts and the proton chemical shifts with the Hückel π-electron densities of the diazoles and triazoles.

D. Methyl Derivatives of Azoles

To negate acidic properties of azoles used in this study, derivatives which did not contain a free imino hydrogen were investigated. The 1-methyl derivatives were selected because of their structural simplicity. However, in the case of tetrazole, the 1,5-dimethyl derivative was used in an attempt to determine the coordination site.

1-Methylpyrazole

The 1-methylpyrazole ligand was first synthesized by Wedichen (33) by reaction of methyl iodide and the parent pyrazole. Methyl hydrazine (34) has also been used to synthesize this ligand. The properaties of 1-methylpyrazole were not studied extensively until the mid 1900s. Mangini and Casoni (35) reported that the absorption spectrum of 1-methylpyrazole had an absorption maximum at 214 nm which shifted only slightly upon protonation. Zerbi and Alberti(36) identified the infrared spectrum of 1-methylpyrazole for the region from 20

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the region from 2000-600 cm^{-1}. Strong bands occurring at 1050 and 940 cm^{-1} and a weak doublet occurring at 675 and 650 cm^{-1} were shown to be good indicators of the presence of a monosubstituted pyrazole ring. The 1-substituted pyrazoles were also different from other substituted pyrazoles because they contained distinctive bands at 1520, 1397, 1279, cm^{-1}; a doublet at 1100 and 1180, and a very strong band at 755 cm^{-1}.

Broadus and Vaughan (37) subsequently studied the dipole moments of 1-methylpyrazole in nine different solvents. When the dipole moment of the azole was plotted as a function of the dielectric constant of the solvents, a smooth curve was not observed. The deviations were attributed to the weak donor-acceptor interactions of 1-methylpyrazole and the solvent and/or to the ability of the solvents to form weak hydrogen bonds with the 2-nitrogen of the pyrazole ring.

With the development of nmr as an instrumental tool, 1-methylpyrazole proton magnetic resonance assignments in various solvents were investigated. Prominent investigators in this field of study were Batterham and Bigum (38), Elguero et al. (39), Cola and Perotili (40), and Bystrov et al. (41). Rees and Green (42) studied the carbon-13 nmr of this ligand and reported the chemical shifts of the pure ligand with respect to the benzene resonance an external standard.

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Although some work has been reported on the protonation the 1-methylpyrazole (30), no coordination compounds ve been reported.

1-Methylimidazole

That the imidazole moiety occurs in an amino acid and several biologically active substances is known. However, ttle is known about the biological activity of 1-methyl- idazole. It has been shown that this compound changes e pH of biological systems through protein interactions d coordinates with specific receptor sites on biomacro- lecules (43). The 1-methylimidazole also produces con- lsions in rabbits when administered in doses of 45 mg/kg, d it is lethal at doses of 75 mg/kg (44).

The 1-methylimidazole was first prepared by Wyss in 77 (45). Several of its physical properties are listed Table I. Perchard and Novak (46) have reported the frared and Raman spectra from 4000-200 cm^{-1} for 1-methyl- idazole, 1-methylimidazole-d_3, and 1-methyl-d_3-imidazole. ey also reported the vibrational spectra of ligand com- exes (47,48) with zinc(II) halides, copper(II) halides, d silver(I) nitrate between 4000-500 cm^{-1}.

Proton nmr studies have been conducted by Reddy et al. 9). They determined the chemical shifts of 1-methylimid- ole in deuterochloroform (internal reference TMS) and ported values of 7.90, 7.20, and 7.39 ppm for the 2-, 4-, 5-protons respectively. Barlin and Batterham (30)

studied the proton
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tudied the protonation of 1-methylimidazole in trifluoro-
cetic acid by proton nmr and found protonation to occur at
he 3-nitrogen. The fact that the 3-nitrogen is a good
onor site for the coordination of metal ions has been
emonstrated in the investigations of solid complexes (47,
8,50-53). The 1-methylimidazole complexes have been formed
ith silver, magnesium, calcium, manganese, iron, cobalt,
ickel, copper, zinc, and cadmium ions and have the general
ormula $[M(1\text{-MeIz})_n{}^{m+}]$, where n is 2, 4, or 6 and the
harge, m+, is 1 or 2. These complexes have been charac-
erized and identified with the aid of chemical analysis,
-ray powder patterns, ligand field spectra, infrared and
aman spectra, magnetic susceptibility measurements, and
or spectra.

Formation constants for the silver(I) complexes with
-methylimidazole (51,52) have been reported as $\log k_1$ =
.00 and $\log k_2 = 3.89$ at 25^0 for the formation of
$g(1\text{-MeIz})_1{}^{1+}]$ and $[Ag(1\text{-MeIz})_2{}^{1+}]$ respectively. These
nstants were obtained by potentiometric measurements of
I followed by data treatment using Bjerrum's method (54).
uman and Wang (51) also found the heat of complex forma-
on (-15.6 kcal mole^{-1}) by calorimetric methods at 25^0 and
re then able to determine the change in free energy
9.4 kcal mole^{-1}) and the change in entropy (21 e.u.) by
ing the previously reported formation constant for the
action.

The 1-methyl-

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In 1912 Wolff (56)

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picric acid. The

4-position to giv

1-Methyl-1,2,3-triazole

The 1-methyl-1,2,3-triazole was first prepared in 1910
imroth and Fester (55) when they allowed the silver
of the parent triazole to react with methyl iodide.
912 Wolff (56) prepared the ligand by decarboxylating
5-carboxyl-1-methyl-1,2,3-triazole. No extensive in-
igations of the properties of this compound have been
rtaken. Elguero et al. (57) have investigated the nmr
acteristics of 1,2,3-triazole and its derivatives,
uding the 1-methyl-1,2,3-triazole. They reported posi-
s for the proton absorptions in d_6-DMSO, $CDCl_3$, Py,
, CF_3CO_2H, and pure ligand. To date, no investigations
erning coordination compounds of 1-methyl-1,2,3-triazole
been reported.

1-Methyl-1,2,4-triazole

Pellizari and Soldi (58) first prepared the 1-methyl-
4-triazole in 1905 by alkylation of the sodium salt of
parent azole and by heating N:N'-diformylmethylhydrazine
formamide. Few studies have been performed on this
zole compound. Proton nmr absorptions in $CDCl_3$ and
have been measured and reported by Jacquier et al. (59);
picrate derivatives have also been reported for the 1-
yl-1,2,4-triazole. Greatest downfield shifts of the 5-
otons occurred after interaction of the ligand with
ic acid. Therefore, protonation probably occurs at the
sition to give the 1-methyl-1,2,4-triazolium cation.

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1,5-Dimethyltetrazol

synthesized and pate

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Kaufman *et al*.

1,5-dimethyltetrazol

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tetrazole (66), the

1,5-Disubstitutedtetrazoles

)imethyltetrazole -- The 1,5-dimethyltetrazole was first
esized and patented by A. G. Knoll (60). He allowed
ime to react with hydrazoic acid to produce the 1,5-
hyltetrazole. In 1950, Harvill, et al. (61) prepared
igand by reaction of methylacetamide and hydrazoic acid.
Kaufman et al. (62) measured the dipole moment of the
imethyltetrazole and found it to be of the order of
Debyes. Some other physical properties of this ligand
isted in Table I. McEwan and Rigg (63) have studied
eat of formation and combustion of this ligand at 25^0.
eat of formation of the disubstituted tetrazole
3 kcal $mole^{-1}$) was less than that of the parent
zole (56.66 kcal $mole^{-1}$), although the heat of combus-
(532.19 kcal $mole^{-1}$) was higher than that of the
: tetrazole (219.03 kcal $mole^{-1}$). These data seem to
.te that the 1,5-dimethyltetrazole is much more stable
he parent tetrazole. Markgraf et al. (64) reported
oton magnetic resonance spectra of this ligand in
ochloroform solution (TMS as internal standard) as
two sharp peaks in the ratio of 1:1 observed at
al shifts of 4.05 and 2.58 ppm for the 1-methyl and
yl protons respectively.

oordinating ability of 1,5-dimethyltetrazole has been
ned only once (65) in all the studies reviewed for
ole systems. This seems unusual because the 1-methyl-
ole (66), the 5-methyltetrazole (67), and the

1,5-disubstituted

referred to as **PMT**

have been shown to

Gross and Fea

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,5-disubstituted tetrazole, pentamethylenetetrazole, often eferred to as PMT (68), have been studied extensively and ave been shown to form rather strong complexes.

Gross and Featherstone (1b) have measured the pharmaco- ogical properties of the 1,5-disubstituted tetrazoles and ound that 1,5-dimethyltetrazole is one of the least potent epressants; a dosage of 750 mg/kg had only slight sedative ction on the rat.

entamethylenetetrazole -- The 1,5-disubstituted tetrazole, entamethylenetetrazole (PMT), was first synthesized and aracterized by Schmidt in 1925 (69). Later Knoll im- oved Schmidt's method of preparation and patented the ocedure which is similar to that presently used by Knoll armaceutical Company (70) and Knoll Ltd. in England (71). is synthesis consists of treating cyclohexanone with drazoic acid causing ring expansion and formation of the cyclic ring compound, PMT.

Gross and Featherstone in 1946 (1a) reported the armacological activity of PMT on rabbits and rats. They und the minimum convulsive does for rats was 25 mg/kg, ile the minimum lethal does was 50 mg/kg.

The complex compounds of PMT have been previously idied in this laboratory. This work has recently been nmarized in a review article (68). Complexation of PMT l other 1,5-cyclopolymethylenetetrazoles with such Lewis ds as halogens, interhalogens, silver ions and π-acids e been studied in solution to determine strength of the σ- and π-type inte

tion constants of

PMT and substitute

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The iodine m

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- and π-type interactions of the tetrazole ring. Forma-ion constants of halogen and interhalogen complexes with MT and substituted PMT's (72,73) in carbon tetrachloride olutions as well as formation constants of iodine complexes ith PMT and other cyclopolymethylenetetrazoles (74) in ,2-dichloroethane were determined spectrophotometrically t 25^0. Formation constant values for the iodine mono-hloride-tetrazole interaction were about 2×10^3 $\underline{M}^{-1}$, hile those for the iodine-tetrazole interactions were much ess (1.4 to 2.6 $\underline{M}^{-1}$). D'Itri and Popov (74) measured quilibrium constants for the reaction $Ag^+ + Tz = [Ag(Tz)_2{}^+]$ n aqueous medium at 25^0 by following potentiometrically he silver ion concentration in solutions containing a lver salt and a tetrazole; Tz represents the series of clopolymethylenetetrazoles (trimethylene- through hepta-thylene-). Equilibrium constant values for the silver n-tetrazole interaction were of the order of 1×10^3 $\underline{M}^{-1}$. rmation constant for the PMT complexes with such π-acids tetracyanoethylene, tetracyanoquinodimethane, chloranil, initrobenzene, and trinitrofluorenone (75) were also termined spectrophotometrically in dichloromethane solu-ons at 25^0. Values for the formation constants for the tter systems were very small (0.06 to 1.31 $\underline{M}^{-1}$) and may icate very weak π-type interactions between the π-acids the tetrazole ring.

The iodine monochloride-PMT solid complex was the only ogen complex isolated and structurally characterized.

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M^{II} is Mn, Fe, Co,

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1,2,4-triazole chlo

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ystallographic study by Baenziger, et al. (76) indicated bond between the iodine monochloride and the nitrogen he 4-position (next to the carbon atom on the tetrazole) of the tetrazole ring.

There is little evidence of complexation between transi- metal ions and 1,5-disubstituted tetrazoles (68) except the PMT complexes (77-81). These complexes have the owing general formulae: $M^{II}(PMT)_6(ClO_4)_2$; $(PMT)_4(ClO_4)_2$; $M^{II}(PMT)_2X_2$; and $M^{II}(PMT)_1X_2$, where is Mn, Fe, Co, Ni, Cu, and Zn and X is Cl and Br. lexes containing six PMT molecules per metal ion and perchlorate anion were shown to have an octahedral or orted octahedral structure. They are soluble in water in a number of polar nonaqueous solvents. They melt or npose between 148-240^0, and most probably are ionic in re. However, the mono-PMT complexes with metal halides ess quite different properties. These complexes are uble in polar and nonpolar solvents. They have much r melting or decompositions points than the perchlorate exes. These differences, as well as magnetic suscepti- y and spectroscopic data, indicate that the metal halide exes are probably polymeric and contain halogen bridges force the tetrazole ring into a bridging position. s (82) reported a similar condition for the copper(II) -triazole chloride complex. In this case, copper(II) re octahedrally coordinated; the ring of the triazole le acts as a bridging ligand with two adjacent

nitrogens coordina
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ogens coordinated to two different copper(II) ions, thus
ng long polymeric chains. If a similar structure does
for the PMT-metal halide system, it is the first
case where the tetrazole ring acts as a bidentate
nd.

E. General Theory of NMR

The energy of the resonance frequency of a given
eus obtained by nmr is dependent upon the electronic
onment of that nucleus. It has been shown that elec-
shield the nucleus in such a way that the magnitude
e field felt by the nucleus (H_n) is different from the
ed field (H_0) by a value known as the shielding con-
(σ); therefore,

$$H_n = H_0 (1-\sigma) . \qquad (1)$$

s of the shielding constant are dependent on several
rs. One of the most important factors is the hybridi-
n of the electronic orbitals within the molecule and
lectronegativity of the groups attached to the molecule.
rement of the actual applied field or the field felt
nucleus is very difficult; therefore, a reference
al is employed to measure the difference between the
strength at which the sample nucleus (H_s) and the
nce nucleus (H_r) resonates:

$$H_s - H_r = H_0 (\sigma_r - \sigma_s) . \qquad (2)$$

For a given nmr pr

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Expression 4 can b

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Since $\sigma_s <<< 1$ e

$$\delta = \sigma_s - \sigma$$

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is represented by

tween the field ex

frequency (ν) in H

$$h\nu$$

where h is Planck'

ratio, a constant

a given nmr probe, the total field felt by the nucleus when it undergoes resonance is constant (whether it is he sample or the reference). H_n is only dependent on value of the shielding constant for the particular tronic environment of the nucleus. Thus

$$H_s\ (1 - \sigma_s) = H_r\ (1 - \sigma_r) \qquad (3)$$

h expressed as ratios becomes:

$$\frac{1 - \sigma_r}{1 - \sigma_s} = \frac{H_s}{H_r}\ . \qquad (4)$$

ession 4 can be rearranged and expressed as:

$$\frac{\sigma_s - \sigma_r}{1 - \sigma_s} = \frac{H_s - H_r}{H_r}\ . \qquad (5)$$

e $\sigma_s <<< 1$ expression 5 reduces to:

$$\delta = \sigma_s - \sigma_r = \frac{H_s - H_r}{H_r} \qquad (6)$$

e the difference in the shielding constants of the e and the reference is known as the chemical shift and presented by the symbol, delta (δ). Relationship be- the field experienced by the nucleus (H_n) and the ency (ν) in Hz is expressed by:

$$h\nu = \frac{\gamma\ H_n}{2\pi} \qquad (7)$$

h is Planck's constant and γ is the gyromagnetic a constant characteristic of the given nucleus being measured. Separa

tion is often mea

shift value may b

The values o

are only slightly

probe, ν_0. The e

be written as:

$$\delta =$$

where ν_0 is usu

for proton magnet

difference ν_s -

which allows the

as ppm when subst

Factors with

within the molecu

measurement relat

and solutes, to p

large quadrupole

diamagnetic and p

tion of the total

works which deal

ured. Separation between sample and reference absorp-
is often measured in Hz. Therefore, the chemical
ft value may be written in terms of frequency as:

$$\delta = \sigma_s - \sigma_r = \frac{\nu_s - \nu_r}{\nu_r} \quad . \qquad (8)$$

The values of ν_s and ν_r are large numbers which
only slightly different in frequency from that of the
be, ν_0. The expression for the chemical shift can also
written as:

$$\delta = \frac{\nu_s - \nu_r}{\nu_0} = \frac{\Delta \times 10^6}{\nu_0} \qquad (9)$$

re ν_0 is usually a fixed frequency of 40, 60, or 100 MHz
proton magnetic resonance. The term delta, Δ, is the
ference $\nu_s - \nu_r$ and usually expressed in units of Hz
ch allows the chemical shift value, δ, to be expressed
ppm when substituted into equation 9.

Factors within the equilibrium system, other than those
in the molecule itself, which affect the nucleus under
urement relate to molecular interactions with solvents
solutes, to paramagnetic species, and to nuclei with
e quadrupole moments. These factors are classified as
gnetic and paramagentic effects depending on the direc-
of the total shielding and are discussed in most general
which deal with nmr theory.

F.

Valuable inf
interaction of mo
donor-acceptor sy
netic resonance.
(where A and D
cules and A_nD_m
chemical shift of
the donor molecul
tration. Since t
changing between
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when compared to
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molecules in the
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the acceptor mole
resonance can be

F. Complexation Studies by ^{1}H-NMR

Valuable information pertaining to the structure and teraction of molecular and ionic complexes in the electron nor-acceptor systems may be obtained by using proton mag- tic resonance. For the equilibrium: $nA + mD = A_n D_m$ here A and D represent the acceptor and donor mole- les and A_nD_m the donor-acceptor complex), either the emical shift of the proton nucleus on the acceptor or on e donor molecule can be studied as a function of concen- ation. Since the acceptor and donor molecules are ex- anging between the uncomplexed and complexed states, two change conditions arise. If the exchange is very slow en compared to the life time of the complex, two resonance nes appear. The areas of these lines are proportional to e concentration of the respective complexed and uncomplexed lecules in the system and may be used to calculate the uilibrium constants for the reaction. The position of se lines is determined by the chemical shift values for particular species; assuming the measured nucleus is on eptor molecule, then δ_A, δ_{AD}, δ_{AD_2}, etc. are the chemi- shift values for the free acceptor, the 1:1 complex, the 1:2 complex. However, if the exchange is very fast compared to the life time of the complex, a time-averaged nance is observed. Assuming the measured nucleus is on acceptor molecule, the position of the time-averaged nance can be represented as:

δ_{obs} =

where α, β, a

species at any g

When the la

stoichiometry of

by applying one

1. The che

tion (δ_{obs}) is p

of either the do

concentration is

2. The che

tion (δ_{obs}) is p

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3. The rel

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function of the

The shape c

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*The term Δ_{obs} s
tion 9, but rat
chemical shift
plexed molecule

$$\delta_{obs} = \alpha\,\delta_A + \beta\,\delta_{AD} + \gamma\,\delta_{AD_2} + \text{-----} \qquad (10)$$

ere α, β, and γ are the mole fractions of each
ecies at any given time.

When the latter exchange condition prevails, the
oichiometry of the complex in solution can be obtained
applying one of the following procedures:

1. The chemical shift of the nucleus under investiga-
on (δ_{obs}) is plotted as a function of the concentration
either the donor or acceptor while the other reactant's
ncentration is held constant.

2. The chemical shift of the nucleus under investiga-
on (δ_{obs}) is plotted as a function of the mole ratio of
e donor and acceptor.

3. The relative chemical shift (Δ_{obs})* is plotted as
function of the concentration of the donor or acceptor
lecules while the other reactant's concentration is held
nstant.

4. The relative chemical shift (Δ_{obs}) is plotted as a
nction of the mole ratio of donor and acceptor.

The shape of the plotted function can vary between two
remes: 1. two intersecting lines or, 2. a smooth
ved line. In the first case, two intersecting lines,
composition of the complex in solution corresponds to
represented by the point of intersection. In the other

---

term Δ_{obs} should not be confused with that used in equa-
n 9, but rather equals the difference between the observed
mical shift of the nucleus in the complexed and uncom-
xed molecule thus: $\Delta_{obs} = \delta_{obs} - \delta_A$.

case, a smooth cu

applied to the in

intersect at a po

the complex in so

Once the sto

sirable to evalua

in solution. Han

tigators to devel

quotient (note th

not included in t

librium of the ty

the well-known Be

troscopy (84) to

the chemical shif

(which undergo ra

plexed states) as

tion, they applie

for equilibrium c

by nmr (82) to th

$$\delta^{A}_{obs} - \delta^{A}_{0}$$

The value Q rep

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‡ A similar deriva
molecules are fo

se, a smooth curve, an extrapolation of tangential lines plied to the initial and final portions of the curve will tersect at a point corresponding to the composition of e complex in solution.

Once the stoichiometry has been determined, it is de-rable to evaluate the formation constant of the complex solution. Hanna and Ashbaugh (83) were the first inves-gators to develop a method which gave an equilibrium otient (note that the activity coefficient correction was included in the derivation). They considered an equi-rium of the type expressed in Equation 11 and applied well-known Benesi-Hildebrand method of absorption spec-scopy (84) to the nmr data. Hanna and Ashbaugh considered

$$A + D = AD \qquad (11)$$

chemical shift of the protons on the acceptor molecule* ich undergo rapid exchange between complexed and uncom-xed states) as being concentration dependent. In addi-n, they applied data treatments similar to those used equilibrium constant determination of hydrogen bonding nmr (82) to the complexation equilibrium and showed that:

$$\delta^{A}_{obs} - \delta^{A}_{O} = \frac{[D]\ Q}{(1 - [D])Q} (\delta^{A}_{AD} - \delta^{A}_{O}) \qquad (12)$$

value Q represents the quotient of the concentrations

---

imilar derivation applies if the nuclei on the donor ecules are followed.

of reaction product
chemical shift of t
form, δ^{A}_{obs} is the
protons in the comp
of the acceptor pro
the total concentra
greater than the ac
be simplified to:

$$\Delta^{A}_{obs} = \ldots$$

by expressing the c

$\delta^{A}_{obs} - \delta^{A}_{0}$ as Δ^{A}

The reciprocal form

$$\frac{1}{\Delta^{A}_{obs}} = \frac{1}{\Delta^{A}_{AD}} \ldots$$

This form is analog
However, the concen
and the relative ch
tons in the pure co
tivity of the compl
quotient may be eva
when $\frac{1}{\Delta^{A}_{obs}}$ vs. $\frac{1}{[\ldots}$
complex $(\frac{1}{\Delta^{A}_{AD}})$.

reaction products and reactants, δ_O^A is the observed emical shift of the acceptor protons in the uncomplexed rm, δ_{obs}^A is the observed chemical shift of the acceptor otons in the complexing media, δ_{AD}^A is the chemical shift the acceptor protons in the pure complex AD, and [D] is total concentration of the donor, which is always much eater than the acceptor concentration. Equation 12 can simplified to:

$$\Delta_{obs}^A = \frac{[D]\ Q}{(1 - [D])\ Q} (\Delta_{AD}^A) \qquad (13)$$

expressing the differences of

$\delta_{obs}^A - \delta_O^A$ as Δ_{obs}^A and $\delta_{AD}^A - \delta_O^A$ as Δ_{AD}^A .

reciprocal form of Equation 13 is:

$$\frac{1}{\Delta_{obs}^A} = \frac{1}{\Delta_{AD}^A\ (Q)} \left(\frac{1}{[D]}\right) + \frac{1}{\Delta_{AD}^A} \quad . \qquad (14)$$

s form is analogous to the Bensi-Hildebrand equation. ever, the concentration of the acceptor does not appear, the relative chemical shift value for the acceptor pro- s in the pure complex, Δ_{AD}^A, replaces the molar absorb- ity of the complex. The value of the equilibrium ient may be evaluated from the slope of the line obtained 1 $\frac{1}{\Delta_{obs}^A}$ vs. $\frac{1}{[D]}$ is plotted and extrapolated to pure lex $\left(\frac{1}{\Delta_{AD}^A}\right)$.

It is possible unde

on the donor molecu

methods. Where thi

shift of the accept

Δ^{D}_{AD}, can be determi

measurements on a s

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is quite large; thu

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Two values for

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These are:

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2. Either th
   be greate
   solvent).

3. Nmr absor
   overlap t
   versa if

A second meth

constant for 1:1 a

is possible under certain conditions to study both nuclei the donor molecules and on the acceptor molecules by nmr hods. Where this is possible, the limiting chemical ft of the acceptor nuclei, δ^{A}_{AD}, and the donor nuclei, , can be determined graphically by making chemical shift surements on a series of solutions where the concentra- n of the supporting reactant is varied such that the mole io of the supporting reactant to the measured reactant quite large; thus increasing the amount of the complexed n of the measured molecules and causing the observed nical shift to approach its limiting value, δ^{D}_{AD} or δ^{A}_{AD}.

Two values for the equilibrium quotient can also be ained and should agree with one another. These values ılt from data treatment of two experiments where each of two reactants are held constant while the other is ed. Hanna and Ashbaugh list some criteria for ideal ems in which both the donor and acceptor can be studied. e are:

1. Both donor and acceptor molecules should contain protons (or other magnetic nuclei) which preferably give single sharp lines when the absorption spectra are recorded.

2. Either the donor or acceptor concentration should be greater than the other components (excluding solvent).

3. Nmr absorptions of the donor and solvent should not overlap the absorptions of the acceptor (or _vice versa_ if the donor protons are being studied). (83)

second method for the evaluation of the formation nt for 1:1 acceptor-donor complexes by nmr data has also been proposec

derivation on the

Hammick, and Wardl

expression:

$$\frac{1}{[D]}$$

where Δ correspo

and K correspon

Ashbaugh. Foster

ideal or that the

remains constant

In this method, w

line is obtained

and enables Δ_0

itely dilute solu

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To study com

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is a metal ion, a

should:

1. show a f

donors,

2. have wel

3. be diama

tions of the mea

also been proposed by Foster and Fyfe (86). They base their derivation on the optical method described by Foster, Hammick, and Wardly (87), thereby obtaining the following expression:

$$\frac{1}{[D]} + \Delta K = \Delta_O K \qquad (15)$$

where Δ corresponds to Δ^A_{obs} ; Δ_O corresponds to Δ^A_{AD} and K corresponds to Q in the derivation by Hanna and Ashbaugh. Foster and Fyfe assume that the solutions are ideal or that the activity coefficient quotient $\frac{\gamma_{AD}}{\gamma_A \gamma_D}$ remains constant over the range of solutions being studied. In this method, when $\frac{1}{[D]}$ vs Δ is plotted, a straight line is obtained whose negative slope gives K directly and enables Δ_O to be obtained by extrapolation to infin-
.tely dilute solutions rather than to highly concentrated nes as does the Hanna and Ashbaugh method.

To study complexation in solution by proton nmr, the ıoice of an acceptor is quite important. If the acceptor ; a metal ion, as is the case of this investigation, it ıould:

1. show a fairly strong tendency to complex with weak ıors,

2. have well-defined coordination numbers,

3. be diamagnetic to eliminate magnetic field correc-
ns of the measured resonances,

4. form salts

with low donor prop

Because the silver(

was the most accept

NMR techniques

complexes with silv

and Sheppard (85) u

of the silver(I) ni

hexene in deuterium

perturb the double

single bonds. Quin

silver(I) ion compl

cyclohexene, cis-cy

analogues. The ole

when coordinated to

fact to the stronge

coordination bond.

chemical shifts of

hexene, but-2-ene,

olefin-containing

silver(I) nitrate

containing aromati

which varied with

ferences in the tw

exchange of the si

in the equilibrium

were thought to be

4. form salts which are fairly soluble in solvents
low donor properties.

se the silver(I) ion best met these requirements, it
he most acceptable metal ion for the study.

NMR techniques have been used to study several ionic
lexes with silver(I) salts. As early as 1960, Powell
Sheppard (85) used nmr to study structural properties
ne silver(I) nitrate complex with but-2-ene and cyclo-
ne in deuterium oxide. The silver(I) ion seemed to
urb the double bond of the olefin and not affect the
e bonds. Quinn and VanGilder (89) also studied the
er(I) ion complexes with olefins, such as cyclopentene,
hexene, cis-cyclooctene, and their 1-methyl substituted
gues. The olefinic protons were deshielded by 30-50 Hz
coordinated to the silver(I) ion. They attributed this
to the stronger σ-type than π-type component of the
ination bond. Schug and Martin (90) studied the proton
cal shifts of aqueous silver ion complexes of cyclo-
e, but-2-ene, benzene, and toluene. The nmr spectra of
n-containing aqueous solutions were independent of the
r(I) nitrate concentration. However, aqueous solutions
ning aromatic molecules, produced chemical shift values
varied with the silver(I) nitrate concentration. Dif-
es in the two systems were explained by the rapid
ge of the silver(I) ion between the different species
equilibrium mixture. Species in the aromatic system
hought to be free donor, Ar; 1:1 complex, $Ar-Ag^+$;

1:2 complex, Ar-Ag$_2^2$

shift of the donor

average of the vari

cordingly, where:

The weighting fact

equilibrium constan

which is not the c

1:1 complex is the

by assuming that t

by:

$[Ar]_T = [Ar]_O$

and by plotting th

the total aromatic

a straight line if

complex ($[Ar]_T$ = [

found a linear rel

shift and the tota

and toluene. They

relative chemical

values were 15.6 a

Ag^{1+} respectively

attributed to the

system to the silv

plex, $Ar\text{-}Ag_2^{2+}$; etc. Therefore, the observed chemical f the donor nucleus being measured was written as an of the various ligand environments weighted ac- ly, where:

$$\delta_{obs} = \sum_{i=0}^{n} X_i \delta_i \quad . \qquad (16)$$

ghting factors, X_i, cannot be evaluated unless all rium constants for the system studied are known, s not the case with this system. The fact that the plex is the most predominant one may be established ming that the total aromatic concentration is given

$$[Ar]_T = [Ar]_O + [Ar\text{-}Ag^+] + [Ar\text{-}Ag_2^{2+}] \; \text{-----} \qquad (17)$$

plotting the average observed chemical shift <u>versus</u> al aromatic concentration; this process should yield ght line if the highest complex species is the 1:1 ($[Ar]_T = [Ar]_O + [Ar\text{-}Ag^+]$). Schug and Martin (90) linear relationship between the observed chemical nd the total aromatic concentration for both benzene uene. They were also able to determine the limiting chemical shifts for the pure 1:1 complexes. These were 15.6 and 17.1 Hz for benzene-Ag^{1+} and toluene- pectively when studied at 40 MHz. These shifts were ed to the transfer of electrons from the π-electron the silver(I) ions.

