INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106

STUDIES IN THE CHEMISTRY OF SUBSTITUTED PYRIDINES

by

PAUL SCHWARTZ

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1974

This manuscript has been read and accepted for the University Committe in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

7/26/74
date

Chairman of Examining Committe

7/26/74
date

Executive Officer

Supervisory Committee

The City University of New York

Abstract

STUDIES IN THE CHEMISTRY OF SUBSTITUTED PYRIDINES

by

Paul Schwartz

Adviser: Professor Michael A. Weiner

The thesis discusses the effects substituent groups have on the electronic distribution of the pyridine molecule. It is divided into two parts. The first part describes experiments designed to show the electron withdrawing ability of organosilicon and organogermanium groups when substituted on the 4-position of pyridine N-oxide. It was seen through pKa measurements, and measurements of hydrogen-bond strengths by IR and NMR studies that silicon and germanium are elctron withdrawing relative to Carbon. Electron withdrawal is described in terms of backbonding from the π system of the pyridine ring into empty d-orbitals of silicon or germanium. It was shown that the extent of backbonding is dependent upon the availability of oxygen's electrons to backbond into the pyridine ring.

The second part describes the preparation and spectral investigations of Co(II) and Ni(II) complexes containing the methyldiphenyl-4-pyridylphosphonium and methyldiphenyl-4-picolylphosphonium cations as ligands. Spectral measurements showed that a positive charge conjugated to the pyridine ring increases the field produced by the ligand. The increased field was interpreted in terms of a stabilization of the pyridine π^* orbitals and an increase in M→L backbonding.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Professor Michael Weiner who supervized this research. Ideas generated from our numerous discussions formed the basis of this entire work. He was always ready and willing to lend a helping hand and is genuinely a fine mentor.

I also wish to express my thanks to Professor Juan Villa for the use of his Faraday balance and especially for his kind interest in my progress.

Thanks are also in order to Professors Neil McKelvie and David Goldberg who gave of their time to discuss various aspects of this work with me.

Lastly, my wife Judy's contribution to this thesis will never be forgotten and it is to her that this work is dedicated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES

(continued)

LIST OF DIAGRAMS

PART I

ORGANOSILICON AND ORGANOGERMANIUM SUBSTITUTED PYRIDINE N-OXIDES

INTRODUCTION

According to the Pauling electronegativity scale silicon and germanium have electronegativity values of 1.8 while carbon has a value of 2.5.[1] These values imply that silicon and germanium would be more electron releasing (less withdrawing) than carbon. However silicon and germanium contain empty d-orbitals which can participate in p-d π bonding with appropriate π systems and backbonding into these orbitals would tend to enhance the electron withdrawing abilities of silicon and germanium. Evidence of the dative π bonding capabilities of silicon and germanium was first shown by Chatt and Williams.[2] They measured the dissociation constants of benzoic acid and of para-t-butyl-, para-trimethylsilyl-, and para-trimethylgermyl- substituted benzoic acids by differential potentiometric titration. They concluded from their results (see Table 1) that the enhanced acidity of the organometallic derivatives is a result of dative π bonding, occuring in the silicon-phenyl and germanium-phenyl bonds. This is enough to overcome the positive inductive effect due to the greater electropositive character of silicon and germanium relative to carbon.

Chipperfield and Webster[3] measured the pKa values of organometallic substituted pyridines and found them to be larger than the value obtained for unsubstituted pyridine (Table II). Their results are