In addition t

studies of silver(I

some stability mea

(91) have re-exami

in aqueous solutio

sion:

$$\Delta = \frac{K \ldots}{1 \ldots}$$

which is similar t

for 1:1 complexes,

of the 1:2 complex

$$K_1 = \frac{\ldots}{[A] \ldots}$$

and

$$K_2 = \frac{\ldots}{[A \ldots}$$

In these studies,

benzene and the do

silver(I) nitrate

centrations. When

determination of t

came quite involve

simplify the expre

$A_1 = K_1 \Delta_1$

$A_3 = K_1$

In addition to structural information obtained by nmr es of silver(I) complexes with various organic ligands, stability measurements have been made. Foreman, et al. have re-examined the silver(I) nitrate-benzene system ueous solution by proton nmr. They derived the expres-

$$\Delta = \frac{K_1\Delta_1[D_0] + K_1K_2\Delta_2[D_0]^2}{1 + K_1[D_0] + K_1K_2[D_0]^2} \qquad (18)$$

is similar to that derived by Foster and Fyfe (86) :1 complexes, except they also consider the formation e 1:2 complex as well,

$$K_1 = \frac{[AD]}{[A]\ [D]} \quad \text{for} \quad A + D = AD \qquad (19)$$

$$K_2 = \frac{[AD_2]}{[AD]\ [D]} \quad \text{for} \quad AD + D = AD_2 \qquad (20)$$

se studies, Foreman et al. defined the acceptor as e and the donor as silver(I) ion, and maintained (I) nitrate concentrations in excess of benzene con- tions. When the 1:2 complex was considered, the ination of the formation constants K_1 and K_2 be- uite involved; therefore, several steps were taken to y the expression. First new terms were defined as:

$$= K_1\ \Delta_1 \qquad A_2 = K_1K_2\ \Delta_2 \qquad (21)$$

$$= K_1 \qquad A_4 = K_1K_2$$

and substituted

$$\frac{\Delta}{D_0} = A_1 +$$

A plot of $\frac{\Delta}{D_0}$ vs

when only the 1:1

$K_2 \neq 0$ the gradi

function:

$$\frac{d(\frac{\Delta}{D_0})}{d\Delta} =$$

The nmr data, in

a least square cu

Δ_1, and Δ_2 are

zene complex, For

and 0.48 kg mole^{-1}

shift values for

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Deb *et al.* (

tion between silv

donors in aceton

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shown that silver

94). When aceton

silver(I) ion co

sumed to be in th

Thus the followi

systems studied:

d substituted into Equation 18 and re-arranged to give:

$$\frac{\Delta}{D_0} = A_1 + A_2 [D_0] - A_3 \Delta - A_4 [D_0] \Delta . \qquad (22)$$

plot of $\frac{\Delta}{D_0}$ vs Δ gives a straight line of gradient $-K_1$ en only the 1:1 complex is present, $K_2 = 0$. However, if $\neq 0$ the gradient of the plot is given by a complex iction:

$$\frac{d(\frac{\Delta}{D_0})}{d\Delta} = A_2 - A_4 \Delta (\frac{dD_0}{d\Delta}) - A_3 - A_4 D_0 . \qquad (23)$$

nmr data, in such cases where $K_2 \neq 0$, are treated by east square curve fitting computer program, and K_1, K_2, and Δ_2 are evaluated. In the silver(I) nitrate-ben- e complex, Foreman et al. (91) obtained values of 2.30 0.48 kg $mole^{-1}$ for K_1 and K_2 and limiting chemical ft values for pure $[Ag_1Bz^{1+}]$ and $[Ag_2Bz^{2+}]$ of 26 and 51 Hz pectively when measured at 100 MHz.

Deb et al. (92) used proton nmr to study complex forma- n between silver(I) ions and nitrogen, oxygen, and sulfur ors in acetonitrile. They modified the Hanna-Ashbaugh ation to include solvent effects. Several workers have wn that silver nitrate is complexed by acetonitrile (93, . When acetonitrile is in large excess as compared to ver(I) ion concentrations, all silver(I) ions are as- ed to be in the 1:2, silver(I) ion-acetonitrile complex. s the following equilibrium was considered for the donor tems studied:

where S repres

represents accep

the donors (indo

molal concentrat

expression:

$$\frac{1}{\Delta_0} = \frac{m_S}{K\Delta_c}$$

for the determin

m_A and m_S wer

solvent and Δ_0

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Observed ch

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the calculated e

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Re-arrangem

(5-1-0)octa-2,5-

sites 1-4) prot

technique (95).

$$AS_2 + D = DAS + S \qquad (24)$$

ere S represents solvent molecules (acetonitrile), A
presents acceptor (silver(I) ions), and D represents
e donors (indol, benzofuran, and benzothiophene). Using
al concentration units, they derived the following
pression:

$$\frac{1}{\Delta_0} = \frac{m_S}{K\Delta_c}\left(\frac{1}{m_A}\right) + \frac{1}{\Delta_c}\left(1 - \frac{2}{K}\right) \qquad (25)$$

the determination of the formation constant, K, where
and m_S were the molal concentrations of acceptor and
vent and Δ_0 and Δ_c were the observed relative chemi-
shift for the donor and limiting relative chemical
ft of the pure complex DAS for the donor protons.

Observed chemical shifts of each proton environment on
se heterocyclic ligands were recorded and used in the
culation of equilibrium constants for each site. Although
calculated equilibrium constant values varied for the
ferent sites on a particular ligand molecule, valuable
ormation was obtained concerning the presence or absence
localized interactions.

Re-arrangement studies of the bullvalene or bicyclo-
1-0)octa-2,5-diene (containing four equivalent proton
es 1-4) protons have been studied using the spin-echo
nique (95). The protons participate in rapid exchange

reactions and th

bonds can be det

presence of the

line width for t

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Rates of bullval

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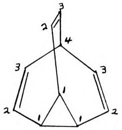
$\delta = 1/2\ \delta_c\{$

where δ is the



actions and the effect of silver(I) ion upon the olefinic nds can be detected. Rate of exchange was slowed by the esence of the silver(I) cation. Also, the steady state ne width for the two active proton sites at 2 and 3 earest the double bonds) was increased upon complexation. es of bullvalene proton exchange were determined to be perature dependent both in the presence of silver(I) ions in the free state. Activation energy for the rearrange-t of bullvalene was shown to be higher when silver(I) s were present.

The univalent potassium cation has also been used in elucidation of formation constants for ionic complexes. stegard and Chan (96) have studied the nature of the ding of potassium(I) ion to macotetrolide, nonactin, by ton magnetic resonance spectroscopy at 220 MHz. They lied a least squares curve fitting program to their nmr a to obtain an apparent formation constant of $7 \pm 2 \times 10^4$ ncentration expressed in mole fraction) for the K^{1+}-actin complex. Their theoretical expression was:

$$\delta = 1/2\ \delta_c\{(1 + \phi + \eta) - [(1 + \phi + \eta)^2 - 4\phi]^{1/2}\} \quad (26)$$

e δ is the observed chemical shift

δ_C is th[e]

state,

ϕ is the

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η is the

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their experiment

They compared th

δ/δ_C vs ϕ with

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Another nov

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species created

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$[D_0] = [A_O]$, the

than under the p

librium constant

can be expressed

δ_c is the observed chemical shift in the complexed state,

ϕ is the stoichiometric concentration ratio of K^{1+} to nonactin,

η is the reciprocal of the apparent formation constant, K, and the stoichiometric nonactin concentration.

The stoichiometric concentration of nonactin was fixed in eir experiments and $KClO_4$ concentration was varied.) ey compared the family of curves derived by plotting /δ_c vs ϕ with their experimental data to obtain the equi- brium constant.

Another novel method for the determination of formation nstants for donor-acceptor complexes by nmr has recently en outlined by Foster and Twiselton (97). The nmr chemi- l shift measurements were obtained on a series of solu- ons where the initial concentrations of the reactants are ried and the acceptor/donor ratio is always 1:1. This ocedure was employed to minimize the use of termolecular ecies created when the reaction conditions are $[D_0]>>>[A_O]$ he usual conditions). Under these new conditions, o] = $[A_O]$, the relative chemical shift is much smaller an under the previous condition, $[D_0]>>>[A_O]$. The equi- orium constant, K , for the formation of the 1:1 complex 1 be expressed as:

$K =$

which combined w

chemical shift,

becomes:

$$\frac{\Delta}{[A_0]}$$

Equilibrium cons

shifts, Δ_0, wer

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Informatio

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Sodium-23

sodium salts in

this laboratory

shift of the sc

$$K = \frac{\frac{[AD]}{[A_O]}}{[A_O] \quad (1 - \frac{[AD]}{[A_O]})^2} \qquad (27)$$

hich combined with the usual expression for the observed hemical shift,

$$\delta = \alpha \quad \delta_A + \beta \quad \delta_{AD} \qquad (28)$$

ecomes:

$$\frac{\Delta}{[A_O]} = K \Delta \left(\frac{\Delta_O}{\Delta} - 2 + \frac{\Delta}{\Delta_O}\right) \quad . \qquad (29)$$

quilibrium constants, K, and limiting relative chemical hifts, Δ_O, were evaluated on both the molar scale and olal scale for a series of values for $[A_O]$ and Δ using computer curve fitting program.

G. Sodium-23 NMR

Information obtained from proton nmr studies on donor cceptor systems is often valuable in the elucidation of olution structure and strength of interaction, but it is ot always obtained directly from the site of interaction. he site of interaction can be studied by using more direct ethods such as sodium-23 nmr.

Sodium-23 nmr is a useful tool in solvation studies of odium salts in non-aqueous solvents. Nmr data obtained in is laboratory (98) have recently shown that the chemical ift of the sodium-23 magnetic resonance is dependent upon

cation-anion and c
anion interactions
solvents having sc
to 0.50 M. The ch
and iodide solutic
while the chemical
tetraphenylborate
to within the limi
to ±0.3 ppm). The
using both sodium
solutions in 10 d
interactions were
the changes in el
shown to be a res
abilities of the
was related to th
proposed a scale
of the reaction (
antimony pentachl
donor numbers (th
solute and solver
the chemical shif
chlorate and tetr
acetonitrile, ace
methylformamide,
phosphoramide, ar
panded this study

cation-anion and cation-solvent interactions. The cation-anion interactions were studied in a variety of non-aqueous solvents having sodium salt concentrations ranging from 0.10 to 0.50 M. The chemical shifts of the sodium thiocyanate and iodide solutions were shown to be concentration dependent, while the chemical shifts of the sodium perchlorate and tetraphenylborate solutions were not concentration dependent to within the limits of detectability of the instrument (up to ±0.3 ppm). The cation-solvent interactions were studied using both sodium perchlorate and sodium tetraphenylborate solutions in 10 different solvents. When the cation-anion interactions were absent from the system under investigation, the changes in electron density around the sodium ion were shown to be a result of solvent interactions. The varying abilities of the solvents to change the electron density was related to the solvent's donor ability. Gutmann (99) proposed a scale of donor numbers defined as the enthalpy of the reaction (Kcal $mole^{-1}$) between a given solvent and antimony pentachloride in 1,2-dichloroethane solution. These donor numbers (the enthalpy of complex formation between solute and solvent) were shown to be linear functions of the chemical shift for the sodium ion for both sodium perchlorate and tetraphenylborate solutions in nitromethane, acetonitrile, acetone, ethyl acetate, tetrahydrofuran, dimethylformamide, dimethylsulfoxide, pyridine, hexamethylphosphoramide, and water. Herlem and Popov (97) have expanded this study to include some very basic solvents (liquid ammonia, e

amine, t-butylamine

quanidine). The hi

more negative the

was saturated aque

resonance; for exa

15.6 ppm; acetone,

29.8, $\delta_{^{23}Na}$ = 0.72

The chemical

been measured in m

phenylborate anion

of the solvents fo

around the sodium(

as that point at w

sodium-23 resonanc

way between the va

value obtained in

an equal solvation

solvents. When a

sodium ion vs the

smooth curve is ob

The study of

should give some

strengths of these

liquid ammonia, ethylenediamine, ethylamine, iso-propyl-
mine, t-butylamine, hydrazine, and 1,1,3,3-tetramethyl-
uanidine). The higher the donor number of the solvent the
ore negative the chemical shift value (external reference
as saturated aqueous sodium chloride) for the sodium-23
esonance; for example nitromethane D.N. = 2.7, $\delta_{^{23}Na}$ =
5.6 ppm; acetone, D.N. = 17.0, $\delta_{^{23}Na}$ = 8.56; DMSO, D.N. =
9.8, $\delta_{^{23}Na}$ = 0.72; and Py, D.N. = 33.1, $\delta_{^{23}Na}$ = -0.72 ppm.

The chemical shift of the sodium-23 resonance has also een measured in mixed solvent systems (98) using the tetra-henylborate anion. The study demonstrates the competition f the solvents for the solvation or coordination positions round the sodium(I) ion. An iso-solvation point was defined s that point at which the chemical shift value of the odium-23 resonance has reached a value 50 percent of the ay between the value obtained in pure solvent A and the alue obtained in pure solvent B. At this point, there is n equal solvation or complexation of the cation by the two olvents. When a plot of observed chemical shift for the odium ion vs the mole fraction of one solvent is made, a nooth curve is obtained.

The study of the azole systems using this technique ould give some information about the relative donor rengths of these ligands.

Nitromethane

Amine impur

grade obtained f

an Amberlite IR-

rate of 1-2 ml p

activated with 7

three 75 ml wash

a column 20 cm l

then washed with

discarded, befor

The eluted nitro

tained from Bari

and fractionally

The boiling poin

to be 101^0 at 7

of 100.8^0 (101)

Acetonitrile

Two liters

grade obtained

III. EXPERIMENTAL

A. Chemicals

Jitromethane

Amine impurities were removed from nitromethane (c.p. jrade obtained from Fisher Scientific) by passing it through in Amberlite IR-120 (acid form) cation exchange resin at a :ate of 1-2 ml per minute. The resin had previously been ictivated with 75 ml of 0.1 N hydrochloric acid followed by :hree 75 ml washings of anhydrous methanol and packed into . column 20 cm long and 1 cm in diameter. The column was :hen washed with about 100 ml of nitromethane, which was iscarded, before the nitromethane to be purified was added. he eluted nitromethane was refluxed over barium oxide (ob-ained from Barium and Strontium Chemicals) for 12 hours nd fractionally distilled directly into dark storage bottles. he boiling point of the purified nitromethane was determined o be 101^{0} at 760 mm, as compared to the literature value f 100.8^{0} (101).

:cetonitrile

Two liters of acetonitrile (A.C.S. analyzed reagent :ade obtained from J. T. Baker Co.) were purified by washing with two

hydroxide solutic

portions of anhy

then decanted an

12 hours. It wa

pentoxide and fr

was determined t

nitrile was stor

sieves until nee

Pyridine

Pyridine (r

and Bell) was dr

followed by frac

The boiling poin

be 101^{0} at 760 m

Other Solvents

Reagent gra

this study were

to use.

Silver Perchlora

Anhydrous s

organics) was us

it was divided

cator to ensure

ashing with two 300 ml portions of saturated potassium ydroxide solution followed by shaking twice with 60 gram ortions of anhydrous sodium carbonate. The solvent was hen decanted and allowed to stand over calcium sulfate for 2 hours. It was then dried by refluxing over phosphorus entoxide and fractionally distilled. The boiling point as determined to be 81.0^{0} at 750 mm. The purified acetoitrile was stored in dark bottles over type 5A molecular ieves until needed.

yridine

Pyridine (reagent grade obtained from Matheson Coleman nd Bell) was dried over barium oxide by refluxing for 12 hr ollowed by fractional distillation into storage bottles. he boiling point of the dried pyridine was determined to e 101^{0} at 760 mm.

ther Solvents

Reagent grade acetone and all other solvents used in his study were dried over type 5A molecular sieves prior o use.

ilver Perchlorate Anhydrous

Anhydrous silver perchlorate (obtained from Alfa Inrganics) was used without further purification. However, : was divided into smaller portions and stored in a desicator to ensure dryness.

Sodium Tetrapheny

Sodium tetra
was used without

Sodium Perchlora

Anhydrous so
organics) was use

Tetrabutylammoniu

Tetrabutylam
method outlined
amounts (0.10 mo
from Eastman Org
dissolved in a m
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tion by the addi
volume of aceton
crystallized fro
until no yellow
tion, about 30 m
by dissolving it
perchlorate; if
butylammonium pe
for 12 hours in

odium Tetraphenylborate

Sodium tetraphenylborate (obtained from J. T. Baker) as used without further purification.

odium Perchlorate

Anhydrous sodium perchlorate (obtained from Alfa Inrganics) was used without further purification.

etrabutylammonium Perchlorate

Tetrabutylammonium perchlorate was prepared by the ethod outlined by Coetzee and McGuire (102). Equivalent mounts (0.10 mole) of tetrabutylammonium iodide (obtained rom Eastman Organic Chemicals) and sodium perchlorate were issolved in a minimum amount of acetone. The tetrabutylmmonium perchlorate was precipitated from the acetone soluion by the addition of 10 volumes of ice water to each olume of acetone present. The solid was isolated and recystallized from acetone-water mixtures several times, ntil no yellow iodide residue was observed. A samll porion, about 30 mg, was tested for the presence of the iodide dissolving it in acetone and adding a solution of silver erchlorate; if no silver iodide was detected, the tetraitylammonium perchlorate was dried in a vacuum oven at 80^0 r 12 hours in the presence of phosphorus pentoxide.

Hydrazoic Acid

A solution

by the method o

sodium azide (2

The mixture was

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point.

CAUTION: Hydra

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1,5-Dimethylte

The 1,5-d

Hydrazoic Acid

A solution of hydrazoic acid in benzene was prepared by the method of Braun (103) by suspending practical grade sodium azide (210 grams, 3.23 moles) in 210 ml of water. The mixture was placed in a 3-liter three-necked round-bottomed flask equipped with a dropping funnel, mechanical stirrer, and an alcohol thermometer. One liter of benzene was added to the aqueous slurry, and the mixture was cooled and maintained between 0-10^0 by an external ice bath. Concentrated sulfuric acid (85 ml, 1.60 moles) was added dropwise to the vigorously stirred slurry. When the addition of sulfuric acid was complete, the benzene layer, with hydrazoic acid dissolved in it, was decanted from the almost solid sludge of sodium sulfate. The hydrazoic acid-benzene solution was stored over anhydrous sodium sulfate until needed. The normality of the acid was determined by extracting the acid into water and titrating with standardized sodium hydroxide solution to the phenolphthalein endpoint.

CAUTION: Hydrazoic acid vapors are highly toxic; therefore, all reactions involving this reagent should be carried out in a well-ventilated hood.

B. Ligands

1,5-Dimethyltetrazole (1,5-DiMeTz)

The 1,5-dimethyltetrazole was prepared by the method outlined by Mar

tion medium con

hydroxide solut

$(CH_3)_2C{=}N{-}OH$ —— (C

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ide (65 grams,

of 30-40 minute

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Sodium azide (2

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extractions wi

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the reaction m

the residue wa

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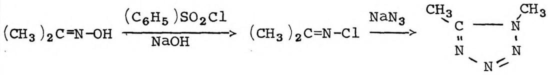
method was the

outlined by Margraf, Bachmann, and Hollis (64). The reaction medium consisted of 345 ml of 1.0 N aqueous sodium hydroxide solution in which acetone oxime (26 grams, 0.556



mole) was dissolved. The reaction mixture was mechanically stirred and externally chilled while benzenesulfonyl chloride (65 grams, 0.353 mole) was added dropwise over a period of 30-40 minutes. During the addition of benzenesulfonyl chloride to the reaction mixture, a white solid was formed. Sodium azide (24 grams, 0.353 mole) was dissolved in a minimum amount of water and added dropwise to the chilled suspension over a period of 30 minutes. The solution was allowed to reach room temperature, warmed slowly by a heating mantle, and was refluxed for 12-15 hours. The solvent, water, was removed under reduced pressure, and a solid residue was obtained. This solid material was extracted three times with 400-500 ml of hot benzene followed by two extractions with 300 ml of hot chloroform. The solvent extracts were combined and allowed to evaporate to dryness to yield the crude tetrazole. If the solid residue from the reaction mixture retained a large amount of solvent, the residue was slurried with acetone and filtered. The acetone and water filtrate was placed in an evaporating dish and concentrated. The solid residue obtained using this method was then extracted as previously described. The product was rec

mixture followe

of 14.7 grams (

point of 71.5-7

71.8-72.6°. Th

are shown in Fi

Analysis:

<u>1-Methyl-1,2,4-</u>

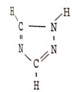
The 1-meth

of Pellizzari (

Ten grams of 1,

Co.) were disso

sodium methoxid



transferred to

9 ml of methyl

in an <u>iso</u>-prop

tube was then

return to room

placed in an c

to the high pr

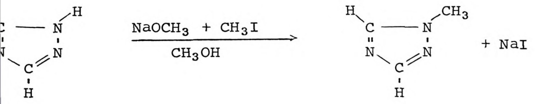
oduct was recrystallized from a benzene-ether (40:60) xture followed by vacuum sublimation which gave a yield 14.7 grams (41%). The 1,5-DiMeTz obtained had a melting int of 71.5-72^{0} as compared to the literature value of .8-72.6^{0}. The infrared and nmr spectra of this compound e shown in Figures 1, 3 and 21 in Appendix II.

Analysis: Calc. %C, 36.72; %H, 6.18; %N, 57.11

Found %C, 36.54; %H, 6.12; %N, 56.85.

<u>Methyl-1,2,4-triazole (1-Me-1,2,4-Trz)</u>

The 1-methyl-1,2,4-triazole was prepared by the method Pellizzari (58) as outlined by Alkinson and Polya (104). n grams of 1,2,4-triazole (obtained from Aldrich Chemical .) were dissolved in a solution containing 7 grams of dium methoxide in 60 ml of methanol. The mixture was



ansferred to an 100 ml high pressure tube and about nl of methyl iodide was added. The solution was cooled an <u>iso</u>-propyl alcohol-dry ice bath. The pressure e was then sealed. The sealed tube was then allowed to urn to room temperature, shaken gently to ensure mixing, ced in an oil bath and heated to 120^{0} for 2 hours. (Due the high pressure generated upon heating the reaction

mixture, the rea
The reaction ves
ture, placed in
The unreacted t
mixture by evap
concentrated mi
and three 30 ml
tracts were coo
recovered by fi
duct (1-Me-1,2,
tion boiling at
a dark bottle u
this compound a
II.

Analysis:

1-Methyl-1,2,3-

The 1-meth
using two diff
synthesis.

The first
triazole follo
1,2,3-triazole
by decarboxyla
prepared by re
and a portion

ıixture, the reaction was carried out in a safety room.) The reaction vessel was allowed to return to room tempera- :ure, placed in liquid nitrogen until frozen and opened. The unreacted triazole was removed from the yellow reaction ıixture by evaporation of the methanol and extracting the :oncentrated mixture with two 30 ml portions of hot benzene ınd three 30 ml portions of hot chloroform. When the ex- :racts were cooled, the 1,2,4-triazole precipitated and was ecovered by filtration. The residue containing the pro- łuct (1-Me-1,2,4-Trz) was fractionally distilled. The frac- .ion boiling at 172° at 735 mm was collected and stored in dark bottle until used. The infrared and nmr spectra of his compound are shown in Figures 5, 7, and 22 in Appendix I.

Analysis: Calc. %C, 43.35; %H, 6.08; %N, 50.57.

Found %C, 43.24; %H, 5.97; %N, 50.87.

-Methyl-1,2,3-triazole (1-Me-1,2,3-Trz)

The 1-methyl-1,2,3-triazole preparation was attempted ;ing two different methods, each involving a two-step ,nthesis.

The first method involved the preparation of 1,2,3- iazole followed by methylation of the 1-position. The 2,3-triazole was prepared from 4-carboxy-1,2,3-triazole decarboxylation. The 4-carboyx-1,2,3-triazole (105) was epared by refluxing propionic acid (35 grams, 0.50 mole) d a portion of the benzene stock solution of hydrazoic acid (page 46)

This reaction w

$$HC{\equiv}CCOOH \xrightarrow[\text{Benzen}]{HN_3}$$

F

flask equipped

water-cooled c

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caped during t

began to separ

tion mixture w

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218-222°. The

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distilled unde

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Attempts

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(55) or the s

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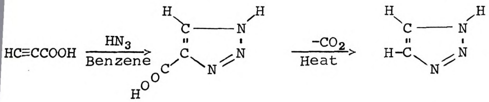
The seco

boxylation of

by Pedersen (

triazole, it

acid (page 46) equivalent to 1.5 moles of hydrazoic acid. This reaction was performed in a three-necked round-bottomed



flask equipped with a mechanical stirrer and an effective water-cooled condenser. The reaction was carried out in the hood due to the toxicity of hydrazoic acid which escaped during the heating process. A solid white product began to separate after a few hours of heating. The reaction mixture was cooled in an ice-water bath and the solid product was removed by filtration. (This step was performed in a well-ventilated hood, due to the presence of unreacted hydrazoic acid.) The solid was recrystallized from water and found to have a melting or decarboxylation point at 218-222^0. The 4-carboxy-1,2,3-triazole was decarboxylated at 220^0. The resulting 1,2,3-triazole was then fractionally distilled under reduced pressure at a b.p. of 100^0 at 29 mm as compared to the literature value of 205-206^0 at 760 mm.

Attempts to methylate the 1,2,3-triazole using either the silver salt of the triazole and methyl iodide in ether (55) or the sodium salt of the triazole and dimethylsulfate in methanol (106) were unsuccessful.

The second method involved the preparation and decarboxylation of 1-methyl-4-carboxy-1,2,3-triazole, as reported by Pedersen (105). To prepare the 1-methyl-4-carboxy-1,2,3-triazole, it was necessary to prepare gaseous methyl azide and pass it thr

of dry toluene

Methyl azide (1

$$HC{\equiv}CCOOH \xrightarrow[\text{Toluen}]{CH_3N_3}$$

azide (39 grams

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0.39 mole) fron

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allowed to sta

solid formed

The reaction

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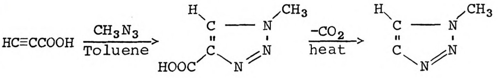
and pass it through the reaction mixture containing 100 ml of dry toluene and propiolic acid (14 grams, 0.20 mole). Methyl azide (107) was generated from a solution of sodium



azide (39 grams, 0.60 mole) and 100 ml of 0.25 N sodium hydroxide by the dropwise addition of dimethylsulfate (37 ml, 0.39 mole) from a graduated addition buret. The sodium azide solution was warmed to 40^0 in order to increase the rate of liberation of the generated methyl azide. Methyl azide was passed over anhydrous calcium chloride and then bubbled into the reaction mixture in a high pressure bottle, through a disposable Pasteur pipette at a rate of 2 bubbles per second. The rate of methyl azide evolution was adjusted by the regulation of the rate of addition of dimethylsulfate to the sodium azide solution. After all the dimethylsulfate was added, the sodium azide solution was heated for an additional 30 minutes before the toluene reaction mixture was sealed off with a pinch clamp. The toluene solution was allowed to stand overnight at room temperature. A white solid formed on the inner surface of the reaction vessel. The reaction vessel, a high pressure bottle, was sealed and heated in boiling water for 2 hours. After cooling the reaction vessel in ice water, the seal was removed, and the precipitate was filtered. Since the mixture had charred during the heating process, the product was dissolved in hot

toluene and tr
crude product
recrystallized
(7.8 grams, 0.
repeated with
heating of the
8.4 grams of t
tions of the l

The 1-met
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equipped with
flask was heat
taining molten
dioxide ceased
pressure, b.p.
of this compou
pendix II.

Analysis:

1-Methylimidaz

The 1-met
Co.) was vacu
liquid. The i
shown as Figu

Analysis:

toluene and treated with Norit-A decolorizing carbon. The crude product was recovered from the hot filtrate and then recrystallized from water. A white crystalline material (7.8 grams, 0.094 mole) was isolated. The preparation was repeated with the omission of the last step, sealing and heating of the pressure bottle. The latter method yielded 8.4 grams of the triazole. Therefore, all further preparations of the ligand omitted the heating step.

The 1-methyl-4-carboxy-1,2,3-triazole was decarboxylated by heating 5-10 grams portions in a round-bottomed flask equipped with a distillation head and a receiver. The flask was heated to 245° by lowering it into a beaker containing molten Wood's metal. Once the evolution of carbon dioxide ceased, the product was distilled under reduced pressure, b.p. 140° at 20 mm. The infrared and nmr spectra of this compound are shown as Figures 9, 11, and 23 in Appendix II.

Analysis: Calc. %C, 43.35; %H, 6.08; %N, 50.57.

Found %C, 43.25; %H, 5.88; %N, 50.44.

1-Methylimidazole (1-MeIz)

The 1-methylimidazole (obtained from Aldrich Chemical Co.) was vacuum distilled at 63° at 6 mm to give a colorless liquid. The infrared and nmr spectra of this compound are shown as Figures 17, 19, and 25 in Appendix II.

Analysis: Calc. %C, 58.50; %H, 7.38; %N, 34.12.

Found %C, 58.28; %H, 7.28; %N, 33.94.

1-Methylpyrazol

The 1-meth

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(10 ml), and wa

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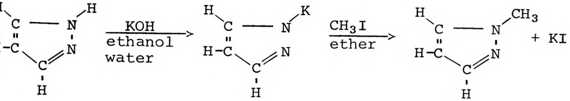
Appendix II.

Analysis:

1-Methylpyrazole (1-MePz)

The 1-methylpyrazole was prepared by the methylation of pyrazole (obtained from Aldrich Chemical Co.) in the 1-posi- tion by using the method outlined by Finar and Lord (108). A reaction mixture consisting of pyrazole (15 grams, 0.22 mole), potassium hydroxide (12.4 grams, 0.22 mole), ethanol (10 ml), and water (2 ml) was warmed in a 50 ml round-bottomed flask equipped with a condenser and stirrer. The mixture was



tirred until homogeneous, then 50 grams (22 ml, 0.35 mole) f methyl iodide, dissolved in 20 ml of anhydrous ether, ere added dropwise during a period of 1 hour. The reaction ixture was refluxed for an additional hour. The product as extracted from the cooled mixture with two 30 ml por- ions of ether followed by two 30 ml portions of chloroform. he extracts were combined and concentrated before the pro- uct was fractionally distilled, yielding 9.8 grams (0.12 ole) of 1-MePz. The boiling point of the ligand was etermined to be 117° at 735 mm. The infrared and nmr spec- ra of this compound are shown as Figures 13, 15, and 24 in ppendix II.

Analysis: Calc. %C, 58.50; %H, 7.38; %N, 34.12.

Found %C, 58.56; %H, 7.20; %N, 34.07.

C.

Bis(1,5-dimethylt

Mono(1-methyl-1,2

Mono(1-methyl-1,2

Each of the

nitromethane solu

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the ligand in nit

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these complexes a

[Ag(1,5-DiMe

Analysis

[Ag(1-Me-1,

Analysi

C. Solid Compounds Isolated

,5-dimethyltetrazole)silver(I) Perchlorate
1-methyl-1,2,4-triazole)silver(I) Perchlorate
1-methyl-1,2,3-triazole)silver(I) Perchlorate

Each of the above complexes was prepared in 20 ml of methane solution containing 0.01 mole of silver per-ate, by the dropwise addition of a 2.0 M solution of igand in nitromethane. When the ligand to silver ion ratio was greater than 4:1, the solution was allowed to for an additional 15 minutes. The solid complex was isolated by filtration. The complex was washed first nitromethane to remove excess silver perchlorate then anhydrous ether. The solid was dried at 30° for several before the infrared spectra and melting points were ved. The infrared spectra obtained on a Nujol mull of of the complexes are listed in Figures 2,4,6,8,10, and Appendix II. Melting points and chemical analysis for complexes are as follows:

$[Ag(1,5\text{-DiMeTz})_2]ClO_4$ m.p. opaque at 40° melts at 139-141°.

Analysis: Calc. %C, 17.85; %H, 3.00; %N, 27.77.

Found %C, 17.59; %H, 3.12; %N, 26.68.

$[Ag(1\text{-Me-}1,2,4\text{-Trz})_1]ClO_4$ m.p. dec. ~ 285°.

Analysis: Calc. %C, 12.40; %H, 1.74; %N, 14.47.

Found %C, 12.30; %H, 1.70; %N, 14.68.

[Ag(1-Me-

Analys

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Bis(1-methylpy

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was stirred for
which had forme
was washed with
then with anhyd
melting point
complex at 30^{0}
shown in Figur
ysis and melti

[Ag(1-MeI

Analy

$[Ag(1\text{-}Me\text{-}1,2,3\text{-}Trz)_1]ClO_4$ m.p. dec. ~ 230°.

Analysis: Calc. %C, 12.40; %H, 1.74; %N, 14.47.

Found %C, 12.45; %H, 1.68; %N, 14.49.

Bis(1-methylimidazole)silver(I) Perchlorate

Bis(1-methylpyrazole)silver(I) Perchlorate

No solid complexes could be isolated in nitromethane solutions of the ligands, 1-methyl- imidazole and -pyrazole even when diethylether was added in order to lower the dielectric constant of the reaction medium. Therefore, each of the complexes was prepared from absolute ethanol solutions containing 0.01 mole of silver perchlorate by the dropwise addition of 2.0 M solution of the ligand in ethanol. When the ligand to silver ion ratio was 4:1, the solution was stirred for an additional 15 minutes. The solid complex which had formed was isolated by filtration. The complex was washed with a small portion of absolute ethanol and then with anhydrous ether. The infrared spectrum and the melting point of the complex were obtained after drying the complex at 30° for several hours. The infrared spectra are shown in Figures 14, 16, 18, and 20 in Appendix II. Analysis and melting points for the complexes are:

$[Ag(1\text{-}MeIz)_2]ClO_4$ m.p. 119-119.5°.

Analysis: Calc. %C, 25.86; %H, 3.26; %N, 15.08.

Found %C, 25.75; %H, 3.78; %N, 15.20.

[Ag(1-MePz

Analys

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All the pr

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Model 4202 A fr

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A model V 4310C

operating at 15

line width for

order of 10 Hz

were employed a

reference was a

$[Ag(1\text{-}MePz)_2]ClO_4$ m.p. 126-128°.

Analysis: Calc. %C, 25.86; %H, 3.26; %N, 15.08.

Found %C, 25.68; %H, 3.24; %N, 15.06.

D. Instrumentation

Proton Nuclear Magnetic Resonance Spectra

All the proton nuclear magnetic resonance spectra were obtained on a Varian A 56/60 D spectrometer. Tetramethylsilane was used as an internal standard. Sweep calibration on the spectrometer was checked daily by employing the sideband technique (109). Several of the ligand proton nuclear magnetic resonance positions were more precisely determined by linear interpolation between two TMS sidebands. The sidebands were generated through the use of a Hewlett Packard Model 4202 A frequency oscillator (10 Hz to 1 MHz).

Sodium Nuclear Magnetic Resonance Spectra

The majority of the sodium nuclear magnetic resonance spectra were obtained on the Varian DA-60 spectrometer in the wideline configuration which was modified to allow the recorder sweep potentiometer to sweep the magnet power supply. A model V 4310C <u>rf</u> unit, modified for phase detection and operating at 15.88 MHz was employed. Because the natural line width for the sodium-23 resonance in water is on the order of 10 Hz (98), standard non-spinning, 15-mm test tubes were employed as sample tubes for the measurements. The reference was a co-axial 8 mm tube containing saturated

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aqueous sodium chloride solution. The spectra were calibrated by means of the sidebands produced by the wideline modulation unit operating at 400 Hz and the chemical shift of the samples was determined by linear interpolation from the sidebands. A sweep rate of 250 seconds (or more) per sweep was employed, and the spectra were retraced at least three times to average the effects of field drift.

A saturated solution of sodium tetraphenylborate in nitromethane, as a secondary standard, was used in cases where the chemical shift of the sample was masked by the saturated aqueous sodium chloride reference resonance.

The sodium nuclear magnetic resonance spectrum of a few samples was obtained on a Nuclear Magnetic Resonance Specialties MP 1000 pulsed nmr spectrometer operating in the time sharing mode. In this configuration, the spectrum obtained is a plot of the integrated free induction decay signal from the sample as the ordinate versus the radio frequency as the abscissa. The spectrum appears as a frequency swept continuous wave nmr spectrum but at a much higher signal to noise ratio and at a scan rate of 20 seconds. Scans were collected on a time averaging computer (Fabri-Tek Model 1080) until the resonance absorption signal of the sample could be observed on the computer's readout oscilloscope. The sample was then replaced with the reference solution of saturated aqueous sodium chloride and the computer was allowed to continue collecting data until the reference peak and the sample peak were both discernible. This spectrum was then transf

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vas then transferred to the recorder, and the chemical shift vas determined. Calibration was obtained by accurately setting the time base of the pulse synthesizer and matching che scan length of the recorder to the spectrometer.

During the time required for one spectrum (two minutes) che instrument drift was less than 5 Hz. No corrections vere made for susceptibility changes from one sample to another as these were shown in previous work (98) to be small in the case of Na-23 studies.

Infrared Spectra

The infrared spectra of all the ligands and their respective silver perchlorate complexes as well as the 1-nethylimidazolium tetraphenylborate salt were obtained on che Perkin Elmer 237 spectrometer in the 4000-650 cm^{-1} region and on the Digit Lab FTS-16 interferometric spectrometer in the 600-150 cm^{-1} region. The interferometer was equipped with a 3 micron beam splitter. A reference, consisting of three 2 mm thick polyethylene windows, was scanned 500 times and stored. The sample was then placed between two 2 mm thick polyethylene windows and scanned 500 times. The ratioed spectra were then plotted as percent transmittance from 600-150 cm^{-1}. The samples were either run as neat liquids or as Nujol mulls.

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pH Determinations

A Beckman Model 76 expanded scale pH meter equipped with a Beckman 41263 glass electrode and a standard saturated calomel electrode was used to determine the changes in pH of the 1-methylimidazole and sodium tetraphenylborate system in water. The pH meter was calibrated with Beckman pH 7.00 buffer solution.

Melting Points

Melting points of the isolated solids were determined on a Fisher-Johns melting point apparatus.

Microanalysis

Microanalyses were performed by the Spang Microanalytical Laboratory in Ann Arbor, Michigan, and by F. M. D'Itri of the Institute of Water Resources at Michigan State University.

E. Solution Preparations

Proton Nuclear Magnetic Resonance

The solutions to be studied were prepared, either by direct weighing of the reactants or by preparing concentrated stock solutions of silver perchlorate and ligand and pipetting the appropriate amounts of each stock solution into a 2 ml volumetric flask and diluting to the reference mark with the appropriate solvent. An aliquot of this solution, or in some case

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or in some cases when precipitation occurred, an aliquot of the supernatant liquid was transferred to the standard 8 mm O.D. nmr tubes, and tetramethylsilane was added as internal reference. The samples were then allowed to equilibrate to the probe temperature of about 38^0 before the nmr spectra were obtained. All scans were repeated at least twice and some times as many as four times to ensure reproducibility.

In all cases, except 1-methylimidazole, the silver perchlorate-ligand solutions were stable for several days. Thus the series of solutions to be measured could be prepared and measured on different days, if necessary, without changing the observed nmr spectra. In the case of nitromethane solutions of 1-methylimidazole, however, a slow reduction of silver ion was observed. Therefore, these solutions were prepared and measured immediately after preparation.

Sodium Nuclear Magnetic Resonance

The solutions to be studied were prepared by directly weighing the sodium salts, sodium tetraphenylborate or sodium perchlorate, into 5 ml volumetric flasks and then adding the appropriate aliquots of concentrated ligand stock solutions followed by dilution to the reference mark with the solvent.

Samples used in the determination of donor numbers of the 1-methyl derivatives of the ligands were prepared by weighing the sodium tetraphenylborate into 2 ml volumetric flasks and then

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flasks and then adding the pure ligand. These solutions were very near saturation, thus they were placed in a sonicator for about 10 minutes and then were allowed to stand overnight to ensure solubility.

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IV. RESULTS AND DISCUSSION

Proton Nuclear Magnetic Resonance Studies in Nitromethane

Nitromethane was selected as the solvent for a proton nmr study of the coordination site of azole ligands to silver ion. Gutmann (99) has shown that nitromethane possesses very low donor ability. Therefore, it should not compete with the azoles in the complexation reactions. However, because of its high dielectric constant (ϵ = 35.9) and its polarity, it is a good solvent for silver(I) perchlorate.

To ensure that in these complexation studies the ligands reacted as neutral molecules the acidic imino proton was removed by substitution in the 1-position. The PMT molecule represents the most throughly studied 1,5-disubstituted tetrazole, but this ligand is not especially suited for pmr studies due to the complexity of the methylene proton resonances (77). Therefore, in order to study the coordination of a tetrazole to silver ion by pmr, it was felt that the pentamethylene ring of PMT should be replaced with simpler substituents. Substitution of the 1- and 5-positions can take many forms. The substituents can be aromatic, aliphatic, or mixed aromatic-aliphatic. The

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-dimethyltetrazole was selected for this study because of observed simplicity of its proton magnetic resonance ctrum (64). Single resonance lines are observed at chemi- shift values of 4.05 ppm of the 1-methyl protons and at 8 ppm for the 5-methyl protons in deuteriochloroform. se lines provide a simple and very suitable means of dying the donor-acceptor interaction in solution.

It seems reasonable to assume that if coordination urs through the 2-nitrogen, the 1-methyl resonance would shifted more than the 5-methyl resonance. If, however, coordination occurs through the 4-nitrogen (as was the e for the isolated solid ICl-PMT complex), then the 5- hyl resonance absorption would shift more than the 1- hyl resonance absorption. The remaining possibilities that coordination could occur at the 3-nitrogen or have equal probability of occurring at the 2-, 3-, and 4-nitro- s. In these latter cases the differences in the long ge shielding through the 1-nitrogen and 5-carbon by the ghtly aromatic ring should be small, and the magnitudes of chemical shifts of 1-methyl and 5-methyl protons should comparable.

Chemical shift data (for each equivalent proton environ- t) of the ligands, 1,5-dimethyltetrazole, 1-methyl-1,2,4- azole, 1-methyl-1,2,3-triazole, 1-methylimidazole, and thylpyrazole in nitromethane solutions were obtained er two conditions: 1) constant ligand concentration with ying concentration of silver ion and 2) constant silver ion concentrati

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concentration with varying ligand concentration. Assign-ts of observed chemical shifts for the ligands in nitro-hane were made on the basis of the literature values ted in Table II for these ligands in various other sol-ts.

The 1,5-DiMeTz had two singlet proton resonances in romethane, one for the 1-methyl protons at 3.98 ppm and for the 5-methyl protons at 2.50 ppm (TMS as internal ndard). When the concentration of the ligand was held stant at 0.130 M and the silver perchlorate concentration ied from 0.0120 to 1.211 M (corresponding to a silver ion ligand mole ratio of from 0.10 to 9.32), the chemical ft of the 1-methyl protons gradually increased from 4.01 until it became obscured by the solvent resonance at ues >4.26 ppm. Chemical shift values of the 5-methyl tons gradually increased from 2.55 to 2.83 ppm (Table III). n reversing the reaction conditions, where the silver chlorate concentration was held constant at 0.101 M and ligand concentration was varied from 0.0101 to 0.406 M rresponding to a ligand to silver ion mole ratio of from 0 to 4.0), the chemical shift gradually decreased from 0 to 4.08 ppm for the 1-methyl protons and from 2.78 to 9 ppm for the 5-methyl protons respectively (Table IV). mole ratios (Lig/Ag^{+}) > 2.00, the solutions became slight-cloudy. Only the supernatant liquid of these solutions used in the measurements.

Chemical shift assignments of the azole ligands

δ(ppm)

		Ref.	1-CH_3	2-H	3-H	4-H	5-CH_3 or H
	$CDCl_3$	64	4.05	--	--	--	2.58
-4-Trz	$CDCl_3$	30	4.00	--	7.99	--	8.17
	$CDCl_3$	59	3.93	--	7.94	--	8.09
	DMSO	59	3.88	--	7.95	--	8.47
1-Me-1,2,3-Trz	$CDCl_3$	30	4.13	--	--	7.80	7.18
	$CDCl_3$	57	4.10	--	--	7.74	7.59
	C_6D_6	57	3.37	--	--	7.40	6.80
	DMSO-d_6	57	4.09	--	--	7.72	8.08
	Py-d_5	57	3.95	--	--	7.78	7.83
	Pure ligand	57	4.20	--	--	7.89	8.12
1-MeIz	$CDCl_3$	30	3.70	7.47	--	7.08	6.88
	$CDCl_3$	110	--	7.43	--	7.05	6.90
	CH_3NO_2	30	--	7.57	--	7.08	7.08
1-MePz	CCl_4	40	3.862	--	7.268	6.999	7.169
	CCl_4*	111	*3.81	--	*7.30	*6.14	*7.36
	$CDCl_3$	110	--	--	7.33	6.22	7.35

1-MePz	CCl_4	40	3.862	--	7.268	6.999	7.169
	CCl_4*	111	*3.81	--	*7.30	*6.14	*7.36
	$CDCl_3$	110	--	--	7.33	6.22	7.35
	$CDCl_3$	112	3.88	--	7.33	6.23	7.55
	CH_3NO_2	39	3.81	--	7.37	6.28	7.40
	CH_3CN	39	3.80	--	7.36	6.18	7.42
	CH_3OH-d_1	39	3.83	--	7.40	6.20	7.48
	$(CH_3)_2CO$	39	--	--	7.36	6.27	7.52
	DMF	39	3.86	--	7.38	6.18	7.60
	DMSO	39	--	--	7.41	6.21	7.66

Internal reference tetramethylsilane except * cyclohexane.

Table III. Proton magnetic resonance study of the 1,5-dimethyltetrazole and silver perchlorate system in nitromethane.

$AgClO_4$ (<u>M</u>)	Ag^+/Lig	1-CH_3 δ(Hz)	1-CH_3 Δ(Hz)	5-CH_3 δ(Hz)	5-CH_3 Δ(Hz)
--	free lig.	238.6	--	150.1	--
*0.0129	0.10	240.5	1.9	153.2	3.1
*0.0260	0.20	242.6	4.0	156.3	5.2
*0.0388	0.30	244.7	5.1	159.6	9.5
*0.0518	0.40	246.6	8.0	161.8	11.7
0.0648	0.50	247.0	8.4	165.2	15.1
0.0778	0.60	249.2	10.6	165.2	15.1
0.104	0.80	249.9	11.3	165.9	15.8
0.130	1.00	251.6	13.0	166.7	16.6
0.156	1.20	251.8	13.2	167.5	17.4
0.182	1.40	252.6	14.0	168.0	17.9
0.208	1.60	253.2	14.6	168.5	18.4
0.234	1.80	253.4	14.8	168.9	18.8
0.259	1.99	253.4	14.8	169.1	19.0
0.286	2.20	254.1	15.5	169.1	19.0
0.337	2.59	254.7	16.1	169.0	18.9
0.389	2.99	255.0	16.4	169.5	19.4

0.286	2.20	254.1	15.5	169.1	19.0
0.337	2.59	254.7	16.1	169.0	18.9
0.389	2.99	255.0	16.4	169.5	19.4
0.441	3.39	254.8	16.2	169.4	19.3
0.519	3.99	255.4	16.8	169.6	19.5
0.623	4.79	under solvent peak		169.5	19.4
0.778	5.98			169.5	19.4
0.882	6.78			170.2	20.1
0.986	7.58			169.8	19.7
1.167	8.98			169.9	19.8
1.211	9.32			170.0	19.9

$[1,5\text{-DiMeTz}]_{constant} = 0.130\ \underline{M}$

*Solutions became slightly cloudy, only supernatant liquid was used in measurements.

Table IV. Proton magnetic resonance study of the 1,5-dimethyltetrazole and silver perchlorate system in nitromethane.

1,5-DiMeTz	Lig/Ag^+	$1-CH_3$		$5-CH_3$	
(M)		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
0.0101	0.10	--	--	165.1	15.0
0.0203	0.20	251.4	12.8	166.1	16.0
0.0304	0.30	252.2	13.4	166.6	16.5
0.0406	0.40	251.8	13.2	166.7	16.6
0.0507	0.50	251.6	13.0	166.5	16.4
0.0608	0.60	251.1	12.5	166.4	16.3
0.0811	0.80	250.6	12.0	166.0	15.9
0.101	1.00	249.9	11.3	165.8	15.7
0.122	1.20	249.8	11.2	165.2	15.1
0.142	1.41	249.1	10.5	165.2	15.1
0.162	1.61	248.4	9.8	164.8	14.7
0.183	1.82	248.3	9.7	164.4	14.3
0.203	2.01	247.9	8.7	164.0	13.9
*0.243	2.41	246.7	8.1	162.4	12.3
*0.284	2.81	246.0	7.4	161.0	10.9
*0.324	3.21	245.5	6.9	160.0	9.9

[illegible]	2.41	246.7	8.1	162.4	12.3
*0.284	2.81	246.0	7.4	161.0	10.9
*0.324	3.21	245.5	6.9	160.0	9.9
*0.365	3.62	245.2	6.6	157.3	7.2
*0.406	4.02	245.1	6.5	155.5	5.4
0.130	free lig.	238.6	--	150.1	--

$[AgClO_4]_{constant} = 0.101$ M

*Solutions became slightly cloudy, only supernatant liquid was used in measurements.

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The proton magnetic resonance spectrum for 1-Me-1,2,4-Trz in nitromethane consisted of three singlets at 3.89, 7.77, and 8.08 ppm from TMS with relative intensities of 3:1:1. The high field peak at 3.89 ppm, therefore, was assigned to the 1-methyl protons; the peak at 7.77 ppm was assigned to the 3-proton; and the low field peak at 8.08 ppm was assigned to the 5-proton based on literature values for this ligand shown in Table II.

When the concentration of the 1-Me-1,2,4-Trz was held constant at 0.476 M and the silver perchlorate concentration was varied from 0.00112 to 0.972 M (corresponding to a silver ion to ligand mole ratio of from 0.002 to 2.04), the chemical shift gradually increased from 3.90 to 4.06 ppm for the 1-methyl protons, from 7.77 to 8.11 ppm for the 3-proton; and from 8.08 to 8.58 ppm for the 5-proton, (Table V). When the reaction conditions were reversed and the silver perchlorate concentration was held constant at 0.238 M and the 1-Me-1,2,4-Trz concentration was varied from 0.0577 to .730 M (corresponding to a ligand to silver ion mole ratio of from 0.24 to 7.27), the chemical shift gradually decreased from 4.08 to 3.93 ppm for the 1-methyl protons, from .59 to 8.26 ppm for the 3-proton, and from 8.12 to 7.88 ppm for the 5-proton (Table VI).

In all cases the complex formed in solution exceeded its solubility limit in nitromethane, therefore, all solutions contained solid material. Only the supernatant liquid was used in the pmr measurements. At constant ligand

Table V. Proton magnetic resonance study of the 1-methyl-1,2,4-triazole and silver perchlorate system in nitromethane.

$AgClO_4$ (M)	Ag^+/Lig	1-CH_3		5-H		3-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
0.972	2.04	--	--	--	--	--	--
0.888	1.86	--	--	--	--	--	--
0.775	1.63	--	--	--	--	--	--
0.675	1.42	--	--	--	--	--	--
0.585	1.23	--	--	--	--	--	--
0.495	1.04	--	--	--	--	--	--
0.405	0.85	243.9	10.3	514.9	29.9	486.4	20.4
0.315	0.66	243.4	9.8	515.2	30.2	486.6	20.6
0.225	0.47	243.1	9.5	516.4	31.4	487.8	21.8
0.180	0.38	241.7	8.1	512.6	27.6	484.5	18.5
0.135	0.28	240.2	6.6	505.9	20.9	480.4	14.4
0.0900	0.19	238.2	4.6	499.4	14.4	475.7	9.7
0.0450	0.10	236.5	2.9	491.6	6.6	470.8	4.8

0.0225	0.05	235.3	1.7	488.2	3.2	468.8	2.8
0.0135	0.03	234.4	0.8	486.6	1.6	468.0	2.0
0.0046	0.01	234.2	0.6	487.2	2.2	468.6	2.6
0.0023	0.005	234.3	0.7	485.0	0.0	466.8	0.8
0.0011	0.002	234.3	0.7	485.1	0.1	466.0	0.0
free ligand	--	233.6	--	485.0	--	466.0	--

$[1\text{-Me-}1,2,4\text{-Trz}]_{constant}$ = 0.476 M

*All solutions contained precipitate; thus, only the supernatant liquid was used for each measurement.

Table VI. Proton magnetic resonance study of 1-methyl-1,2,4-triazole and silver

1-Me-1,2,4-Trz ($\underline{M}$)	Lig/Ag^+	$1-CH_3$		5-H		3-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
Pure ligand	--	233.6	--	485.0	--	466.0	--
1.730	7.27	236.0	2.4	495.9	10.9	472.6	6.6
1.500	6.30	236.6	3.0	497.4	12.4	473.8	7.8
1.269	5.33	237.1	3.5	498.4	13.4	474.2	8.2
1.038	4.36	237.6	4.0	501.2	16.2	476.1	10.1
0.807	3.39	238.7	5.1	504.5	19.5	478.8	12.8
0.692	2.91	239.5	5.9	507.4	22.4	480.2	14.2
0.577	2.42	240.9	7.3	510.2	25.2	482.8	16.8
0.461	1.94	242.0	8.4	513.8	28.8	486.4	20.4
0.346	1.45	243.0	9.4	515.6	30.6	486.9	20.9
0.231	0.97	244.2	10.6	--	--	--	--
0.115	0.48	--	--	--	--	--	--
0.058	0.24	--	--	--	--	--	--

$[AgClO_4]_{constant} = 0.238\ \underline{M}$

All solutions contained precipitate; thus, only the supernatant liquid was used for each measurement.

concentration when the mole ratios (Ag^+/Lig) were > 0.85 and at constant silver ion concentration when the mole ratios (Lig/Ag^+) were < 0.97, the amount of free 1-Me-1,2,4-Trz and soluble [$Ag(1\text{-Me-}1,2,4\text{-Trz})_n{}^{1+}$] complex in the supernatant liquid were undetectable by pmr measurements.

The proton magnetic resonance spectrum for the 1-Me-1,2,3-Trz was very similar to that of the 1-Me-1,2,4-Trz. It consisted of three singlets at 4.09, 7.52, and 7.71 ppm from TMS with relative intensities of 3:1:1. The peak at 4.09 ppm was assigned to the 1-methyl protons. The high field peak at 5.52 ppm was assigned to the 5-proton, and the low field peak at 7.71 ppm was assigned to the 4-proton based on literature values for this ligand shown in Table II.

When the concentration of the ligand was held constant at 0.122 M and the silver perchlorate concentration varied from 0.00994 to 0.248 M (corresponding to a silver ion to ligand mole ratio of from 0.08 to 2.03), the chemical shift of the 1-methyl protons gradually increased from 4.12 ppm until it was obscured by the solvent peak at > 4.26 ppm. The results, therefore, are analogous to those observed in the 1,5-DiMeTz - Ag^+ system. The chemical shift for the 4-proton gradually increased from 7.79 to 8.08 ppm while the chemical shift for the 5-proton gradually increased from 7.68 to 7.96 ppm from TMS (Table VII). At silver ion to ligand mole ratios ≥ 0.82 the solutions contained precipitate, and only the supernatant liquid was used for the measurements. In solutions with silver to ligand mole ratios

$AgClO_4$ (M)	Ag^+/Lig	1-CH_3 δ(Hz)	1-CH_3 Δ(Hz)	5-H δ(Hz)	5-H Δ(Hz)	4-H δ(Hz)	4-H Δ(Hz)
0.00994	0.08	247.0	1.7	467.2	4.7	460.8	4.4
0.0199	0.16	248.5	3.2	470.4	7.9	464.3	7.9
0.0298	0.24	250.1	4.8	473.3	10.8	467.1	10.7
0.0397	0.33	251.8	6.5	477.5	15.0	471.8	15.4
0.0494	0.41	252.9	7.6	480.0	17.5	473.8	17.4
0.0732	0.60	253.7	8.4	482.3	19.8	476.4	20.0
*0.0994	0.82	255.6	10.3	484.1	21.6	478.2	21.8
*0.149	1.22	under	solvent	485.1	22.6	477.4	21.0
*0.199	1.63	"	"	--	--	--	--
*0.248	2.03	"	"	--	--	--	--
free ligand	--	245.3	--	462.5	--	456.4	--

$[1\text{-Me-}1,2,3\text{-Trz}]_{constant} = 0.122\ \underline{M}$

*These solutions contained precipitate; thus, only the supernatant liquid was used in the measurements.

)0, the 1-methyl proton absorption was obscured by the
ent absorption. At silver ion to ligand mole ratios
53, the amount of ligand remaining in solution was so
n either free or complexed state that it could not
tively be measured with any degree of accuracy.

When the reaction conditions were reversed and the sil-
perchlorate concentration was held constant at 0.248 M
the ligand concentration was varied from 0.0244 to
M (corresponding to ligand to silver ion mole ratios
0.10 to 5.90), the observed chemical shift gradually
ased from 4.27 to 4.09 ppm for the 1-methyl protons,
8.09 to 7.89 ppm for the 4-proton, and from 7.97 to 7.77
or the 5-proton (Table VIII). At constant ligand con-
ation, when the mole ratio Ag^+/Lig was > 1.22 and at
ant silver ion concentration, when the mole ratio Lig/Ag^+
0.98, the amount of free 1-Me-1,2,3-Trz and soluble
-Me-1,2,3-$Trz_n$$^{1+}$] complex in the supernatant liquid
undetectable by pmr measurements.

The 1-MeIz proton magnetic resonance spectrum in nitro-
ne has been reported by Barlin and Batterham (30). They
ned the chemical shift at 7.57 ppm to the 2-proton and
08 to the 4- and 5-protons. They did not distinguish
en the 4- and 5-positions. We observed two singlet
ances at 3.66 ppm and at 7.36 ppm with relative intensi-
of 3:1. We also observed what appears as a doublet
g shoulders at 6.92 ppm (Figure 3a) with a relative
sity of about twice that of the smaller singlet peak.

1-Me-1,2,3-Trz ($\underline{M}$)	Lig/Ag^+	$1-CH_3$		5-H		4-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
*0.0244	0.10	--	--	--	--	--	--
*0.0488	0.20	--	--	--	--	--	--
*0.0732	0.30	--	--	--	--	--	--
*0.0976	0.39	--	--	--	--	--	--
*0.122	0.49	--	--	--	--	--	--
*0.183	0.74	--	--	--	--	--	--
*0.244	0.98	256.4	11.1	485.4	12.9	478.3	21.9
*0.366	1.48	255.6	10.3	486.0	13.5	478.6	22.2
0.488	1.97	254.0	8.7	484.4	11.9	478.1	21.7
0.610	2.46	252.7	7.4	481.6	9.1	475.2	18.8
0.732	2.95	251.4	6.1	479.1	6.8	472.4	16.0
0.976	3.94	249.9	4.6	475.4	2.9	468.7	12.3
1.220	4.92	249.2	3.9	474.3	1.8	467.4	11.0
1.464	5.90	249.0	3.7	473.2	0.7	466.2	9.8
free ligand		245.3	--	462.5	--	456.4	--

$[AgClO_4]_{constant}$ = 0.248 $\underline{M}$

*These solutions contained some precipitate; thus, only the supernatant liquid was used in the measurements.

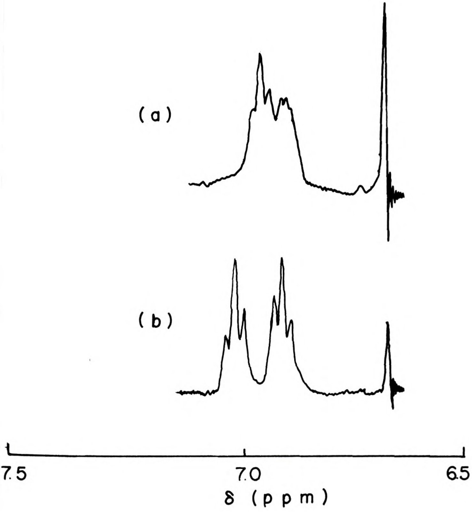


Figure 3. Comparison of the pmr spectrum of the 4- and 5-protons of a) 1-MeIz and b) 1-MeIz-$AgClO_4$ system in nitromethane.

apparent doublet, however, was shown to consist of two
lets at 6.91 and 6.93 ppm, respectively. Upon the addi-
of silver perchlorate such that (Lig/Ag^+) mole ratio
≤ 0.05, the two triplets became well defined, as illus-
ed in Figure 3b. Chemical shift values were assigned as
ows: 3.66 ppm to the 1-methyl protons, 7.36 ppm to the
oton, 6.93 ppm to the 4-proton, and 6.91 ppm to the 5-
on. These results agreed with those reported for the
d in other solvents (Table II).

When the concentration of the 1-MeIz was held constant
333 M and the silver perchlorate concentration was
d from 0.0393 to 1.180 M (corresponding to silver ion
gand mole ratios from 0.12 to 3.54), the chemical shift
ally increased from 3.72 to 3.86 ppm for the 1-methyl
ns, from 7.48 to 7.90 ppm for the 2-proton, from 7.02
38 ppm for the 4-proton, and from 6.94 to 7.27 ppm for
-proton (Table IX). When the reaction conditions were
sed and the silver perchlorate concentration was held
ant at 0.268 M and the ligand concentration was varied
).146 to 2.080 M (corresponding to ligand to silver
ole ratios from 0.51 to 7.30), the chemical shift grad-
decreased from 3.84 to 3.69 ppm for the 1-methyl pro-
from 7.84 to 7.50 ppm for the 2-proton; from 7.25 to
ppm for the 4-proton; and from 7.14 to 6.95 ppm for the
ton (Table X). No precipitation was observed in this
n. Slight reduction of the silver ion was observed
the solutions were prepared 1 hour before measurement or

$AgClO_4$ (M)	Ag^+/Lig	$1-CH_3$		5-H		4-H		2-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
0.0393	0.12	223.4	4.0	416.3	1.6	421.4	7.4	449.0	7.0
0.0786	0.24	225.3	5.9	419.2	4.5	425.1	9.1	454.8	12.8
0.118	0.35	227.5	8.1	422.7	8.0	428.8	12.8	461.2	19.2
0.157	0.47	229.2	9.8	425.5	10.8	431.9	15.9	466.7	24.7
0.197	0.59	230.3	10.9	427.4	12.7	433.8	17.8	470.3	28.3
0.393	1.18	230.2	10.8	428.5	13.8	435.1	19.1	470.2	28.2
0.688	2.07	230.8	11.4	431.3	16.6	437.9	21.9	471.2	29.2
0.983	2.95	231.4	12.0	433.9	19.2	440.3	24.3	472.5	30.5
1.180	3.54	231.8	12.4	436.2	21.5	442.8	26.8	474.0	32.0
free ligand	--	219.4	--	414.7	--	416.0	--	442.0	--

$[1\text{-MeIz}]_{constant}$ = 0.333 M.

1-MeIz ($\underline{M}$)	Lig/Ag^+	1-CH_3 δ(Hz)	1-CH_3 Δ(Hz)	5-H δ(Hz)	5-H Δ(Hz)	4-H δ(Hz)	4-H Δ(Hz)	2-H δ(Hz)	2-H Δ(Hz)
0.146	0.51	230.3	10.9	428.2	13.5	435.1	18.1	470.1	28.1
0.245	0.68	230.0	10.6	427.8	13.1	434.5	18.5	470.3	28.3
0.374	1.31	230.0	10.6	427.2	12.5	433.8	17.8	470.0	28.0
0.489	1.72	230.2	10.8	427.3	12.6	433.5	17.5	470.5	28.5
0.568	1.99	229.1	9.7	426.8	12.1	432.7	16.7	469.0	25.0
0.649	2.27	228.6	9.2	425.1	10.4	431.3	15.3	466.0	24.0
0.734	2.58	227.3	7.9	423.1	8.4	429.6	13.6	462.9	20.9
0.979	3.44	225.5	6.1	420.4	5.7	426.8	10.8	458.1	16.1
1.224	4.29	224.5	5.1	419.0	4.3	425.2	9.2	455.8	13.8
1.468	5.15	223.5	4.1	417.8	3.1	423.7	7.7	453.0	11.0
1.713	6.01	223.0	3.6	417.5	2.8	422.9	6.9	451.8	9.8
2.080	7.30	221.7	2.3	416.4	1.7	421.3	5.3	449.7	7.7
free ligand	--	219.4	--	414.7	--	416.0	--	442.0	--

$[AgClO_4]_{constant} = 0.268\ \underline{M}$

en they were exposed for more than 10 minutes to the probe nperature (~ 38^{o}C). To minimize the effect of the reducon upon the data obtained, the solutions were mixed and asured immediately. This reduction was most noticeable Lig/Ag^{+} mole ratios > 2.

The observed chemical shift values for the 1-MePz in tromethane have been reported by Elquero, et al. (39). emical shift values of 3.81 ppm, 7.37 ppm (doublet), 6.18 (triplet), and 7.40 ppm (doublet), were assigned to the ethyl protons, and the 3-, 4-, and 5-proton respectively. observed one very sharp singlet at 3.82 ppm with a relae intensity of 3 as compared to a triplet at 6.19 ppm. absorption at 3.82 ppm was assigned to the 1-methyl pros and the absorption at 6.19 ppm was assigned the 4-pro-. We did not observe two distinguishable doublets as reted by Elquero, et al. but rather a broad combination of doublets whose center appeared at about 7.39 ppm as wn in Figure 4a. These doublets were shown to be at 7.37 7.40 ppm and were assigned to the 3- and 5-protons rectively based on those values listed by Elquero, et al. n the addition of silver perchlorate such that the g/Ag^{+}) mole ratio was ≥ 0.05, the broad doublet was split o two distinct doublets (Figure 4b).

When the concentration of the 1-MePz was held constant 0.299 M and the silver perchlorate concentration varied m 0.00494 to 0.742 M (corresponding to silver ion to ligand ios from 0.02 to 3.24), the chemical shift gradually

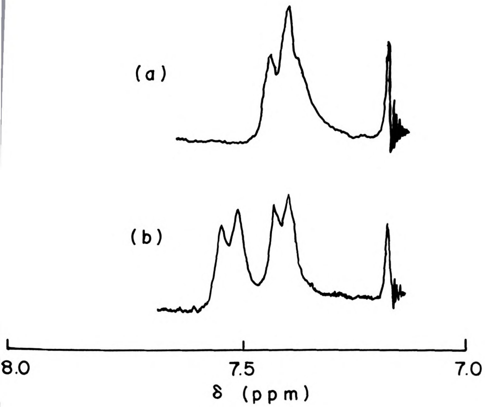


Figure 4. Comparison of the pmr spectrum of the 3- and 5-protons of a) 1-MePz and b) 1-MePz - $AgClO_4$ system in nitromethane.

eased from 3.85 to 4.10 ppm for the 1-methyl protons, 7.36 to 7.78 ppm for the 3-proton, from 6.20 to 6.55 for the 4-proton, and from 7.78 to 7.86 ppm for the 5-on (Table XI). When the reaction conditions are re-ed and the silver perchlorate concentration was held tant at 0.223 M while the ligand concentration was varied 0.0229 to 1.375 M (corresponding to ligand to silver nole ratios from 0.10 to 6.77), the chemical shift grad-y decreased from 4.07 to 3.90 ppm for the 1-methyl pro-, from 7.72 to 7.47 ppm for the 3-proton, from 6.50 to ppm for the 4-proton, and from 7.81 to 7.58 ppm for 5-proton (Table XII).

At very low mole ratios ($Lig/Ag^+ < 0.30$), it was very icult to determine the position of the 3-, 4-, and 5-on resonances, because of the broadness of the peaks the lack of reproducibility in determining the center he absorption band within the limits of ± 1 Hz on repeti- scans.

The observed chemical shift, δ_{obs}, for the individual on environments in all cases studied was a weighted age of the ligand environments as free and complexed d. Since the usual coordination number for the silver the acceptor) is 2, the observed chemical shift can be en as the weighted sum of the following three terms: hemical shift of the free ligand, δ_D, the chemical shift e 1:1 complex, δ_{AD}, and the chemical shift of the 1:2 ex, δ_{AD_2}. Therefore, $\delta_{obs} = \alpha\delta_D + \beta\delta_{AD} + \gamma\delta_{AD_2}$ where

$AgClO_4$ (M)	Ag^+/Lig	$1-CH_3$		4-H		3-H		5-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
free ligand	--	229.3	--	371.5	--	442.4	--	444.2	--
0.00494	0.02	231.0	1.7	372.2	0.7	442.9	0.5	446.5	2.3
0.0148	0.06	232.5	3.2	373.3	1.8	443.4	1.0	448.0	3.8
0.0247	0.11	233.0	3.7	375.2	2.7	445.6	3.0	451.1	6.9
0.0371	0.16	234.0	4.7	376.6	5.1	446.6	4.2	451.6	7.4
0.0494	0.22	234.9	5.6	377.8	6.3	448.0	5.6	453.6	9.4
0.0742	0.32	239.2	9.9	380.6	9.1	451.9	9.5	457.3	13.1
0.0989	0.43	244.6	15.3	387.7	16.2	461.9	19.5	466.9	22.7
0.148	0.65	247.2	17.9	388.6	17.1	462.5	20.1	468.7	24.5
0.247	1.08	246.3	17.0	389.6	18.1	464.7	22.3	468.9	24.7
0.346	1.51	246.3	17.0	390.2	18.7	465.6	23.2	469.7	25.5
0.445	1.94	245.8	16.5	391.1	19.6	465.9	23.5	470.1	25.9
0.494	2.16	246.0	16.7	391.4	19.9	466.0	23.6	470.0	25.8
0.618	2.70	245.8	16.5	392.4	20.9	466.4	24.0	471.2	27.0
0.742	3.24	245.8	16.5	393.1	21.6	467.1	24.7	471.8	27.6

$[1\text{-MePz}]_{constant} = 0.229\ \underline{M}$

1-MePz (M)	Lig/Ag$^+$	1-CH_3		4-H		3-H		5-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
0.0229	0.10	244.4	15.1	--	--	--	--	--	--
0.0458	0.21	244.8	15.5	--	--	--	--	--	--
0.688	0.31	245.1	15.8	389.7	18.2	463.4	21.0	468.6	24.4
0.0917	0.41	245.1	15.8	390.5	19.0	462.8	20.4	468.4	24.2
0.115	0.52	246.0	16.7	390.2	18.7	463.9	21.5	468.6	24.4
0.172	0.77	246.0	16.7	390.2	18.7	464.2	21.8	468.8	24.6
0.229	1.03	246.6	17.3	390.5	19.0	465.6	23.2	469.4	25.2
0.344	1.54	246.2	16.9	390.2	18.7	464.6	22.2	468.9	24.7
0.458	2.05	245.8	16.5	389.5	18.0	464.4	22.0	467.8	23.6
0.573	2.59	241.9	12.6	385.7	14.2	459.1	16.7	464.1	19.9
0.688	3.09	239.3	10.0	384.0	11.5	455.9	13.5	461.8	17.6
0.917	4.11	236.8	7.5	381.7	10.2	452.2	9.8	459.0	14.8
1.146	5.14	235.6	6.3	380.0	8.5	449.4	7.0	456.4	12.2
1.375	6.17	233.8	4.5	378.9	7.4	448.1	5.7	455.0	10.8
free ligand	--	229.3	--	371.5	--	442.2	--	444.2	--

$[AgClO_4]_{constant}$ = 0.223 M

and γ are the mole fractions of total ligand in each
: respectively. The observed chemical shift data for
:hese systems are also shown in Tables III through XII
›served relative chemical shifts, Δ_{obs} (in Hz). The
:ved relative chemical shift is defined as the differ-
between the observed chemical shift, δ_{obs}, and the
ical shift of the free ligand, δ_D,

$$\Delta_{obs} = \delta_{obs} - \delta_D \quad . \tag{30}$$

When the observed relative chemical shifts of each pro-
environment for each ligand were plotted as a function
ne silver ion to ligand mole ratios, a variety of curve
es were obtained (Figures 5-9). In each case illustrated
ligand concentration was held constant and the concen-
.on of the silver ion was varied. The shapes of the
es appear to be dependent on the relative strength of
lonor-acceptor interaction, the nearness of the measured
us to the reaction site, the predominant species in
ion, and the limiting chemical shifts for each species
lution.

The extrapolation procedure outlined on page 29 can
y be applied to the three systems 1,5-DiMeTz - $AgClO_4$
re 5), 1-MeIz - $AgClO_4$ (Figure 8), and 1-MePz - $AgClO_4$
re 9). For each case the 1:2 complex (AD_2) appears to
predominant species in solution. However, the
,2,4-Trz - $AgClO_4$ (Figure 6) and 1-Me-1,2,3-Trz -
(Figure 7) systems do not indicate clearly the

Figure 5. Relationship between the observed relative chemical shift of the protons of 1,5-dimethyltetrazole and the Ag^+/Lig mole ratio in nitromethane [Lig] was constant [$AgClO_4$] was varied

o 1-methyl protons

● 5-methyl protons

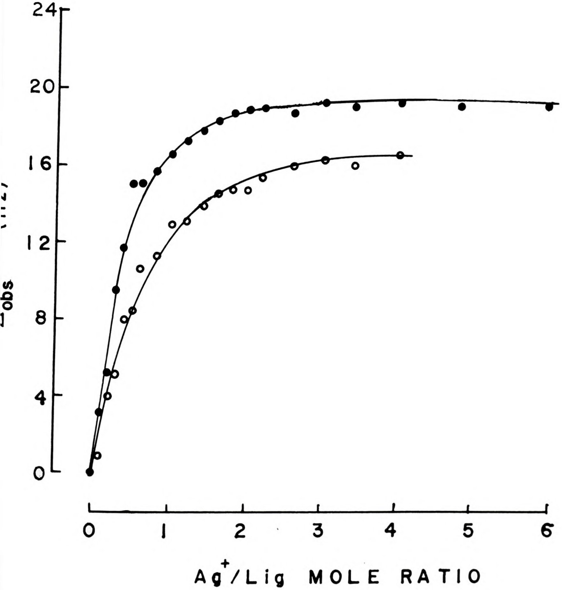


Figure 5.

Figure 6. Relationship between the observed relative chemical shift of the protons on 1-methyl-1,2,4-triazole and the Ag^+/Lig mole ratio in nitromethane [Lig] was constant [$AgClO_4$] was varied

- o 1-methyl protons
- ● 5-proton
- ■ 3-proton

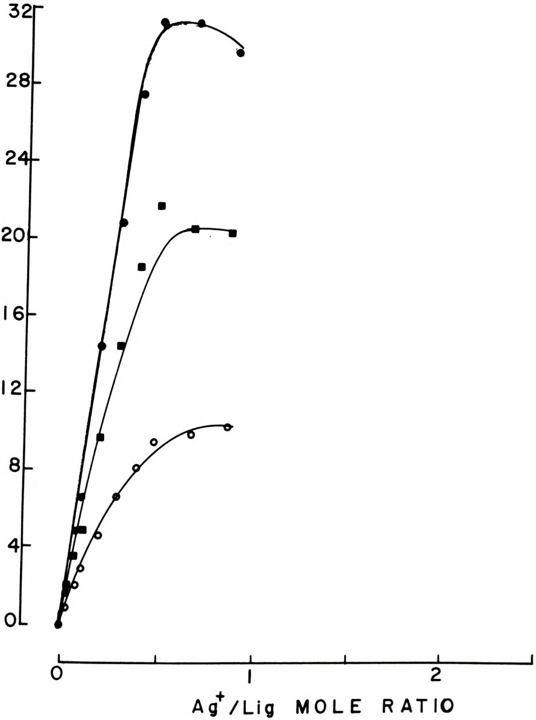


Figure 6.

Figure 7. Relationship between the observed relative chemical shift of the protons of 1-methyl-1,2,3-triazole and the Ag^+/Lig mole ratio in nitromethane [Lig] was constant [$AgClO_4$] was varied

o 1-methyl protons

● 5-proton

■ 4-proton

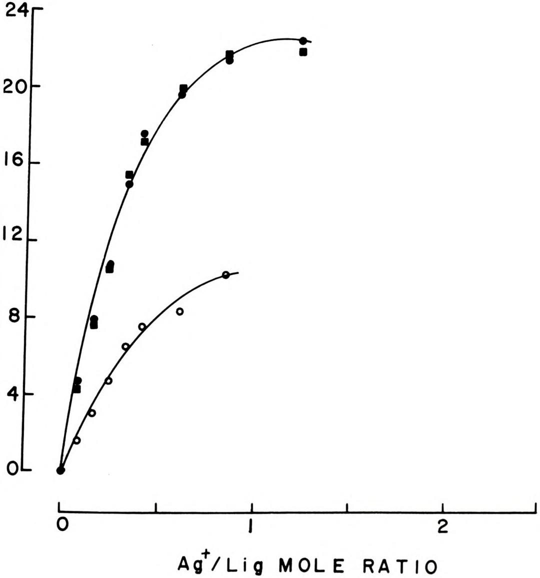


Figure 7.

Figure 8. Relationship between the observed relative chemical shift of the protons of 1-methylimidazole and the Ag^+/Lig mole ratio in nitromethane [Lig] was constant [$AgClO_4$] was varied

- o 1-methyl protons (left ordinate)
- ● 5-proton (left ordinate)
- ▫ 2-proton (right ordinate)
- ▪ 4-proton (right ordinate)

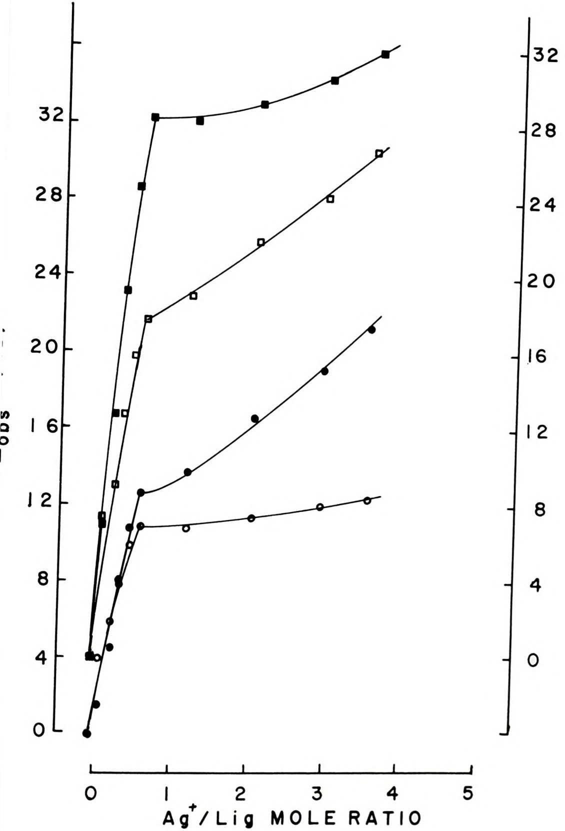

32
28
24
20
16
12
8
4
0
32
28
24
20
16
12
8
4
0
0
1
2
3
4
5
Ag⁺/Lig MOLE RATIO

Figure 8.

Figure 9. Relationship between the observed relative chemical shift of the protons of 1-methylpyrazole and the Ag^+/Lig mole ratio in nitromethane [Lig] was constant [$AgClO_4$] was varied

- ◉ 1-methyl protons (left ordinate)
- ● 5-proton (left ordinate)
- ◻ 3-proton (right ordinate)
- ■ 4-proton (right ordinate)

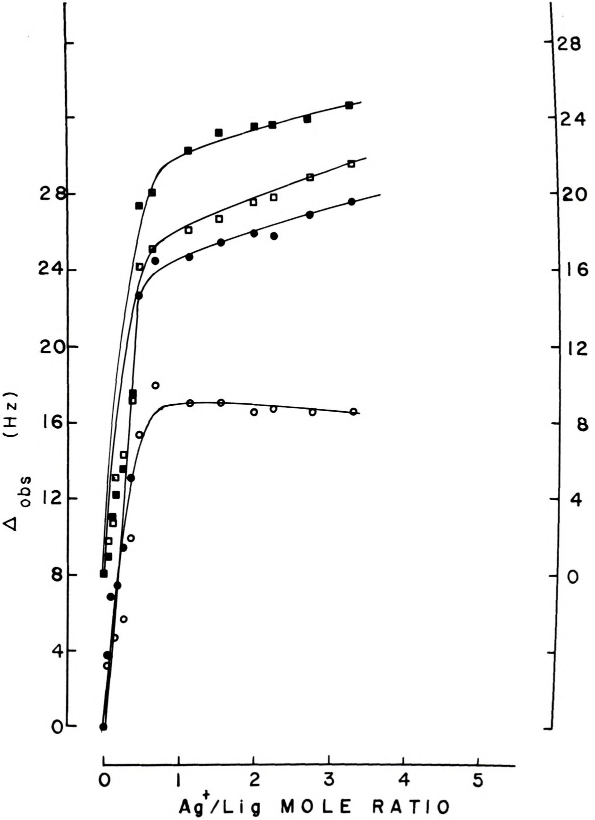

28
24
20
16
12
8
4
0
28
24
20
16
12
8
4
0
Δ obs (Hz)
0
1
2
3
4
5
Ag+/Lig MOLE RATIO

Figure 9.

predominant species in solution. Although there appears to be a slight break in Figure 6 at Ag^+/Lig mole ratio of 0.5, corresponding to a 1:2 complex (AD_2), it is tenuous at most to say that such a species exists in solution. Further support for this fact is that these data were obtained on the supernatant liquid, thus the observed chemical shifts represent not only the strength of the interaction but the solubility of the solid complex $[Ag(1\text{-}Me\text{-}1,2,3\text{-}Trz)_n]ClO_4$.

The limiting relative chemical shift for the 1:2 complex (AD_2) and the 1:1 complex (AD) cannot be easily obtained from these Figure 5-9. Only in the case of 1,5-DiMeTz could the limiting values for the 1:2 complex (Δ_{AD_2}) of 20 Hz for the 5-methyl protons and 17 Hz for the 1-methyl protons be obtained (Figure 5).

In most cases it appears that the limiting relative chemical shift values for the complexed species in solution can be best obtained from the plots of the observed relative chemical shifts (Δ_{obs}) of each equivalent proton environment for each ligand vs the Lig/Ag^+ mole ratios (Figures 10-14). In each case illustrated, the silver ion concentration was held constant while the concentration of the ligand was varied. At very small Lig/Ag^+ mole ratios these figures represent infinitly dilute solutions of the complexed donor, while at large Lig/Ag^+ mole ratios the predominant species are the free donor molecules. By extrapolating the curves to Lig/Ag^+ mole ratios of zero, the limiting relative chemical shifts (Δ_{AD_n}) of the complexed species could be obtained

Figure 10. Relationship between the observed relative chemical shift of the protons of 1,5-dimethyltetrazole and the Lig/Ag^+ mole ratio in nitromethane [$AgClO_4$] was constant [Lig] was varied

o 1-methyl protons

● 5-methyl protons

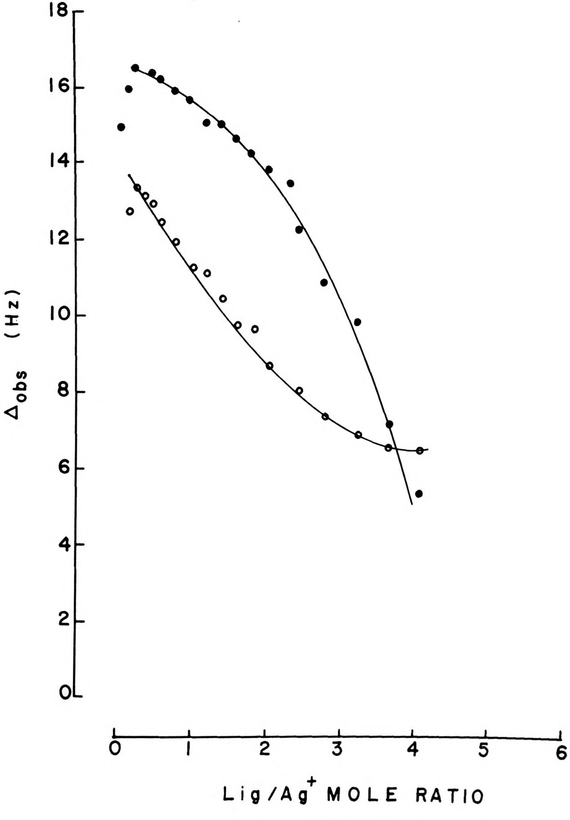


Figure 10.

Figure 11. Relationship between the observed relative chemical shift of the protons of 1-methyl-1,2,4-triazole and the Lig/Ag^+ mole ratio in nitromethane [$AgClO_4$] was constant and [Lig] was varied

- o 1-methyl protons
- ● 5-proton
- ◘ 3-proton

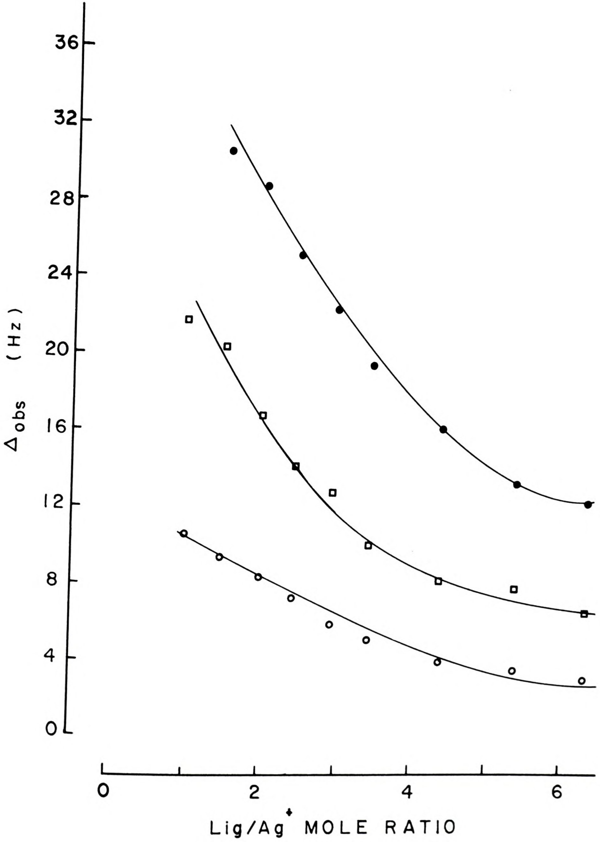


Figure 11.

Figure 12. Relationship between the observed relative chemical shift of the protons of 1-methyl-1,2,3-triazole and the Lig/Ag^+ mole ratio in nitromethane [$AgClO_4$] was constant [Lig] was varied

- o 1-methyl protons
- ● 5-proton
- ■ 4-proton

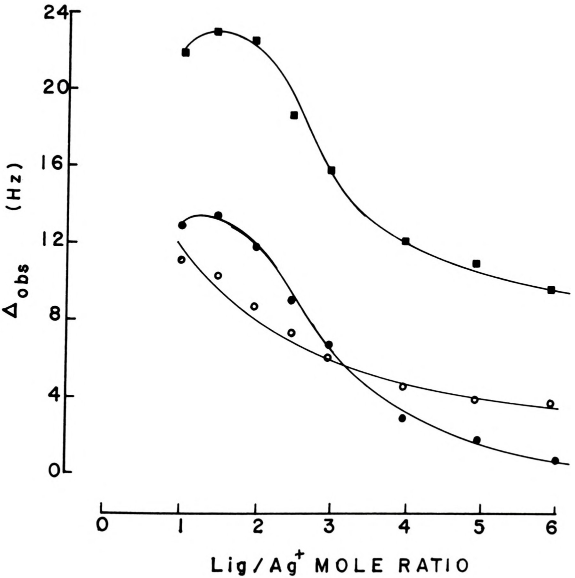


Figure 12.

Figure 13. Relationship between the observed relative chemical shift of the protons of 1-methylimidazole and the Lig/Ag^+ mole ratio in nitromethane [$AgClO_4$] was constant [Lig] was varied

- ○ 1-methyl protons (left ordinate)
- ● 5-proton (left ordinate)
- □ 2-proton (right ordinate)
- ■ 4-proton (right ordinate)

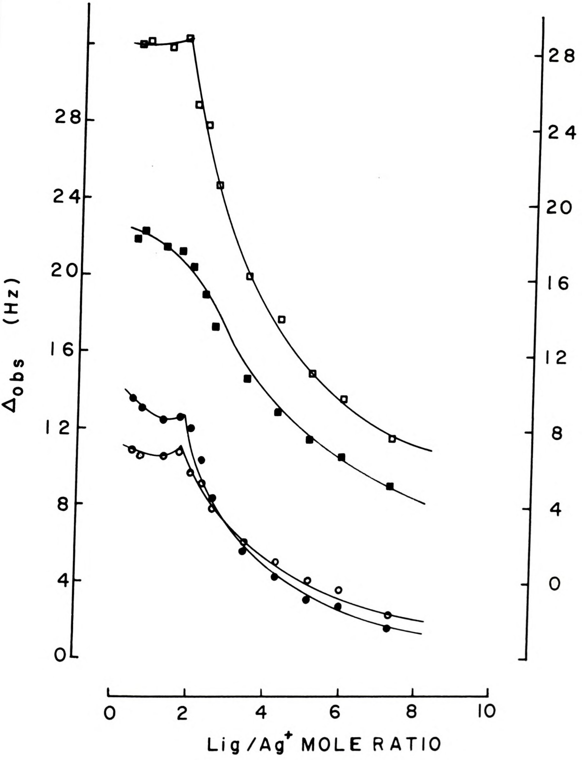

28
24
20
16
12
8
4
0
28
24
20
16
12
8
4
0
Δobs (Hz)
0
2
4
6
8
10
Lig/Ag+ MOLE RATIO

Figure 13.

Figure 14. Relationship between the observed relative chemical shift of the protons of 1-methylpyrazole and the Lig/Ag^+ mole ratio in nitromethane [$AgClO_4$] was constant [Lig] was varied

- ○ 1-methyl protons (left ordinate)
- ● 5-proton (left ordinate)
- ■ 3-proton (right ordinate)
- □ 4-proton (right ordinate)

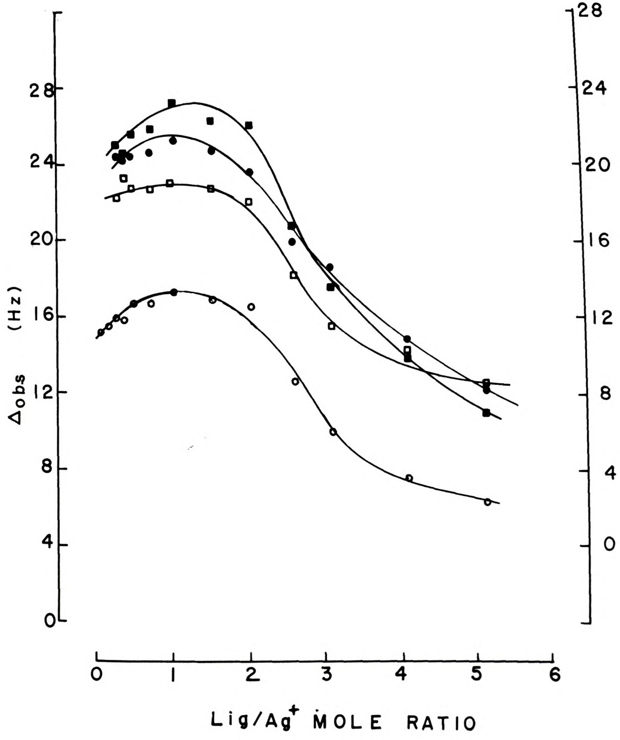

28
24
20
16
12
8
4
0
28
24
20
16
12
8
4
0
Δ_{obs} (Hz)
0
1
2
3
4
5
6
Lig/Ag$^+$ MOLE RATIO

Figure 14.

for each proton environment. The limiting relative chemical shifts for the 1- and 5-methyl resonance of 1,5-DiMeTz was estimated to be 14 and 17 Hz respectively. For the 1-Me-1,2,4-Trz ligand the limiting relative chemical shifts were estimated to be 15, 29, and 42 Hz for the 1-methyl, 3-proton, and 5-proton respectively. The limiting relative chemical shift for the 1-Me-1,2,3-Trz were estimated to be 14, 25, and 18 Hz for the 1-methyl, 4-proton, and 5-proton respectively. The extrapolation procedure could not be applied to the 1-MeIz - $AgClO_4$ and 1-MePz - $AgClO_4$ systems, because in these cases the plots go through a maximum observed relative chemical shift at Lig/Ag^+ mole ratios $\cong 2.00$. These maxima may indicate that there is sufficient amount of the 1:1 complex in solution which has a different relative chemical shift value (Δ_{AD}) from that of the 1:2 complex (Δ_{AD_2}) or that the formation constant $K_1 > K_2$. Either condition might cause the plots to deviate from the smooth curves postulated on page 28. Since these curves go through a maximum, the limiting chemical shift values for the different ligand positions were not clearly defined.

In order to ensure that the shape of the curves obtained in Figures 5-14 were due to complexation and not just solution effects, two additional types of experiments were performed. The solvent resonance was measured as a function of 1,5-DiMeTz concentration (from 0.2212 to 0.7112 M) and silver(I) perchlorate concentration (from 0.0504 to 0.3571 M). The solvent resonance did not vary by more than 1 Hz over

the concentration range for the ligand and not more than 2Hz for the concentration range of the silver(I) perchlorate (Table XIII). The effect of changing the ionic strength of the solution by addition of a noninteracting electrolyte, tetrabutylammonium perchlorate, was also studied. A series of solutions was prepared in which the concentrations of 1,5-DiMeTz and silver(I) perchlorate were held constant at 0.0249 and 0.0254 M respectively. The concentration of the tetrabutylammonium perchlorate was varied from 0.0056 to 0.497 M. The observed resonance frequency of the 5-methyl and 1-methyl protons of the donor molecule remained essentially constant. The differences between the two extreme concentrations of tetrabutylammonium perchlorate were $\sim$ 1 Hz (Table XIV). The effect of the ionic strength was also studied for all the other ligand systems by holding the concentration of the ligand constant at $\sim$ 0.103 M and varying the concentration of tetrabutylammonium perchlorate from $\sim$ 0.01 to 0.50 M (Tables XV through XVIII). In all cases the effect of increasing the salt concentration did not affect the ligand chemical shifts by more than 1 or 2 Hz. Similar results were obtained for the position of the solvent resonance. These studies indicate that the observed chemical shifts of the ligand protons were in fact due to complexation reactions between ligand and silver(I) ions, and that Figures 5-14 are representative of the ligand-silver(I) ion interaction in solution.

Table XIII. Proton magnetic resonance study of the solvent resonance with increasing concentration of 1,5-dimethyltetrazole or silver perchlorate in nitromethane.

1,5-DiMeTz (M)	Sol'v CH_3 δ(Hz)	$AgClO_4$ (M)	Sol'v CH_3 δ(Hz)
0.2212	259.2	0.0504	260.2
0.2998	259.4	0.1009	260.2
0.3604	259.7	0.1503	260.2
0.4970	259.6	0.2522	260.6
0.5827	259.9	0.3026	261.2
0.7112	260.0	0.3571	261.1
--	259.0	--	259.0

Table XIV. Proton magnetic resonance study of the effect of ionic strength on the proton resonances of 1,5-dimethyltetrazole in nitromethane.

Bu_4NClO_4 (<u>M</u>)	δ $1\text{-}CH_3$ (Hz)	δ $5\text{-}CH_3$ (Hz)
--	248.1	164.1
0.0056	248.2	164.1
0.0121	248.8	164.5
0.0248	248.9	164.5
0.0372	248.9	164.6
0.0513	248.9	164.8
0.1262	249.1	164.7
0.2576	248.9	164.8
0.3706	249.2	165.0
0.4968	249.1	165.1

$[1,5\text{-DiMeTz}]_{constant}$ = 0.0249 <u>M</u>

$[AgClO_4]_{constant}$ = 0.0254 <u>M</u>

Table XV. Proton magnetic resonance study of the effect of ionic strength on the proton resonances of 1-methyl-1,2,4-triazole and nitromethane in nitromethane.

Bu_4NClO_4 (M)	$\delta_{1\text{-}CH_3}$ (Hz)	$\delta_{5\text{-}H}$ (Hz)	$\delta_{3\text{-}H}$ (Hz)	$\delta_{sol'v}$ (Hz)
0.0113	233.9	485.5	467.6	260.8
0.0677	234.1	485.6	466.6	260.9
0.181	233.6	486.0	466.9	261.1
0.293	233.8	486.4	467.2	261.1
0.406	233.7	486.9	467.0	261.2
--	233.6	485.9	466.0	261.0

$[1\text{-Me-}1,2,4\text{-Trz}]_{constant}$ = 0.102 M

Table XVI. Proton magnetic resonance study of the effect of ionic strength on the proton resonances of 1-methyl-1,2,3-triazole and nitromethane in nitromethane.

Bu_4NClO_4 (M)	δ_{1-CH_3} (Hz)	δ_{4-H} (Hz)	δ_{5-H} (Hz)	$\delta_{sol'v}$ (Hz)
0.0108	245.0	456.3	462.7	261.1
0.0649	245.0	456.4	463.3	260.4
0.173	245.2	456.0	463.3	261.2
0.281	245.1	456.4	464.2	261.0
0.390	245.4	456.2	464.0	261.1
--	245.3	456.4	462.5	261.3

$[1\text{-Me-}1,2,3\text{-Trz}]_{constant} = 0.108$ M

Table XVII. Proton magnetic resonance study of the effect of ionic strength on the proton resonance of 1-methylimidazole and nitromethane in nitromethane.

Bu_4NClO_4 (M)	δ 2-H (Hz)	δ 4-H (Hz)	δ 5-H (Hz)	δ $1-CH_3$ (Hz)	δ sol'v CH_3 (Hz)
0.034	442.2	416.1	414.7	219.5	259.7
0.093	442.2	416.3	414.8	219.7	259.7
0.172	442.4	416.4	415.0	219.7	259.6
0.222	442.2	416.0	415.2	219.6	259.9
0.318	442.7	416.7	414.8	219.4	259.9
0.349	442.5	416.6	415.2	219.6	260.2
0.420	442.9	416.9	415.4	219.6	260.0
0.492	442.8	417.0	415.7	219.7	260.2
--	442.0	416.0	414.7	219.4	259.6

$[1\text{-MeIz}]_{constant}$ = 0.297 M

Table XVIII. Proton magnetic resonance study of the effect of ionic strength on the proton resonance of 1-methylpyrazole and nitromethane in nitromethane.

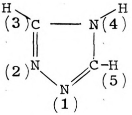
Bu_4NClO_4 ($\underline{M}$)	δ_{1-CH_3} (Hz)	δ_{5-H} (Hz)	δ_{3-H} (Hz)	δ_{4-H} (Hz)	$\delta_{sol'v}$ (Hz)
0.0113	231.0	446.8	442.0	372.0	260.3
0.0677	231.3	446.5	442.4	372.4	260.4
0.181	230.0	447.4	442.3	372.3	260.6
0.293	230.8	447.6	442.4	372.5	260.7
0.406	230.3	447.6	442.3	372.4	260.5
--	229.3	444.2	442.6	371.5	259.4

$[1\text{-MePz}]_{constant} = 0.103\ \underline{M}$

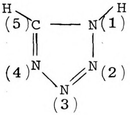
Since so many of the reaction mixtures in nitromethane contained some solid complex, the solid silver(I) perchlorate complexes with the various ligands were prepared and their compositions determined (pages 54-56). Triazole ligands formed 1:1 solid complexes whereas the diazoles and tetrazole formed 1:2 (Ag^+:Lig) complexes with silver(I) perchlorate. A comparison of the infrared spectra of the free ligands with those of the complexes leaves little doubt that the vibrational patterns of the ligands have been influenced by the presence of the silver ion (Figures 1-20, Appendix II).

Reports of solid complexes for the 1-methyl derivatives of diazoles and triazoles are limited to the 1-MeIz system. Reedijk (53) and Perchard and Novak (47,48) have reported solid complexes with silver salts and divalent first row transition metal ions. They propose that 1-MeIz coordinates to the metal ion through the 3-nitrogen. Reedijk (113) has also studied the coordination properties of the parent imidazole and pyrazole ligands with divalent metal perchlorates and tetrafluoroborates. Reedijk's studies indicate that neutral imidazole coordinates through the 3-nitrogen and that neutral pyrazole coordinates through the 2-nitrogen. Reimann, et al. (114,115) have also shown that pyrazole coordinates to first row transition metal ions through the 2-nitrogen. The mono(1,2,4-triazole)copper(II) chloride complex was studied crystallographically by Jarvis (82) (page 23). His studies indicate that the two adjacent nitrogens are involved in coordination. It appears, however, that this is the

1,2,4-4H-triazole isomer whose 1- and 2-nitrogens might possess properties similar to the 3- and 4-nitrogens of the tetrazole ring:



1,2,4-4H-triazole



1,2,3,4-1H-tetrazole

Recently two additional crystallographic studies have been performed on tetrazole complexes. The crystal structure of dichlorobis(1-methyltetrazole)zinc(II) was identified by Baenziger and Schultz (116). The zinc ion is coordinated to the tetrazole ring and is essentially planar with the ring. A charge-transfer σ-bond is formed between the zinc ion and the 4-nitrogen of the tetrazole ring. These data agree with those described for the PMT - ICl complex (page 23). In addition the crystal structure of bis[nitratobis(pentamethylenetetrazole)silver(I)] has been determined in this laboratory (117). The study indicates that a dimer is formed having two silver ions, two nitrate ions and four PMT molecules. Two of the PMT molecules act as bidentate ligands with nitrogen-silver distances of 2.541 and 2.216 Å for the 3- and 4-nitrogens respectively. The other two PMT molecules act as monodentate ligands with nitrogen-silver distances of 2.238 Å for the 4-nitrogen. The nitrate ion also enters into the coordination sphere of the silver ion and acts as a monodentate ligand. The oxygen-silver distance was shown to be 2.422 Å. This crystal structure indicates that the tetrazole ring can indeed form polymer structures (similar to 1,2,4-triazole as proposed in our previous study) by acting as a bridging ligand.

In addition to the location of the preferred sites of interaction for metal ions, some protonation studies by pmr have been performed on the 1-MeIz and 1-Me-1,2,4-Trz ligands (page 12). The 1-MeIz has been shown to protonate at the 3-nitrogen while 1-Me-1,2,4-Trz protonates at the 4-nitrogen. These data support the conclusions of the previous authors concerning metal-ion complexes. It seems reasonable, therefore, that our pmr measurements of the silver(I) perchlorate - ligand systems should indicate some selectivity for the interaction site. To identify this interaction site the following items were compared:

1) The chemical shift of the free ligand, δ_D, in nitromethane solution,

2) The maximum chemical shift observed, $\delta_{c_{max}}$, under the reaction conditions where $[Lig]_{constant}$ $[AgClO_4]_{varied}$,

3) The maximum chemical shift observed, $\delta_{c'_{max}}$, under the reaction conditions where $[AgClO_4]_{constant}$ $[Lig]_{varied}$,

4) The average value of the maximum chemical shift observed minus the chemical shift of the free ligand,

$$\Delta_{c_{max}} = \left(\frac{\delta_{c_{max}} + \delta_{c'_{max}}}{2}\right) - \delta_D \circ$$

A summary of these data are presented in Table XIX. The specific interaction sites appear to be as follows, based on the values of $\Delta_{c_{max}}$: the 2-nitrogen for the 1-MePz, the 3-nitrogen for 1-MeIz, the 3-nitrogen for 1-Me-1,2,3-Trz, and the 4-nitrogen for 1-Me-1,2,4-Trz. However, in the case of 1,5-DiMeTz, the difference in the attachment of the two methyl groups to carbon and nitrogen on the ring and the distance from the interaction site to the probing nucleus leaves some doubt about the proper assignment. Most probably the proper assignment is one of two alternatives; the silver ion either is coordinated to the 3-nitrogen or it is coordinated with equal probability to the 2-, 3-, and 4-nitrogens respectively.

One of the aims of this study was to determine the formation constants for the complexation reactions between the azole ligands and the silver(I) perchlorate in nitromethane solutions. The proton magnetic resonance measurements have indicated that the exchange of the donor environment between free and complexed states is very rapid, thus only one absorption per proton environment was observed. This study has also shown that the predominant component in solution at Lig/Ag^+ mole ratios > 2.00 is the 1:2 complex (AD_2) for the ligands 1-MeIz, 1-MePz, and 1,5-DiMeTz.

An attempt was made to determine the formation constant of the complex $[Ag(1,5\text{-DiMeTz})_2]ClO_4$ in nitromethane solution. It was assumed that the concentration of the 1:1 complex was negligible. Thus the relative fractions of the

Table XIX. Comparison of observed chemical shifts of equivalent proton environments on azole ligands in ligand-silver perchlorate system (δ in ppm).

	$1-CH_3$	2-H	3-H	4-H	5-H or CH_3
1,5-DiMeTz					
δ_D	3.98	--	--	--	2.50
$\delta_{C_{max}}$	4.26	--	--	--	2.83
$\delta_{C'_{max}}$	4.20	--	--	--	2.78
$\Delta_{C_{max}}$	0.25	--	--	--	0.30
1-Me-1,2,4-Trz					
δ_D	3.89	--	7.77	--	8.08
$\delta_{C_{max}}$	4.06	--	8.11	--	8.58
$\delta_{C'_{max}}$	4.08	--	8.12	--	8.59
$\Delta_{C_{max}}$	0.18	--	0.44	--	0.50

1-Me-1,2,3-Trz					
δ_D	4.09	--	--	7.61	7.71
$\delta_{C_{max}}$	>4.26	--	--	8.08	7.96
$\delta_{C'_{max}}$	4.27	--	--	8.09	7.97
$\Delta_{C_{max}}$	0.16	--	--	0.48	0.26
1-MeIz					
δ_D	3.66	7.37	--	6.93	6.91
$\delta_{C_{max}}$	3.86	7.90	--	7.38	7.27
$\delta_{C'_{max}}$	3.84	7.84	--	7.25	7.14
$\Delta_{C_{max}}$	0.19	0.50	--	0.39	0.30
1-MePz					
δ_D	3.82	--	7.37	6.19	7.40
$\delta_{C_{max}}$	4.10	--	7.78	6.55	7.86
$\delta_{C'_{max}}$	4.07	--	7.72	6.50	7.81
$\Delta_{C_{max}}$	0.27	--	0.38	0.34	0.14

complexed and uncomplexed tetrazole were calculated from the chemical shift data (Table III) and the estimated limiting chemical shift values of 20 and 17 Hz for the 5-methyl and 1-methyl protons respectively. The resulting values for the overall formation constant were scattered over at least one order of magnitude (Table XX). It seems, therefore, that the 1:1 complex does indeed play an important role in the complexation reaction.

It appears that the methods outlined for the formation constant determination are limited to that reported by Foreman, et al. (91) (page 35). However, the expression derived by them holds for the case where A, the acceptor (benzene) possesses the nucleus being measured and is complexed to the donor (silver ions) forming the complexed species AD_2. However, if the donor possesses the nucleus being measured, as in our case, a new expression must be derived as follows:

$$A + D = AD \qquad AD + D = AD_2 \tag{31}$$

$$K_1 = \frac{[AD]}{[A]\,[D]} \qquad K_2 = \frac{[AD_2]}{[AD]\,[D]} \tag{32}$$

$$[AD] = K_1[A]\,[D] \qquad [AD_2] = K_1K_2\,[A]\,[D]^2 \tag{33}$$

$$\Delta_{obs} = X_{1:1}\,\Delta_1 + X_{1:2}\,\Delta_2 \tag{34}$$

thus:

Table XX. Overall formation constant determination for the 1:2 complex based on relative fractions of free and complexed ligand.

$[D_0]$	Δ_{obs}	$\frac{\Delta_{obs}}{\Delta_{AD_2}}$	$[AD_2]$	[A]	[D]	K_f
Based on $1\text{-}CH_3$ where $\Delta_{AD_2} = 17$ Hz						
0.259	14.8	0.871	0.113	0.0168	0.033	6,176
0.286	15.5	0.950	0.119	0.0114	0.048	4,531
0.337	16.1	0.945	0.123	0.00689	0.091	2,156
0.389	16.4	0.965	0.125	0.00455	0.139	1,422
0.441	16.2	0.953	0.124	0.00611	0.193	545
0.519	16.8	0.988	0.128	0.00156	0.263	1,186
Based on $5\text{-}CH_3$ where $\Delta_{AD_2} = 20$ Hz						
0.259	19.0	0.950	0.124	0.00650	0.011	157,660
0.286	19.0	0.950	0.124	0.00650	0.038	13,211
0.337	18.9	0.945	0.123	0.00715	0.091	2,077
0.389	19.4	0.970	0.126	0.00483	0.137	1,390
0.441	19.3	0.965	0.125	0.00455	0.191	753
0.519	19.5	0.975	0.127	0.00325	0.265	556
0.623	19.4	0.970	0.126	0.00390	0.371	235
0.778	19.4	0.970	0.126	0.00390	0.526	117

$$[A] = A_0 \left(\frac{1-\Delta_{obs}}{\Delta_{AD_2}}\right) \qquad [D] = D_0 - 2\,[AD_2]$$

$$[AD_2] = A_0 \left(\frac{\Delta_{obs}}{\Delta_{AD_2}}\right)$$

$$K_f = \frac{[AD_2]}{[A]\,[D]^2}$$

$$X_{1:1} = \frac{[AD]}{[D_0]} = \frac{K_1\ [A]\ [D]}{[D_0]} \qquad (35)$$

$$X_{1:2} = \frac{2[AD_2]}{[D_0]} = \frac{2\ K_1\ K_2\ [A]\ [D]^2}{[D_0]} \qquad (36)$$

combining equations 34, 35, and 36:

$$\Delta_{obs} = \frac{K_1\ [A]\ [D]\ \Delta_1 + 2\ K_1\ K_2\ [A]\ [D]^2\ \Delta_2}{D_0} \qquad (37)$$

Since $[A_0] >>> [D_0]$:

$$[A] = [A_0] \qquad (38)$$

and

$$[D] = [D_0] - [AD] - 2[AD_2] = [D_0] - K_1[A][D] - 2K_1K_2[A][D]^2 \qquad (39)$$

Substituting equation 38 into equation 37:

$$\Delta_{obs} = \frac{K_1\ [A_0][D]\ \Delta_1 + 2K_1K_2\ [A_0][D]^2\ \Delta_2}{[D_0]} \qquad (40)$$

Even if one substitutes equation 39 into equation 40 one does not eliminate the value for the equilibrium concentration of the free donor, [D], which we have no way of measuring in our systems. Thus the application of Foreman, Gorton, and Fosters' approach to the determination of the formation constant values for the 1:2 and 1:1 complexes in solution by nmr seems impossible. It is interesting to note, that when the acceptor nucleus is being measured the workable method is obtained, but when the donor molecule is being measured the method is no longer applicable.

Equation 40 may help to explain the shapes of the curves in Figures 5-14. Assuming that 99% of the donor is in the complexed form and only 1% is free in solution, then $[D] = 0.01\ [D_0]$. Under these conditions four factors govern the value of Δ_{obs}, they are Δ_1, Δ_2, K_1, and K_2. In systems where the plots of Δ_{obs} vs Lig/Ag^+ (or Ag^+/Lig) mole ratios give smooth curves with no maxima, it appears that $\Delta_2 > \Delta_1$ and $K_2 > K_1$. However, in the cases where the plots pass through a maximum value, there are two possibilities; either $\Delta_2 < \Delta_1$ and $K_2 > K_1$ or $\Delta_2 > \Delta_1$ and $K_2 < K_1$. The first case assumes that the azole ligands coordinate with silver ions to form stepwise complexes similar to those exhibited for other nitrogen bases where $K_2 > K_1$ (Table XXI). If this condition holds then the terms Δ_1 and Δ_2 must influence the observed relative chemical shift and cause the maximum to occur. This maximum can only occur if $\Delta_1 > \Delta_2$. The second case assumes that $\Delta_2 > \Delta_1$ and indicates that $K_2 < K_1$. This is not the usual ordering of K_1 and K_2 in complex formation but it must not be overlooked as a possible explanation. The formation constants for these systems have not been measured by any other method, except for the 1-MeIz - Ag^+ system in water (51).

In order to check the importance of the 1:1 complex in the 1,5-DiMeTz - $AgClO_4$ system in nitromethane solutions one additional experimental parameter was studied. In these studies the Lig/Ag^+ mole ratio was held constant while the concentration of the reactants was varied. Three systems

Table XXI. Literature values for the formation constants for silver(I) ligand interactions in aqueous solutions.

Ligand	Method Used	Temp °C	Conditions	log K_1	log K_2	Ref.
Ammonia	gl	25	⟶ 0 NH_4NO_3	3.315	3.915	a
	sol	25	0-corr	3.37	3.84	b
	Ag	25	1 KNO_3	3.31	3.91	c
Methyl amine	gl	25	0.5 $CH_3NH_3NO_3$	3.15	3.54	d
Ethyl amine	gl	25	0.5 KNO_3	3.37	3.93	e
Diethyl amine	gl	25	50 mole% C_2H_5OH	3.26	3.17	f
	gl	30	0.5 KNO_3	2.98	3.22	g
Triethylamine	gl	25	0.4 $C_6H_{15}NHNO_3$	2.6	2.1	d
	gl	25	50 mole% C_2H_5OH	2.31	1.79	f
n-Butylamine	gl	25	0.5 $C_4H_{11}NHNO_3$	3.43	4.05	d
i-Butylamine	gl	25	0.5 KNO_3	3.38	3.86	e
t-Butylamine	gl	25	50 mole% C_2H_5OH	4.01	4.25	f
Ethylenediamine	Ag,gl	25	1 KNO_3	6	1.4	d
	gl	20	0.1 $NaNO_3$	4.70	3.00	h
Ethanol amine	gl	25	50 mole% C_2H_5OH	3.41	3.99	f
	gl	30	⟶ 0	3.07	3.57	i
	gl	25	0.5 KNO_3	3.13	3.55	e
Benzylamine	gl	25	0.5 KNO_3	3.29	3.85	e
Imidazole	gl	25	0.058 KCl	3.78	3.26	j
Pyridine	gl	25	⟶ 0	1.97	2.38	k
	sol	25	⟶ 0	2.00	2.11	l
	gl	25	0.5 KNO_3	2.04	2.18	e
α-Picoline	gl	25	0.5 KNO_3	2.27	2.41	e
β-Picoline	gl	25	⟶ 0	2.00	2.35	k
γ-Picoline	gl	25	⟶ 0	2.03	2.36	k
2,4-Dimethylpyridine	gl	25	0.5 KNO_3	2.47	2.71	e
Piperdine	gl	25	0.5 KNO_3	3.16	3.45	d
	gl	25	0.5 KNO_3	3.03	3.45	e
Aniline	gl	25	50 mole% C_2H_5OH	1.38	1.50	f
2,6-Xylidine	gl	25	50 mole% C_2H_5OH	1.47	1.33	f
Quinoline	gl	25	50 mole% C_2H_5OH	1.79	1.95	f
1,10-Phenanthroline	Ag	25	0.1 $NaNO_3$	5.02	7.05	m

Continued

Table XXI. Continued.

gl	glass electrode
sol	solubility measurements
Ag	potentiometrically using silver electrode to follow free silver ions.
⟶ 0	value obtained by extrapolation to infinite dilution
0-corr	corrected to infinite dilution.

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m) J. M. Dale and C. V. Banks, Inorg. Chem., **2**, 591 (1963).

were studied where the Lig/Ag^+ mole ratios were held constant at 0.076, 1.02, and 1.53 (Table XXII). It appears from this study that the magnitude of the chemical shifts were dependent on the total concentration of the reactants as well as the Lig/Ag^+ mole ratio. The shapes of these curves Δ_{obs} vs [Lig] are compared in Figures 15 and 16.

Proton Nuclear Magnetic Studies in Acetonitrile

Proton nmr studies for the complexation of azole derivatives with silver(I) perchlorate were also studied in a competitive solvent, acetonitrile. Acetonitrile has a Gutmann's donor number of 14.1 as compared to 2.3 for nitromethane.

The chemical shift assignments for the various proton environments of the free ligands in acetonitrile were made based on the literature values listed in Table II for other solvents. These assignments are summarized in Table XXIII. The observed chemical shifts for the protons on the ligand molecules were measured on a series of solutions where the silver(I) perchlorate concentration was held constant at about 0.250 M and the concentration of the ligand was varied from about 0.01 to 1.25 M (corresponding to ligand to silver ion mole ratios from 0.04 to 5.00), (Tables XXIV - XXVIII). These values were used to calculate the observed relative chemical shifts (Δ_{obs}), which were plotted as a function of the Lig/Ag^+ mole ratios (Figures 17-21). In most cases, the curves obtained went through a maximum value, however, the

Table XXII. Proton magnetic resonance study of the role of complex dissociation at constant 1,5-dimethyltetrazole to silver perchlorate mole ratios.

$[AgClO_4]$ (M)	[1,5-DiMeTz] (M)	5-CH_3 δ(Hz)	5-CH_3 Δ(Hz)	1-CH_3 δ(Hz)	1-CH_3 Δ(Hz)
1,5-DiMeTz/Ag^+ = 0.765					
0.0502	0.0384	163.7	13.6	247.0	8.4
0.1005	0.0768	164.5	14.4	247.1	8.5
0.1507	0.1153	166.8	16.1	249.5	10.9
0.2009	0.1537	166.1	16.0	250.4	11.8
0.2512	0.1921	167.2	17.1	251.0	12.4
0.3014	0.2306	167.6	17.5	251.8	13.2
0.4018	0.3074	167.8	17.7	252.4	13.8
0.5023	0.3843	168.0	17.9	252.4	13.8
1,5-DiMeTz/Ag^+ = 1.02					
0.0249	0.0254	161.6	11.5	245.6	7.0
0.0499	0.0509	162.4	12.3	246.5	7.9
0.0898	0.0916	163.6	13.5	247.6	9.0
0.1497	0.1521	165.1	15.1	249.2	10.6
0.2495	0.2535	166.2	16.1	250.6	12.0
0.3494	0.3549	166.5	16.4	under	solvent
0.4492	0.4563	166.6	16.5	under	solvent
1,5-DiMeTz/Ag^+ = 1.53					
0.0502	0.0768	164.5	14.4	247.0	8.4
0.1005	0.1537	164.5	14.4	247.2	8.6
0.1507	0.2306	165.0	14.9	248.4	9.8
0.2009	0.3074	166.5	16.5	250.8	12.2
0.2512	0.3843	ppt	--	ppt	--
0.3014	0.4611	ppt	--	ppt	--
0.5100	0.6123	ppt	--	ppt	--

Figure 15. A comparison of the curve shapes obtained when the observed relative chemical shifts of the protons of 1,5-dimethyltetrazole were plotted *versus* [Lig] at constant Lig/Ag^+ mole ratio of 1.02, 0.76, and 1.53

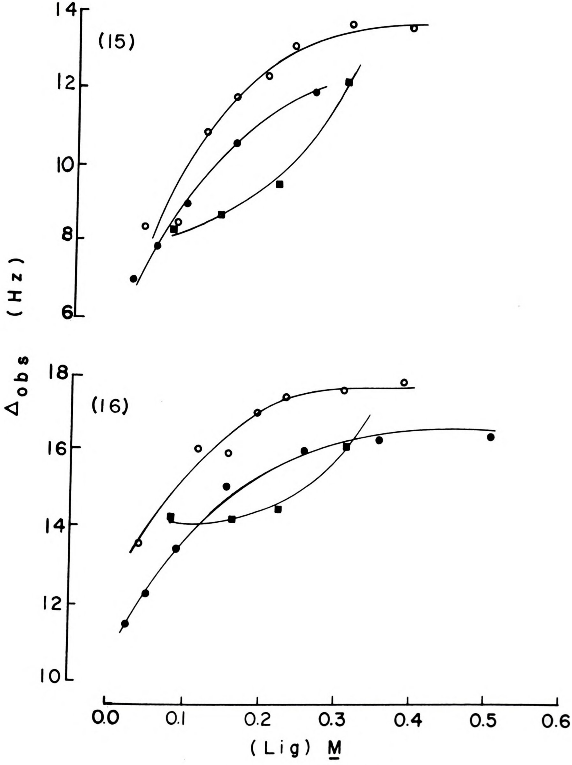
1-methyl protons

- ● mole ratio 0.76
- ○ mole ratio 1.02
- ■ mole ratio 1.53

Figure 16. A comparison of the curve shapes obtained when the observed relative chemical shifts of the protons of 1,5-dimethyltetrazole were plotted *versus* [Lig] at constant Lig/Ag^+ mole ratio of 1.02, 0.76, and 1.53

5-methyl protons

- ● mole ratio 0.76
- ○ mole ratio 1.02
- ■ mole ratio 1.53



Figures 15 and 16.

Table XXIII. Chemical shift assignments for the equivalent protons on the azole ligands in acetonitrile. (ppm)

Compound	δ $1-CH_3$	δ 2-H	δ 3-H	δ 4-H	δ 5-H or CH_3
1,5-DiMeTz	3.92	--	--	--	2.44
1-Me-1,2,4-Trz	3.85	--	7.86	--	8.17
1-Me-1,2,3-Trz	3.89	--	--	8.19	7.86
1-MeIz	3.60	7.39	--	6.94	6.92
1-MePz	3.80	--	7.41	6.19	7.41

Table XXIV. Proton magnetic resonance study of the 1,5-dimethyltetrazole and silver perchlorate system in acetonitrile.

1,5-DiMeTz (M)	Lig/Ag^+	$1-CH_3$		$5-CH_3$	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
0.0107	0.04	151.8	3.4	238.0	2.4
0.0214	0.08	151.8	3.4	238.4	2.8
0.0429	0.17	151.9	3.5	238.3	2.7
*0.0919	0.37	151.8	3.4	238.3	2.7
*0.138	0.55	151.8	3.4	238.3	2.7
*0.207	0.83	151.6	3.2	238.4	2.8
*0.276	1.10	151.7	3.3	238.1	2.5
*0.345	1.38	151.6	3.2	238.1	2.5
*0.460	1.84	151.5	3.1	238.2	2.6
*0.574	2.30	151.3	2.9	237.9	2.3
*0.804	3.22	151.1	2.7	237.8	2.2
*1.034	4.14	150.0	1.6	237.3	1.7
*1.264	5.06	150.0	1.6	237.3	1.7
--	free ligand	148.2	--	235.4	--

$[AgClO_4]_{constant}$ = 0.251 M

*Solutions became slightly cloudy, only supernatant liquid was used in measurements.

Table XXV. Proton magnetic resonance study of the 1-methyl-1,2,4-triazole and silver perchlorate system in acetonitrile.

1-Me-1,2,4-Trz (M)	Lig/Ag^+	$1-CH_3$		3-H		5-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
	free ligand	230.8	--	471.6	--	490.2	--
0.0109	0.04	230.8	--	--	--	--	--
0.0219	0.09	231.5	0.7	476.4	4.8	503.5	13.3
0.0438	0.17	231.9	1.1	476.7	5.1	503.2	13.0
0.0875	0.35	232.9	2.1	477.3	5.7	503.7	13.5
0.131	0.52	233.1	2.3	477.7	6.1	504.6	14.4
0.197	0.78	234.4	3.6	478.0	6.4	504.8	14.6
*0.263	1.04	238.3	7.5	478.7	7.1	505.0	14.8
*0.328	1.30	238.0	7.2	479.0	7.4	505.3	15.1
*0.438	1.74	240.3	9.5	478.9	7.3	504.9	14.7
*0.547	2.17	241.9	11.1	478.7	7.1	504.4	14.2
*0.766	3.04	246.3	15.5	477.1	5.5	502.0	11.8
*0.985	3.91	251.8	21.0	475.6	4.0	499.5	9.3
*1.203	4.78	255.7	24.9	474.6	3.0	498.0	7.8

$[AgClO_4]_{constant}$ = 0.252 M

*Solutions became slightly cloudy, only supernatant liquid was used in measurements.

Table XXVI. Proton magnetic resonance study of the 1-methyl-1,2,3-triazole and silver perchlorate system in acetonitrile.

1-Me-1,2,3-Trz (M)	Lig/Ag^+	$1-CH_3$ δ(Hz)	$1-CH_3$ Δ(Hz)	5-H δ(Hz)	5-H Δ(Hz)	4-H δ(Hz)	4-H Δ(Hz)
1.686	free ligand	232.2	--	491.6	--	471.5	--
0.0506	0.21	236.1	3.9	--	--	--	--
0.0675	0.28	235.6	3.4	503.3	11.7	476.8	4.3
0.0843	0.35	236.0	3.8	503.1	11.5	476.4	4.9
0.169	0.69	235.9	3.7	503.8	12.2	476.8	5.3
0.253	1.04	236.2	4.0	504.3	12.7	477.9	6.4
0.337	1.38	236.6	4.4	504.4	12.8	478.6	7.1
0.422	1.73	236.5	4.3	504.9	13.3	478.6	7.1
0.590	2.42	236.2	4.0	505.2	13.6	478.6	7.1
0.759	3.11	236.4	4.2	505.6	14.0	478.5	7.0
0.927	3.80	236.3	4.1	505.8	14.2	479.2	7.7
1.096	4.49	236.4	4.2	505.6	14.0	479.5	8.0
1.265	5.18	236.3	4.1	505.5	13.9	479.1	7.6

$[AgClO_4]_{constant}$ = 0.244 M

Table XXVII. Proton magnetic resonance study of the 1-methylimidazole and silver perchlorate system in acetonitrile.

1-MeIz (M)	Lig/Ag^+	1-CH_3		5-H		4-H		2-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
0.0123	0.05	223.6	7.6	--	--	--	--	--	--
0.0246	0.10	223.8	7.8	--	--	--	--	--	--
0.0492	0.20	223.8	7.8	417.8	2.7	428.1	11.8	459.0	15.5
0.0984	0.39	224.2	8.2	419.6	4.5	428.8	12.5	460.8	17.3
0.147	0.59	224.3	8.3	420.4	5.3	428.9	12.6	461.3	17.8
0.221	0.89	224.3	8.3	421.3	6.2	429.5	13.2	462.4	18.9
0.295	1.18	224.6	8.6	422.2	7.1	430.0	13.7	463.4	19.9
0.369	1.48	223.8	7.8	423.0	7.9	430.2	13.9	464.6	21.1
0.615	2.46	223.2	7.2	420.4	5.3	427.2	10.9	459.3	15.8
0.861	3.44	221.7	5.7	417.8	2.7	424.6	8.3	455.0	11.5
1.107	4.43	221.1	5.1	416.6	1.5	423.3	7.0	453.0	9.5
1.354	5.41	219.9	3.9	415.6	0.5	421.7	5.4	450.4	6.9
1.600	6.40	219.4	3.4	415.3	0.2	421.1	4.8	449.9	6.4
--	free ligand	216.0	--	415.1	--	416.3	--	443.5	--

$[AgClO_4]_{constant}$ = 0.250 M

Table XXVIII. Proton magnetic resonance study of the 1-methylpyrazole and silver perchlorate system in acetonitrile.

1-MePyz (M)	Lig/Ag^+	$1-CH_3$		4-H		3-H		5-H	
		δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)	δ(Hz)	Δ(Hz)
--	free ligand	228.2	--	371.2	--	444.8	--	444.8	--
0.530	2.22	230.2	2.0	375.4	4.2	445.8	1.0	452.3	7.5
0.434	1.82	230.8	2.6	376.1	4.9	446.2	1.4	453.0	8.2
0.337	1.47	231.6	3.4	376.8	5.6	447.3	2.5	454.2	9.4
0.241	1.01	233.2	5.0	377.8	6.6	448.5	3.7	455.4	10.6
0.193	0.81	234.0	5.8	379.3	8.1	449.6	4.8	456.9	12.1
0.145	0.61	234.0	5.8	379.8	8.6	450.8	6.0	458.2	13.4
0.0964	0.40	234.6	6.4	380.4	9.2	450.8	6.0	458.5	13.7
0.0723	0.30	234.5	6.3	380.7	9.5	450.6	5.8	459.1	14.3
0.0482	0.20	234.0	6.2	380.8	9.6	450.5	5.7	459.6	14.8
0.0385	0.16	234.5	6.3	380.9	9.7	450.5	5.7	459.7	14.9
0.0289	0.12	234.0	5.8	380.7	9.5	450.0	5.2	459.4	14.6
0.0193	0.08	234.0	5.8	380.8	9.6	450.3	5.5	459.4	14.6
0.0096	0.04	234.1	5.9	380.5	9.3	449.5	4.7	459.2	14.4

$[AgClO_4]_{constant}$ = 0.239 M

Figure 17. a) Relationship between the observed relative chemical shift of the protons of 1,5-dimethyltetrazole and the Lig/Ag^+ mole ratio in acetonitrile [$AgClO_4$] was constant [Lig] was varied

- o 1-methyl protons (left ordinate)
- ● 5-methyl protons (right ordinate)

b) Relationship between the observed relative chemical shift of the protons of 1,5-dimethyltetrazole and the Ag^+/Lig mole ratio in acetonitrile [Lig] was constant [$AgClO_4$] was varied

- o 1-methyl protons (left ordinate)
- ● 5-methyl protons (right ordinate)

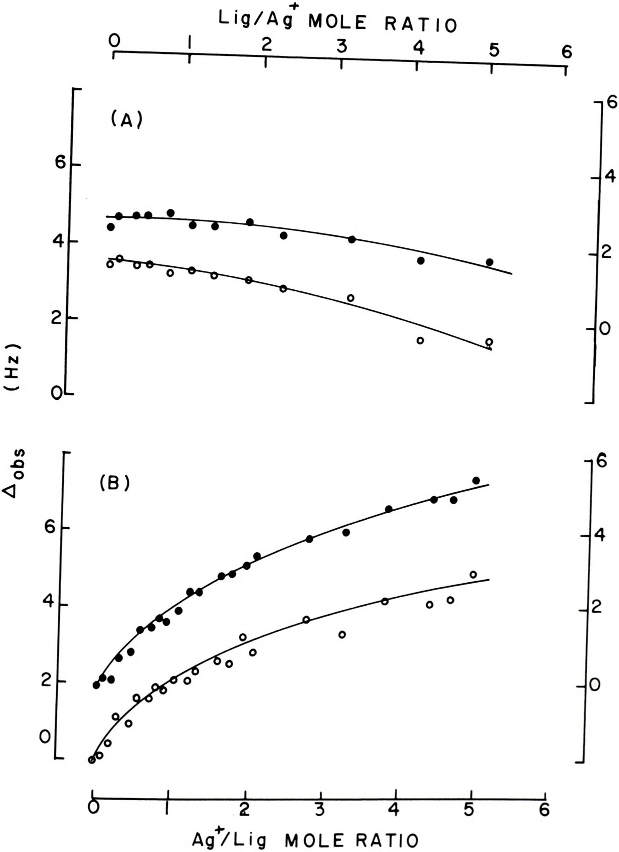


Figure 17.

Figure 18. Relationship between the observed relative chemical shift of the protons of 1-methyl-1,2,4-triazole and the Lig/Ag^+ mole ratio in acetonitrile [$AgClO_4$] was constant [Lig] was varied

- o 1-methyl protons
- ● 5-proton
- ■ 3-proton

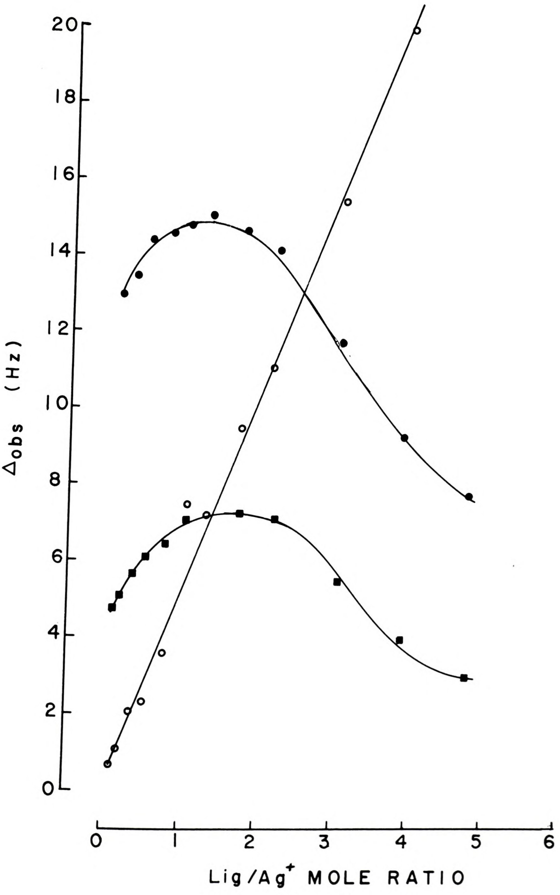


Figure 18.

Figure 19. Relationship between the observed relative chemical shift of the protons of 1-methyl-1,2,3-triazole and the Lig/Ag^+ mole ratio in acetonitrile [$AgClO_4$] was constant [Lig] was varied

o 1-methyl protons

● 5-proton

■ 4-proton

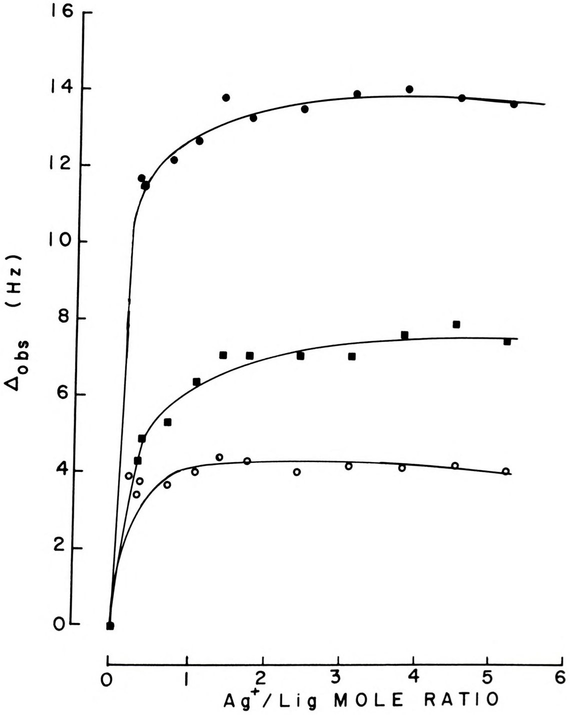


Figure 19.

Figure 20. Relationship between the observed relative chemical shift of the protons of 1-methylimidazole and the Lig/Ag^+ mole ratio in acetonitrile [$AgClO_4$] was constant [Lig] was varied

- o 1-methyl protons (left ordinate)
- ● 5-proton (left ordinate)
- □ 2-proton (right ordinate)
- ■ 4-proton (right ordinate)

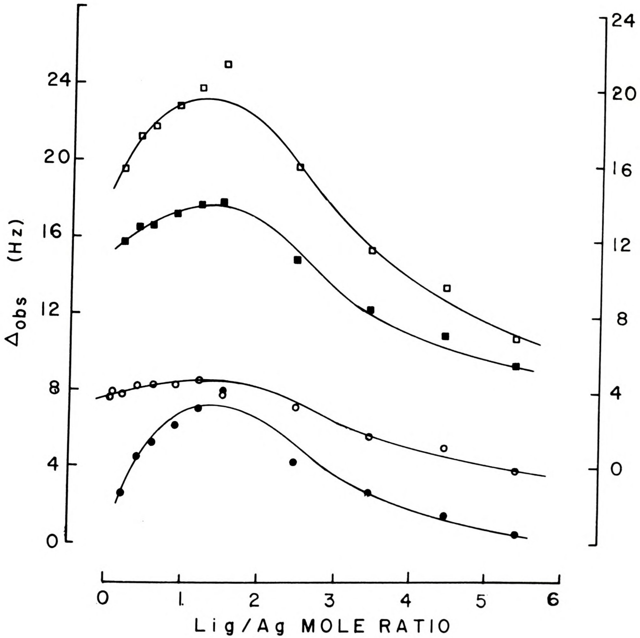

24
20
16
12
8
4
0
24
20
16
12
8
4
0
Δ_{obs} (Hz)
0
1
2
3
4
5
6
Lig/Ag MOLE RATIO

Figure 20.

Figure 21. Relationship between the observed relative chemical shift of the protons of 1-methylpyrazole and the Lig/Ag^+ mole ratio in acetonitrile [$AgClO_4$] was constant [Lig] was varied

- ○ 1-methyl protons (left ordinate)
- ● 5-proton (left ordinate)
- □ 3-proton (right ordinate)
- ■ 4-proton (right ordinate)

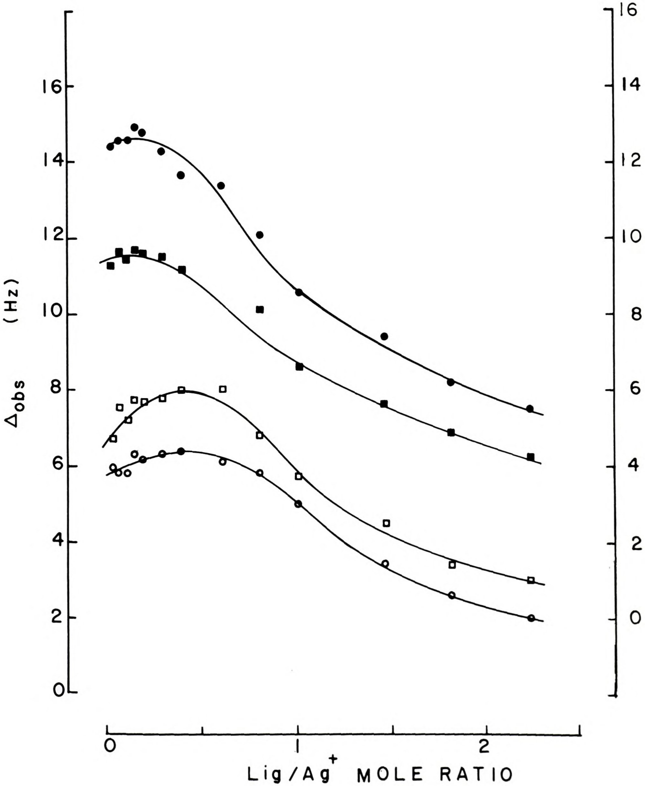


Figure 21.

1-methyl and the 5-methyl protons of the 1,5-DiMeTz (Figure 17a), the 1-methyl protons of 1-Me-1,2,4-Trz (Figure 18), and the 1-methyl protons of 1-Me-1,2,3-Trz (Figure 19) gave smooth curves with no maxima. In addition to the reasons outlined for the systems in nitromethane whose curves went through maximum values, the solvent acetonitrile has a greater influence upon the complexation equilibrium. The ligand molecules are not only involved in the simple AD and AD_2 complexes but are also involved in mixed solvent-ligand complexes (or intermediate solvated species) such as $S_n A D_{2-n}$.

An additional experiment was performed in acetonitrile to compare the complexing ability of 1,5-DiMeTz with the bi-tetrazole, 1,4-bis(1-methyl-5-tetrazolyl)n-butane recently studied by Septemia Policec (118) in this laboratory. In both cases, the ligand concentration was varied, such that the Lig/Ag^+ mole ratios varied from 0.10 to $\leq$ 10. The chemical shifts of the 1-methyl protons of 1,5-DiMeTz increased from 3.92 to 4.01 ppm while the value for the 5-methyl protons increased from 2.47 to 2.56 ppm (Table XXIX). The limiting relative chemical shift for the 1-methyl protons of the bitetrazole was about 6 Hz (0.10 ppm) while that for the 1,5-DiMeTz was about 4 Hz. When the relative chemical shifts observed were plotted as a function of the Ag^+/Lig mole ratios, smooth curves were obtained (Figure 17b).

Table XXIX. Proton magnetic resonance study of the 1,5-dimethyltetrazole and silver perchlorate system in acetonitrile.

DiMeTz (M)	$AgClO_4$ (M)	Ag^+/Lig	1-CH_3 δ(Hz)	1-CH_3 Δ(Hz)	5-CH_3 δ(Hz)	5-CH_3 Δ(Hz)
0.0960	--	free ligand	235.4	--	148.2	--
0.0922	0.0100	0.11	235.5	0.1	148.2	--
0.0924	0.0200	0.22	235.8	0.4	148.3	0.1
0.0938	0.0301	0.32	236.5	1.1	148.9	0.7
0.0912	0.0402	0.44	236.3	0.9	149.0	0.8
0.0907	0.0502	0.55	237.0	1.6	149.6	1.4
0.0865	0.0602	0.70	237.0	1.6	149.7	1.5
0.0889	0.0703	0.79	237.3	1.9	149.9	1.7
0.0926	0.0803	0.87	237.2	1.8	149.9	1.7
0.1018	0.0903	0.89	237.4	2.0	150.1	1.9
0.0975	0.1004	1.03	237.5	2.1	150.3	2.1
0.0936	0.1104	1.18	237.5	2.1	150.4	2.2

0.1003	0.1236	1.23	237.8	2.4	150.6	2.4
0.0944	0.1205	1.28	237.7	2.3	150.6	2.4
0.0887	0.1441	1.62	238.0	2.6	151.0	2.8
0.0958	0.1647	1.72	237.9	2.5	151.1	2.9
0.0956	0.1853	1.94	238.5	3.1	151.4	3.2
0.1001	0.2059	2.06	238.2	2.8	151.6	3.4
0.0936	0.2574	2.75	239.1	3.7	152.0	3.8
0.0948	0.3089	3.26	238.7	3.3	152.2	4.0
0.0944	0.3604	3.82	239.6	4.2	152.8	4.6
0.0940	0.4118	4.38	239.5	4.1	153.1	4.9
0.0999	0.4633	4.64	239.6	4.2	153.1	4.9
0.1062	0.5148	4.85	240.3	4.9	153.6	5.4

$[1,5\text{-DiMeTz}]_{constant} \cong 0.100$ M

Sodium-23 Magnetic Resonance Studies

To determine the relative donor abilities of the azoles, a mixed solvent study (page 42) was performed in nitromethane, acetonitrile, and acetone solutions. However, in all cases the sodium ion resonance line width at half peak height became so broad that at mole fractions (Ligand/Ligand + solvent) > 0.10 the data could not be collected using the Varian DA60 spectrometer in wideline configuration Thus only solutions Lig/Lig + solvent mole fraction < 0.10 were studied in order to note trends in the sodium ion electron density changes. Since the amount of solvent was nearly constant, the chemical shift of the sodium-23 resonance was observed as a function of the mole ratios Lig/Na^+ (Tables XXX-XXXIV). Figures 22, 23, and 24 represent the five ligands in nitromethane, acetonitrile, and acetone respectively.

If the donor ability of the azole ligands is greater than the solvent, one would expect a rapid decrease in the sodium-23 chemical shift. In the least donating solvent nitromethane (D.N. = 2.3), this type of trend is noted. All five ligands show a decrease in the chemical shift with increasing Lig/Na^+ mole ratio. When acetonitrile (D.N. = 14.1) is used as the reaction medium, the donating abilities of the azole ligands begin to differentiate (Figure 23). When a solvent with donor number 17.0 (acetone) was chosen, the ligands are clearly differentiated and 1-MeIz appears to have the greatest donating ability with

Table XXX. Sodium-23 nuclear magnetic resonance study of 1,5-dimethyltetrazole and sodium tetraphenylborate in nitromethane, acetonitrile, and acetone.

[1,5-DiMeTz] (M)	$[NaB(C_6H_5)_4]$ (M)	Lig/Na^+	δ Na-23 (Hz)	(ppm)	L.W. (Hz)
in nitromethane					
--	0.250	--	247	15.6	26
0.0776	0.255	0.30	238	15.0	37
0.155	0.253	0.61	221	13.9	42
0.233	0.258	0.90	215	13.5	46
0.388	0.257	1.51	194	12.9	55
0.776	0.252	3.08	175	11.0	70
1.164	0.256	4.55	144	9.1	83
in acetonitrile					
--	0.250	--	131	8.25	18
0.0693	0.241	0.29	131	8.25	30
0.139	0.245	0.57	133	8.38	38
0.208	0.240	0.87	133	8.38	35
0.346	0.245	1.41	135	8.50	35
0.693	0.241	2.88	121	7.62	38
1.039	0.244	4.26	117	7.37	35
in acetone					
--	0.250	--	164	10.3	17
0.0736	0.258	0.29	146	9.19	29
0.147	0.247	0.60	148	9.32	27
0.221	0.262	0.84	141	8.88	30
0.368	0.254	1.45	147	9.26	26
0.736	0.260	2.83	142	8.94	27
1.104	0.257	4.30	140	8.82	26

Table XXXI. Sodium-23 nuclear magnetic resonance study of 1-methyl-1,2,4-triazole and sodium tetraphenylborate in nitromethane, acetonitrile, acetone, and pyridine.

[1-Me-1,2,4-Trz] (M)	[NaB)C_6H_5)$_4$] (M)	Lig/Na^+	δ Na-23 (Hz)	δ Na-23 (ppm)	L.W. (Hz)
in nitromethane					
--	0.247	--	245	15.4	28
0.0726	0.241	0.30	219	13.8	52
0.145	0.243	0.60	202	12.7	63
0.218	0.244	0.89	179	11.3	74
0.363	0.243	1.49	153	9.63	109
0.726	0.249	2.92	103	6.49	very broad
1.089	0.250	4.36	74	4.66	very broad
in acetonitrile					
--	0.250	--	130	8.19	18
0.0912	0.243	0.38	127	8.00	26
0.182	0.243	0.75	123	7.75	33
0.274	0.241	1.14	113	7.12	31
0.456	0.243	1.88	101	6.36	36
0.912	0.242	3.77	74	4.66	38
1.368	0.241	5.65	55	3.46	43
in acetone					
--	0.250	--	162	10.2	19
0.0904	0.246	0.37	143	9.01	37
0.181	0.242	0.75	131	8.25	37
0.271	0.242	1.12	127	8.00	37
0.452	0.242	1.87	117	7.37	37
0.904	0.243	3.72	91	5.73	41
1.356	0.239	5.67	76	4.79	47
in pyridine					
--	0.246	--	-3	-0.19	30
0.0990	0.236	0.42	-4	-0.25	33
0.198	0.236	0.84	-6	-0.35	35
0.297	0.236	1.26	-6	-0.38	35
0.495	0.236	2.10	-7	-0.44	36
0.989	0.236	4.19	-16	-1.01	38
1.485	0.234	6.35	-21	-1.32	41

Table XXXII. Sodium-23 nuclear magnetic resonance study of 1-methyl-1,2,3-triazole and sodium tetraphenylborate in nitromethane, acetonitrile, and acetone.

[1-Me-1,2,3-Trz] (M)	[NaB(C_6H_5)$_4$] (M)	Lig/Na^+	δ Na-23 (Hz)	(ppm)	L.W. (Hz)
in nitromethane					
--	0.250	--	247	15.6	27
0.0868	0.240	0.36	236	14.7	38
0.174	0.241	0.72	221	13.9	39
0.347	0.242	1.43	190	12.0	51
0.521	0.240	2.17	172	10.8	79
0.868	0.241	3.60	133	8.38	99
1.302	0.239	5.45	--	--	very broad
in acetonitrile					
--	0.250	--	130	8.19	18
0.0923	0.250	0.37	130	8.19	27
0.184	0.242	0.76	128	8.06	31
0.369	0.241	1.53	123	7.75	31
0.554	0.238	2.33	116	7.30	32
0.923	0.240	3.85	110	6.93	31
1.384	0.239	5.79	101	6.36	31
in acetone					
--	0.250	--	163	10.3	18
0.0875	0.240	0.36	146	9.19	36
0.175	0.242	0.72	143	9.01	35
0.350	0.238	1.47	146	9.19	29
0.525	0.247	0.213	135	8.50	27
0.875	0.242	3.62	129	8.12	31
1.313	0.233	5.64	128	8.06	32

Table XXXIII. Sodium-23 nuclear magnetic resonance study of 1-methylimidazole and sodium perchlorate in nitromethane, acetonitrile, acetone and pyridine.

[1-MeIz] (M)	$[NaB(C_6H_5)_4]$ (M)	Lig/Na^+	δ_{Na-23} (Hz)	δ_{Na-23} (ppm)	L.W. (Hz)
in nitromethane					
--	0.250	--	247	15.6	28
0.0272	0.252	0.11	216	13.6	46
0.0950	0.256	0.37	178	11.2	63
0.149	0.256	0.58	173	10.9	69
0.336	0.258	1.30	144	9.07	72
0.506	0.256	1.98	138	8.69	86
0.674	0.254	2.65	115	7.24	119
1.010	0.258	3.91	86	5.42	144
in acetonitrile					
--	0.500	--	132	8.31	31
0.0800	0.496	0.16	134	8.44	34
0.198	0.506	0.39	123	7.75	37
0.274	0.500	0.55	114	7.18	39
0.352	0.508	0.70	109	6.86	43
0.524	0.508	1.03	100	6.30	46
0.720	0.504	1.43	89	5.60	51
0.984	0.508	1.93	77	4.85	63
1.180	0.490	2.41	72	4.53	
in acetone					
--	0.500	--	163	10.3	43
0.0694	0.498	0.14	149	9.38	43
0.278	0.502	0.57	134	8.44	46
0.556	0.502	1.11	103	6.49	49
0.832	0.508	1.63	89	5.60	58
1.25	0.496	2.52	72	4.53	63
1.64	0.506	3.24	49	3.09	75
1.96	0.504	3.90	34	2.14	81
2.50	0.508	4.52	26	1.64	81
in pyridine					
--	0.500	--	-3.0	-0.19	30
0.214	0.514	0.42	-3.0	-0.19	80
0.428	0.516	0.83	-7.0	-0.44	90
0.854	0.538	1.59	-18	-1.13	95
1.28	0.498	2.57	-29	-1.83	97
1.71	0.520	3.29	-43	-2.71	100

Table XXXIV. Sodium-23 nuclear magnetic resonance study of 1-methylpyrazole and sodium tetraphenylborate in nitromethane, acetonitrile, and acetone.

[1-MePz] (M)	$[NaB(C_6H_5)_4]$ (M)	Lig/Na^+	δ_{Na-23} (Hz)	(ppm)	L.W. (Hz)
in nitromethane					
--	0.250	--	247	15.6	28
0.0769	0.261	0.29	240	15.1	33
0.154	0.261	0.59	226	14.2	39
0.231	0.260	0.89	212	13.4	45
0.384	0.261	1.47	191	12.0	53
0.769	0.260	2.96	159	10.0	59
1.153	0.260	4.44	120	7.56	>86
in acetonitrile					
--	0.250	--	131	8.25	20
0.0781	0.259	0.30	101	6.36	28
0.156	0.263	0.59	76	4.79	30
0.234	0.263	0.89	62	3.90	33
0.391	0.260	1.50	63	3.97	34
0.781	0.263	2.97	60	3.78	35
1.172	0.259	4.52	54	3.40	38
in acetone					
--	0.250	--	163	10.3	19
0.0793	0.256	0.31	134	8.44	29
0.159	0.244	0.65	139	8.75	30
0.238	0.257	0.93	139	8.75	28
0.397	0.256	1.55	135	8.50	32
0.793	0.255	3.11	123	7.75	34
1.190	0.257	4.63	116	7.30	34

Figure 22. Relationship between the observed chemical shift of the sodium-23 ion and the Lig/Na^+ mole ratio for the azole ligands in nitromethane.

○ 1,5-DiMeTz

△ 1-Me-1,2,3-Trz

▽ 1-Me-1,2,4-Trz

□ 1-MeIz

◇ 1-MePz

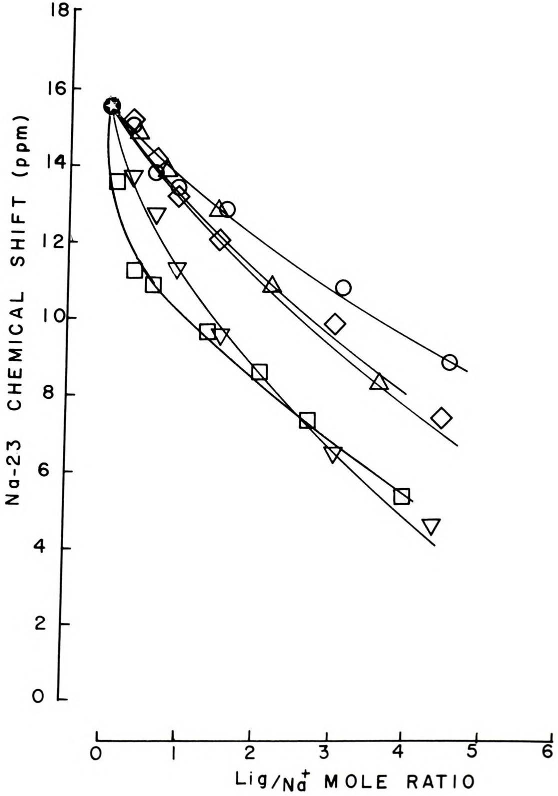

Na-23 CHEMICAL SHIFT (ppm)
18
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
Lig/Na+ MOLE RATIO

Figure 22.

Figure 23. Relationship between the observed chemical shift of the sodium-23 ion and the Lig/Na^+ mole ratio for the azole ligands in acetonitrile.

○ 1,5-DiMeTz
△ 1-Me-1,2,3-Trz
▽ 1-Me-1,2,4-Trz
□ 1-MeIz
◇ 1-MePz

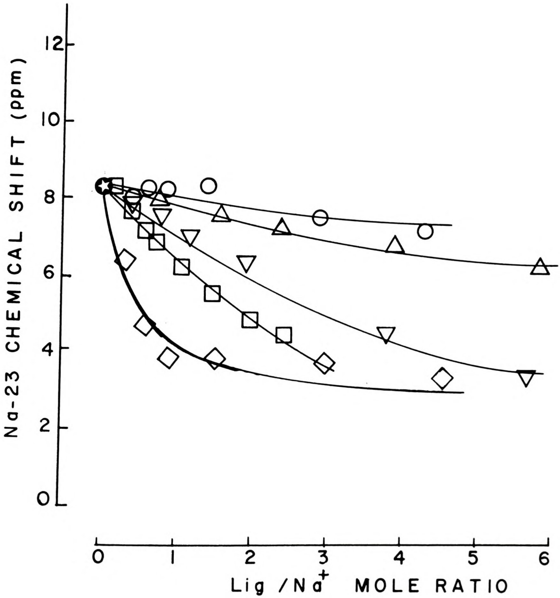

Na-23 CHEMICAL SHIFT (ppm)
12
10
8
6
4
2
0
0
1
2
3
4
5
6
Lig /Na+ MOLE RATIO

Figure 23.

Figure 24. Relationship between the observed chemical shift of the sodium-23 ion and the Lig/Na^+ mole ratio for the azole ligands in acetone.

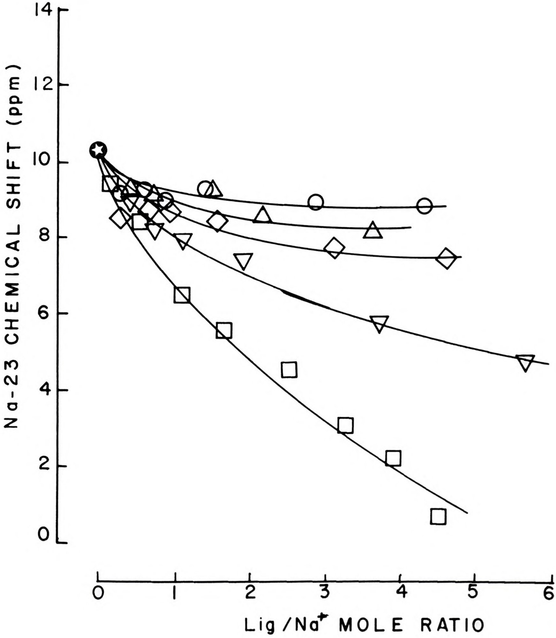
○ 1,5-DiMeTz

△ 1-Me-1,2,3-Trz

▽ 1-Me-1,2,4-Trz

□ 1-MeIz

◇ 1-MePz



Na-23 CHEMICAL SHIFT (ppm)
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
Lig / Na+ MOLE RATIO

Figure 24.

1-Me-1,2,4-Trz > 1-MePz > 1-Me-1,2,3-Trz > 1,5-DiMeTz (Figure 24). Since 1-Me-1,2,4-Trz and 1-MeIz were similar in donor abilities in nitromethane and acetonitrile, a fourth solvent (pyridine) was also studied in order to substantiate the donor order observed in acetone. The results are shown in Figure 25 and do indicate that 1-MeIz has better donor ability than 1-Me-1,2,4-Trz.

In order to check on the relative donor strengths of these compounds four nearly saturated solutions of sodium tetraphenylborate in the pure ligands 1-Me-1,2,3-Trz ($[Na^+]$ = 0.250 M), 1-Me-1,2,4-Trz ($[Na^+]$ = 0.125 M), 1-MePz ($[Na^+]$ = 0.250 M) and 1-MeIz ($[Na^+]$ = 0.250 M) were measured on the NMR Specialities MP100 Pulsed Spectrometer. The absorptions (referenced to saturated aqueous sodium chloride solution) were very broad ~ 200 Hz at half peak height. Therefore, only the positions of the sodium-23 resonance were recorded. The chemical shifts for 1-Me-1,2,3-Trz, 1-MePz, 1-Me-1,2,4-Trz, and 1-MeIz were -1.23, -4.08, -4.32, and -11.02 ppm respectively. These chemical shift values correspond to donor numbers of 36, 41, 41.5, and 54 based on the data presented by Erlich and Popov (98) and Herlem and Popov (100) (Figure 26). From these data, it seems that the azoles are comparatively strong donors.

Figure 25. Relationship between the observed chemical shift of the sodium-23 ion and the Lig/Na^+ mole ratio for 1-methylimidazole and 1-methyl-1,2,4-triazole in pyridine.

□ 1-MeIz

▽ 1-MePz

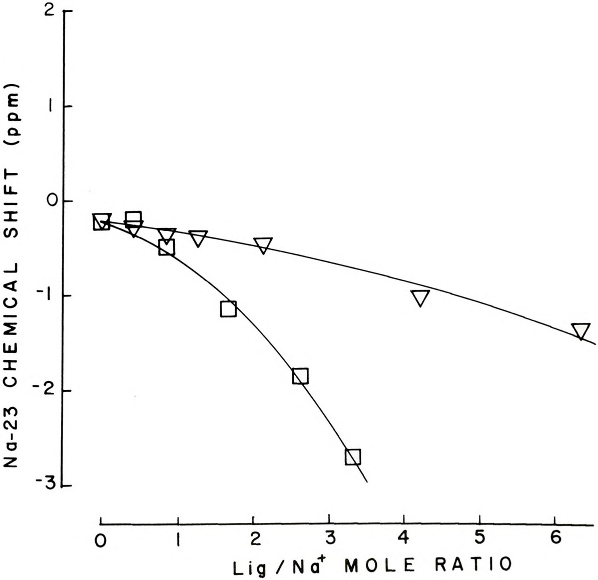


Figure 25.

Figure 26. Relationship between the observed chemical shift of the sodium-23 ion in nonaqueous solvents and the donor number of the solvent.

1 nitromethane, 2 benzonitrile, 3 acetonitrile
4 acetone, 5 ethyl acetate, 6 tetrahydrofuran,
7 dimethylformamide, 8 dimethylsulfoxide,
9 pyridine, 10 hexamethylphosphoramide,
11 hydrazine, 12 ethylenediamine, 13 ethylamine
14 iso-propylamine, 15 ammonia, 16 1-Me-1,2,3-Trz,
17 1-MePz, 18 1-Me-1,2,4-Trz, 19 1-MeIz.

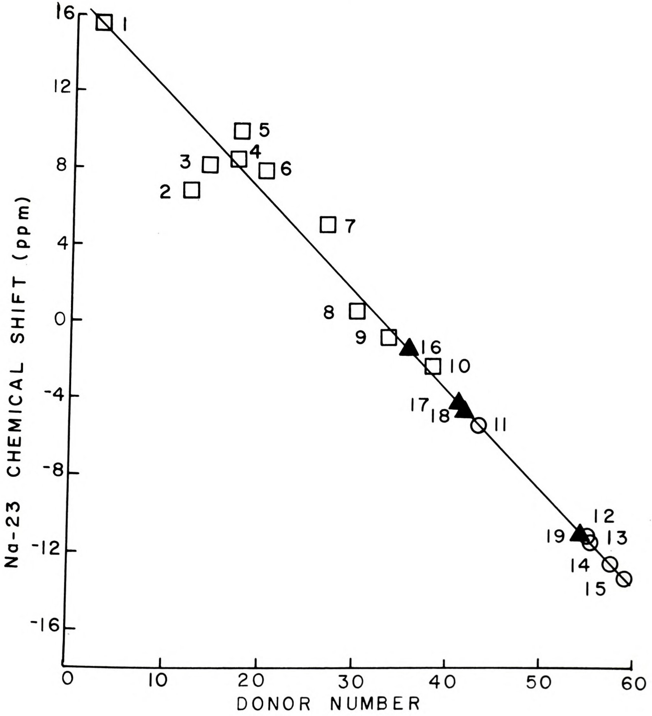

Na-23 CHEMICAL SHIFT (ppm)
DONOR NUMBER
16
12
8
4
0
-4
-8
-12
-16
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

Figure 26.

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APPENDIX I

1-Methylimidazolium tetraphenylborate

APPENDIX I

1-Methylimidazolium Tetraphenylborate

Sodium tetraphenylborate is a prominent analytical reagent for the determination of potassium ions by quantitative precipitating potassium tetraphenylborate from aqueous solutions. Pflaum and Howick (1) have shown that dissolution of this salt in acetonitrile leads to a system that is especially suited for spectrophotometric measurements of the tetraphenylborate ion at 266 and 274 nm. In addition the tetraphenylborate anion forms insoluble salts in aqueous medium with many organic bases (1-9). Included in these studies has been a recent study of organo sodium compounds of N-substituted imidazoles by Tertov and Burykin (9).

During this study, when an aqueous solution of sodium tetraphenylborate was mixed with an aqueous solution of 1-methylimidazole, a white solid formed which appears to be 1-methylimidazolium tetraphenylborate $C_4H_6N_2H\ \ B_1(C_6H_5)_4$. Two experiments seem to support this hypothesis. When 1-methylimidazole was added to a 1 N sodium hydroxide solution of sodium tetraphenylborate, no precipitate was formed. However, when 1-methylimidazole was added to 1 N HCl solution of sodium tetraphenylborate, a white precipitate was formed which dissolved upon the addition of 2 N NaOH solution.

When the pH of a 0.0103 M aqueous solution of sodium tetraphenylborate was measured with the addition of 0.403 M aqueous 1-methylimidazole (Figure 1), the pH of the system increased rapidly. It appears that the equilibrium:

$$\text{1-MeIz} + (C_6H_5)_4B^- + HOH = \text{1-MeIzH}(C_6H_5)_4B + OH^-$$

is shifted to the right by the presence of the tetraphenylborate anion and the formation of the insoluble 1-methylimidazolium tetraphenylborate.

A small portion of this solid was isolated in order to study some of its properties. The solid appears to be soluble in acetone, dimethylsulfoxide, pyridine, ammonium hydroxide and other strong bases. It is insoluble in benzene, chloroform, alcohol and water. The infrared spectrum from 4000-600 cm^{-1} was recorded (Figure 2). A comparison of this spectrum with that of 1-methylimidazole molecule (Figure 13, Appendix II) indicates that there are several bands present which are characteristic of the 1-methylimidazole. In addition, there is a strong band at 3280 cm^{-1} which is in the region, 3300-3030 cm^{-1}, observed for the N-H stretching vibrations of amine salts.

Three samples, A, B, and C, were prepared from aqueous solution containing 4:1, 1:1, and 1:6 mole ratios of sodium tetraphenylborate to 1-methylimidazole. The samples were recrystallized from 10% acetone-water. Chemical analyses indicate that they all have the same composition:

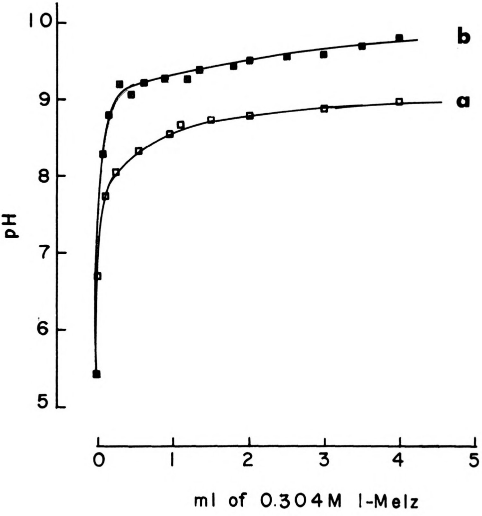

Figure 1. Comparison of the pH changes upon the addition of 0.304 M aqueous 1-MeIz to a) 100 ml of distilled water b) 100 ml of 0.103 M aqueous sodium tetraphenylborate

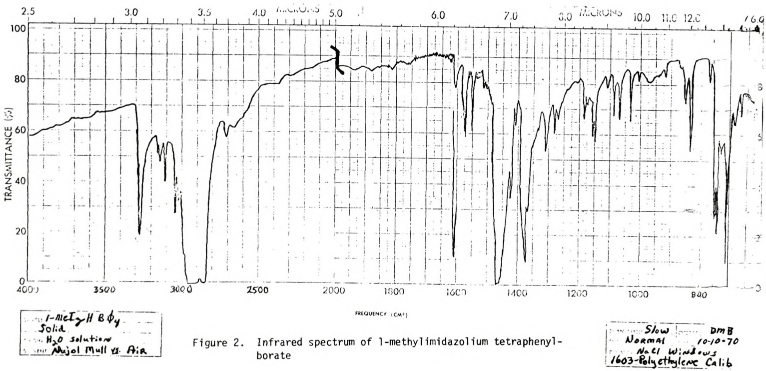

Figure 2. Infrared spectrum of 1-methylimidazolium tetraphenylborate

	A	B		C	Theor
%C	83.68[a]	83.25[a]	83.29[b]	83.51[a]	84.01
%H	6.87	6.73	6.87	6.70	6.29
%N	6.60	6.58	7.00	6.72	7.00

[a]Analysis by F. M. D'Itri.

[b]Analysis by Spang Microanalytical Laboratory in Ann Arbor, Michigan.

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APPENDIX II

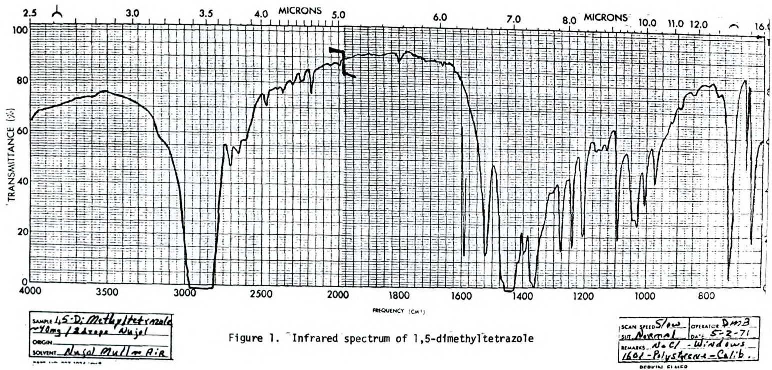

Figure 1. Infrared spectrum of 1,5-dimethyltetrazole

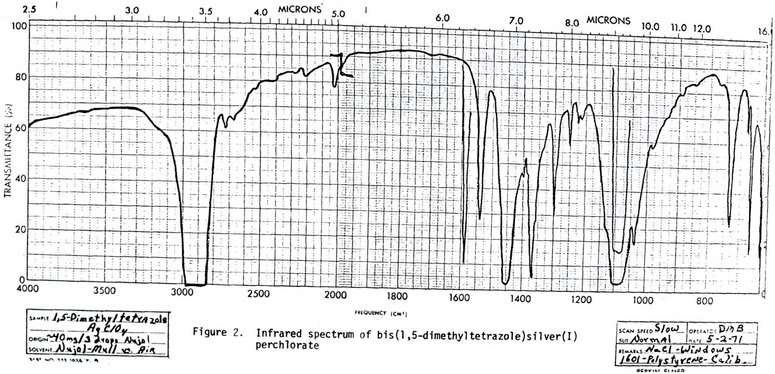

Figure 2. Infrared spectrum of bis(1,5-dimethyltetrazole)silver(I) perchlorate

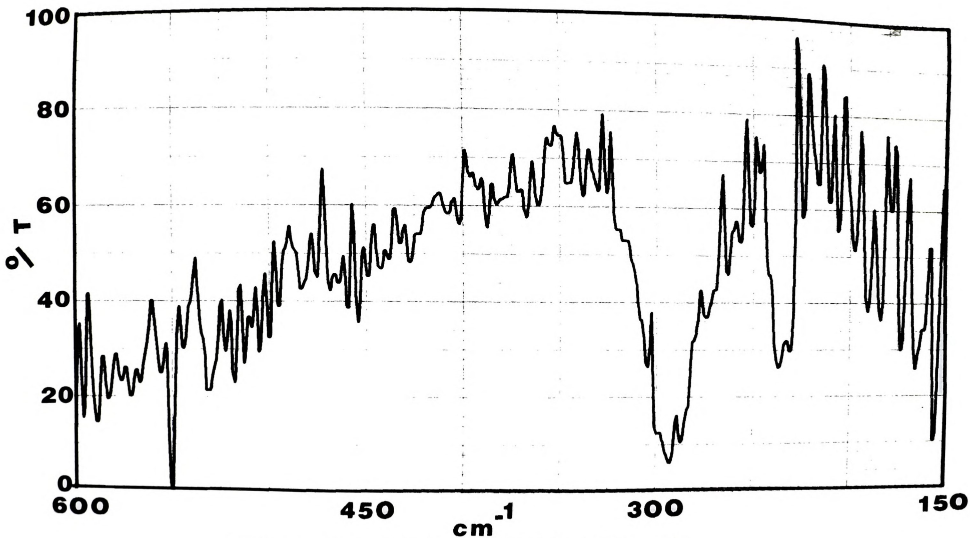

Figure 3. Far infrared spectrum of 1,5-dimethyltetrazole
(Nujol mull)

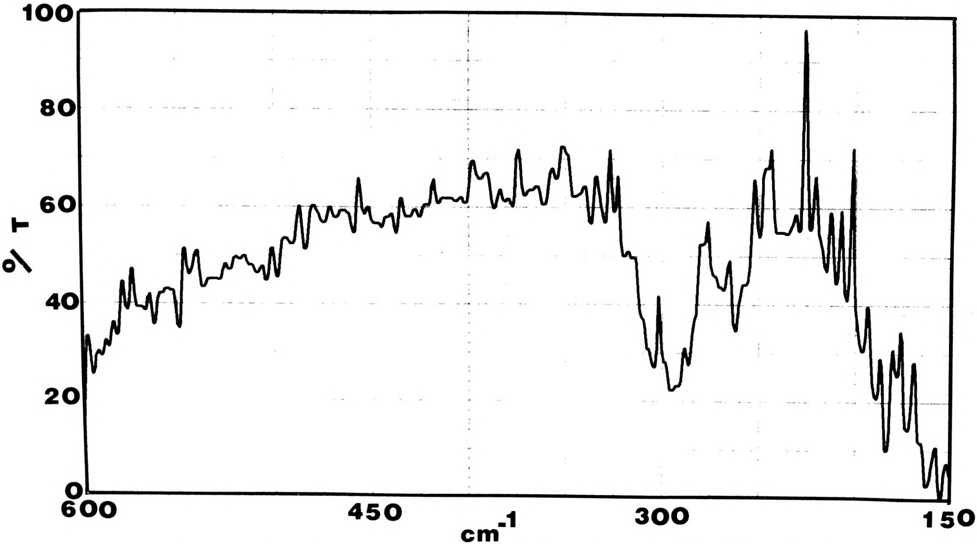

Figure 4. Far infrared spectrum of bis(1,5-dimethyltetrazole)silver(I) perchlorate

(Nujol mull)

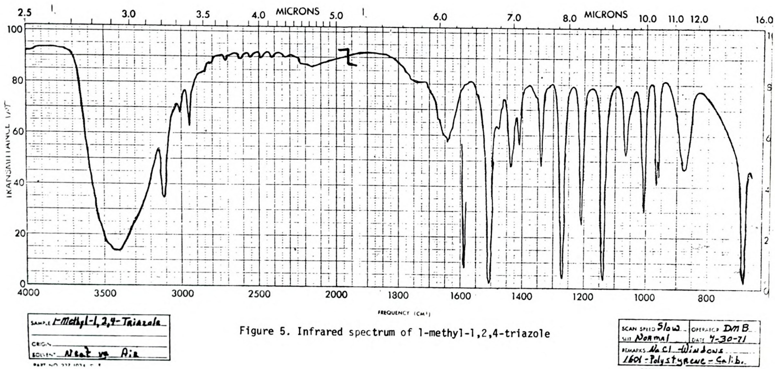

Figure 5. Infrared spectrum of 1-methyl-1,2,4-triazole

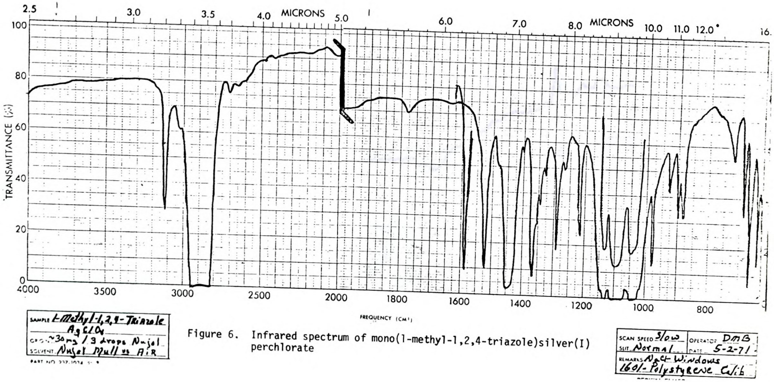

Figure 6. Infrared spectrum of mono(1-methyl-1,2,4-triazole)silver(I) perchlorate

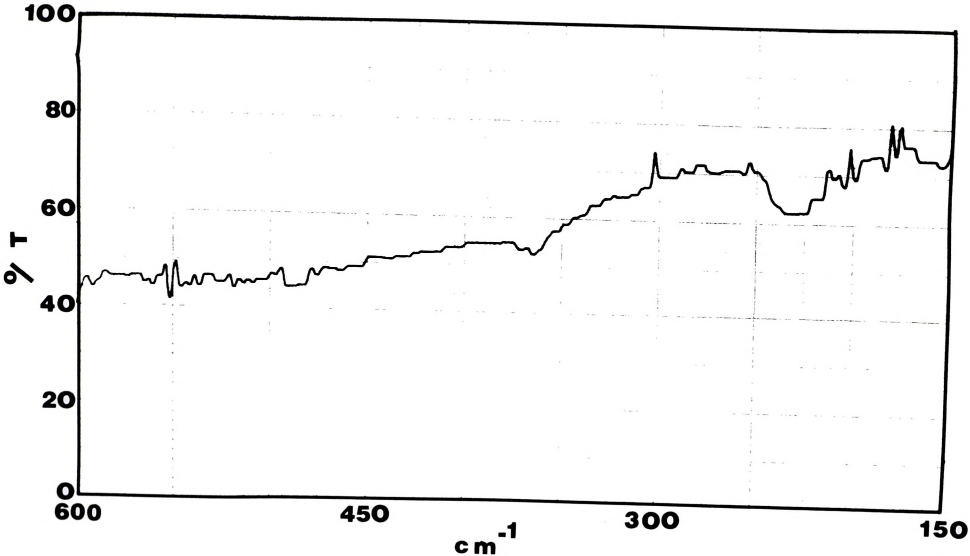

Figure 7. Far infrared spectrum of 1-methyl-1,2,4-triazole

(Neat)

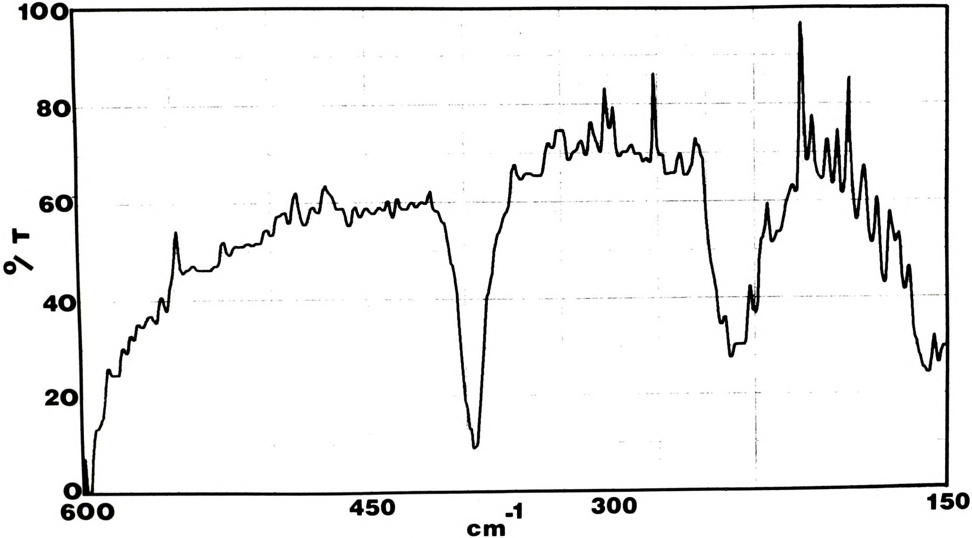

Figure 8. Far infrared spectrum of mono(1-methyl-1,2,4-triazole)silver(I) perchlorate (Nujol mull)

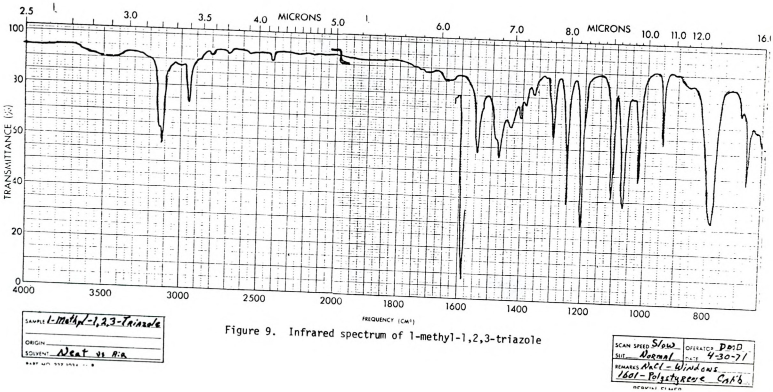

Figure 9. Infrared spectrum of 1-methyl-1,2,3-triazole

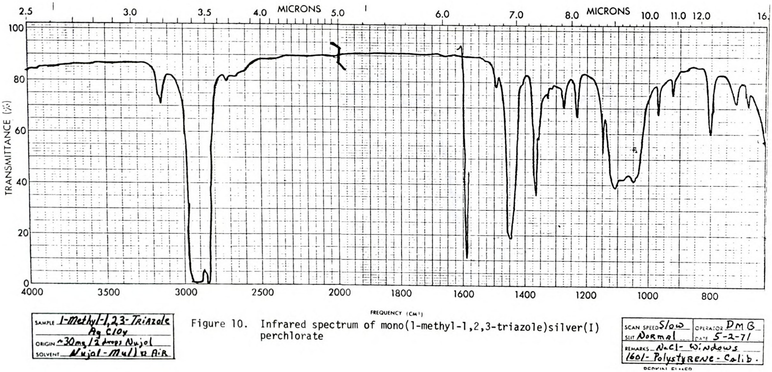

Figure 10. Infrared spectrum of mono(1-methyl-1,2,3-triazole)silver(I) perchlorate

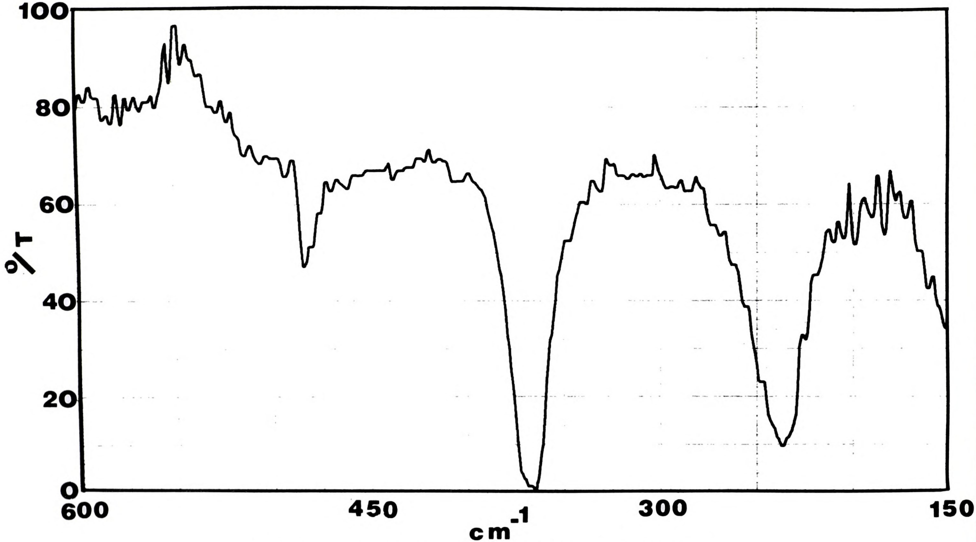

Figure 11. Far infrared spectrum of 1-methyl-1,2,3-triazole

(Neat)

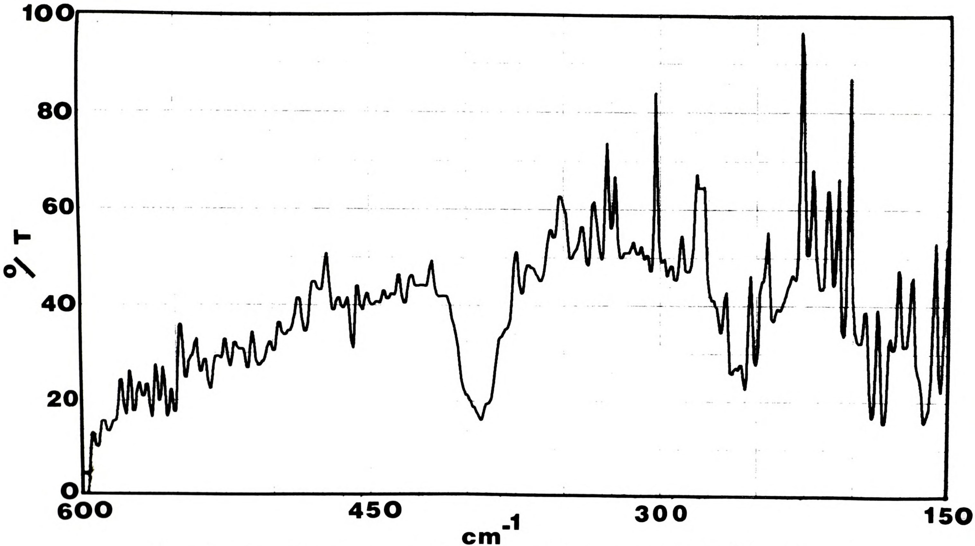

Figure 12. Far infrared spectrum of mono(1-methyl-1,2,3-triazole)silver(I) perchlorate (Nujol mull)

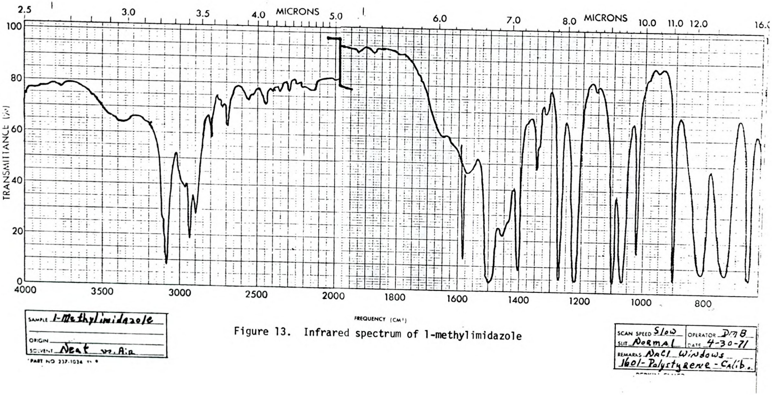

Figure 13. Infrared spectrum of 1-methylimidazole

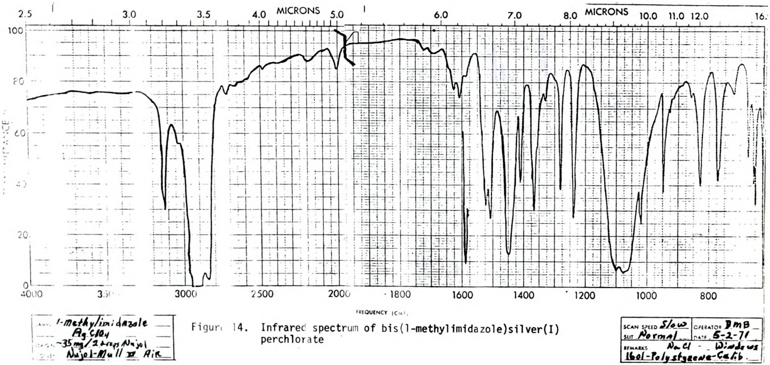

Figure 14. Infrared spectrum of bis(1-methylimidazole)silver(I) perchlorate

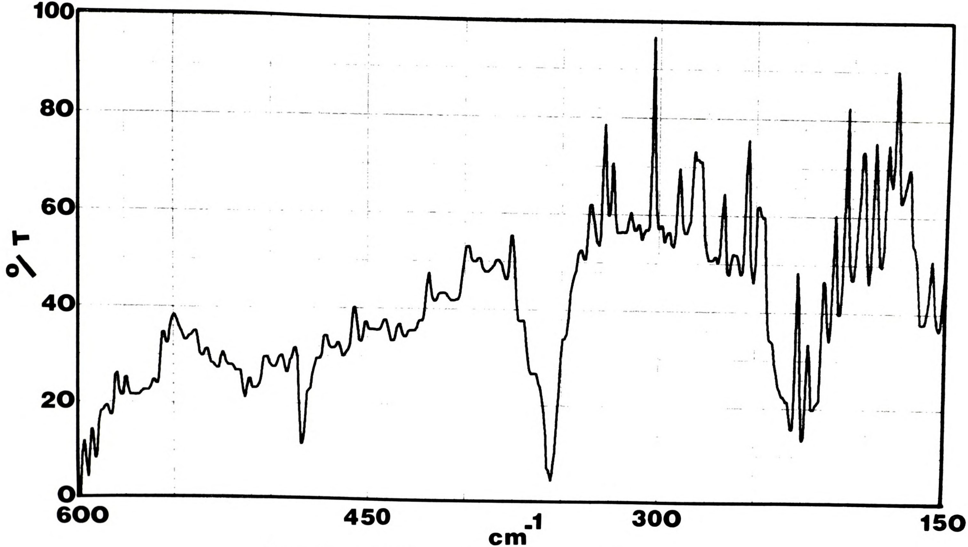

Figure 15. Far infrared spectrum of 1-methylimidazole

(Neat)

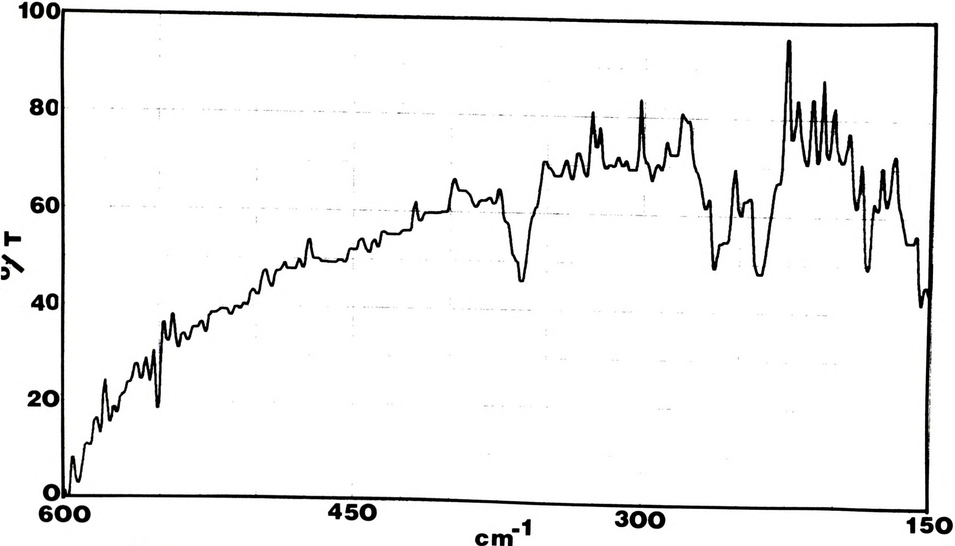

Figure 16. Far infrared spectrum of bis(1-methylimidazole)silver(I) perchlorate

(Nujol mull)

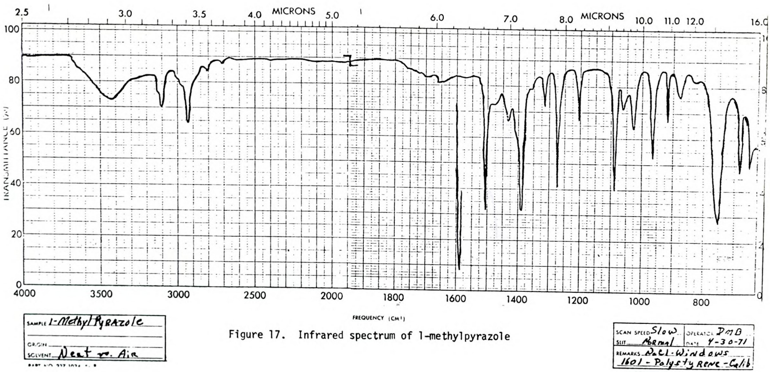

Figure 17. Infrared spectrum of 1-methylpyrazole

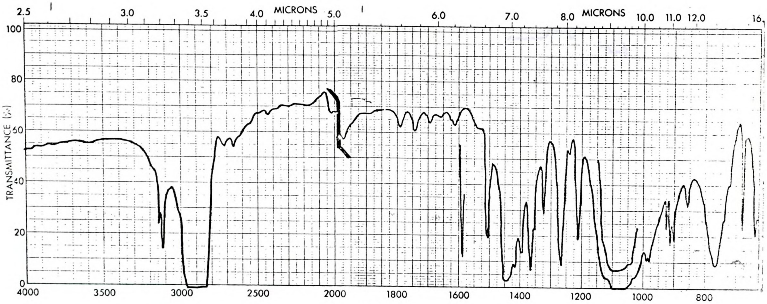

Figure 18. Infrared spectrum of bis(1-methylpyrazole)silver(I) perchlorate

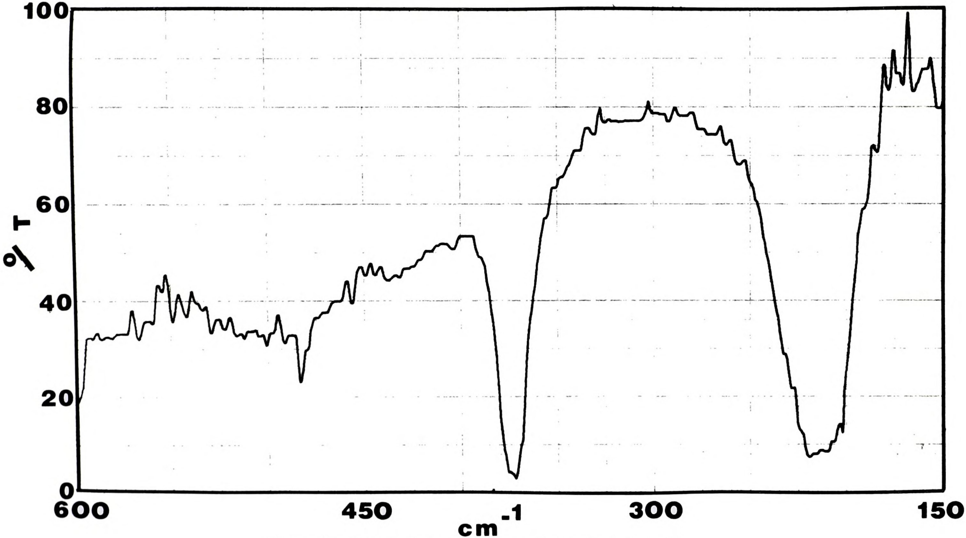

Figure 19. Far infrared spectrum of 1-methylpyrazole

(Neat)

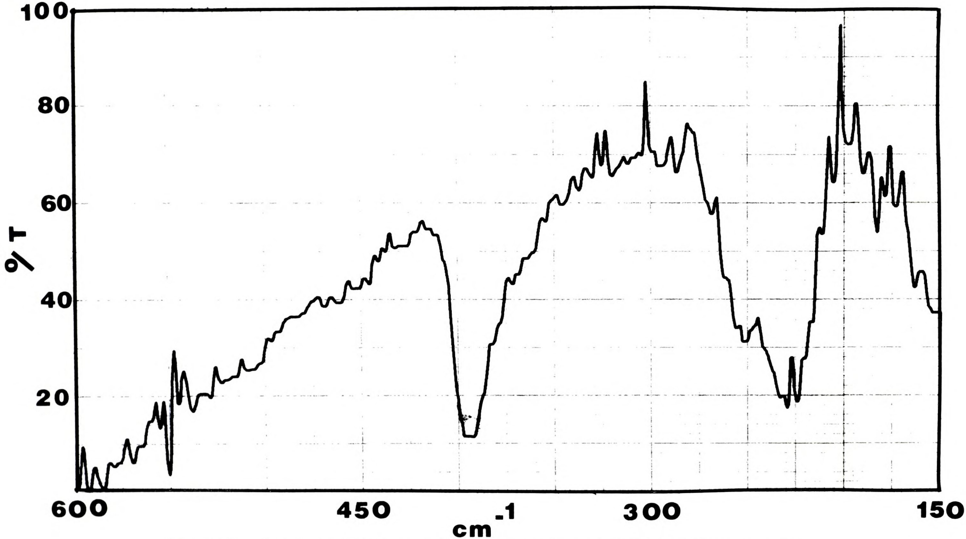

Figure 20. Far infrared spectrum of bis(1-methylpyrazole)silver(I) perchlorate

(Nujol mull)

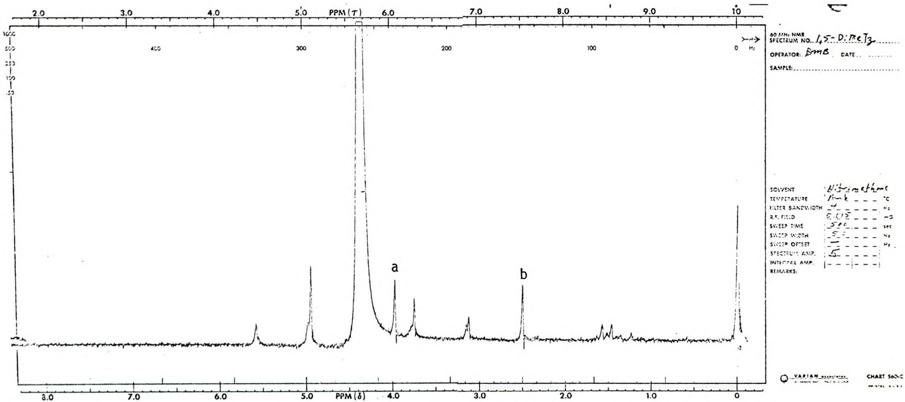

Figure 21. Proton magnetic resonance spectrum of 1,5-dimethyltetrazole in nitromethane
a) 1-methyl protons b) 5-methyl protons

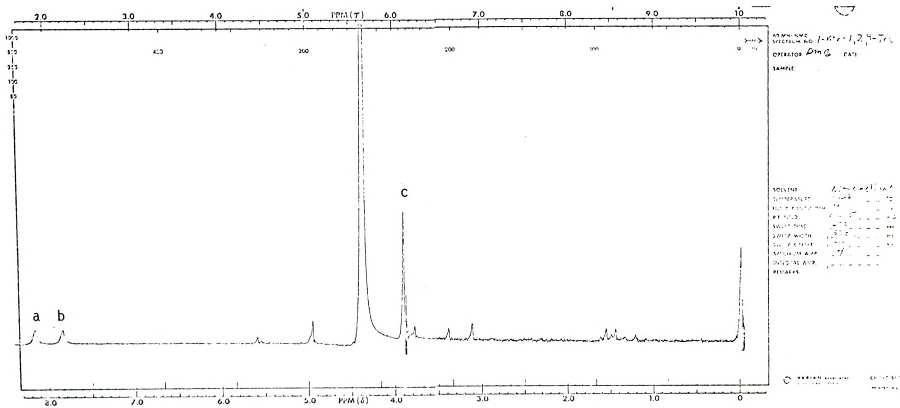

Figure 22. Proton nagnetic resonance spectrum of 1-methyl-1,2,4-triazole in nitromethane a) 5-proton b) 3-proton c) 1-methyl protons

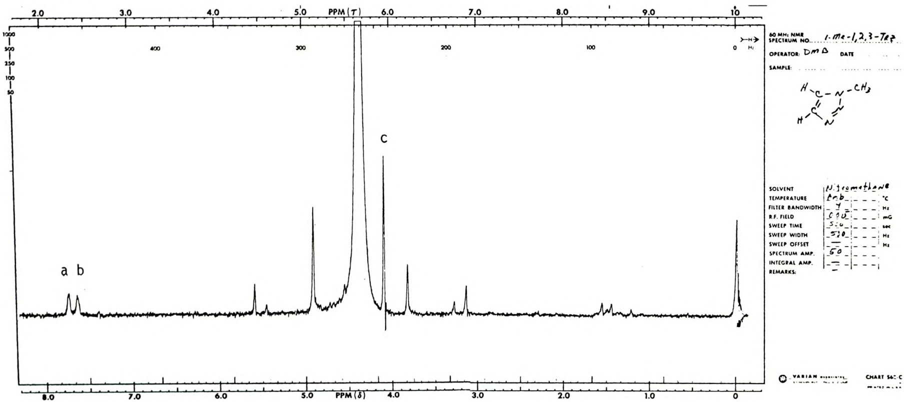

Figure 23. Proton magnetic resonance spectrum of 1-methyl-1,2,3-triazole in nitromethane

a) 4-proton b) 5-proton c) 1-methyl protons

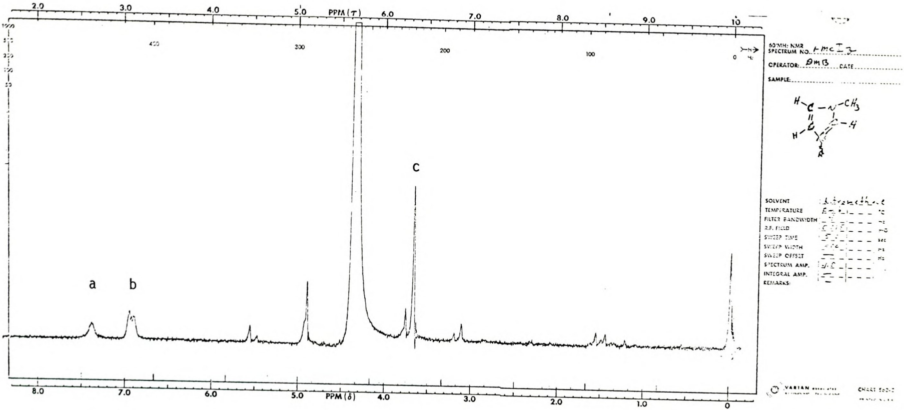

Figure 24. Proton magnetic resonance spectrum of 1-methylimidazole in nitromethane a) 2-proton b) 4- and 5-protons c) 1-methyl protons

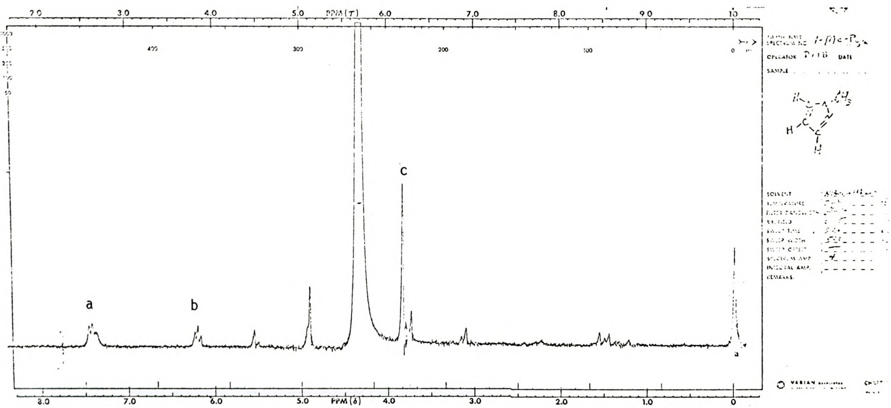

Figure 25. Proton magnetic resonance spectrum of 1-methylpyrazole in nitromethane
a) 3- and 5-protons b) 4-proton c) 1-methyl protons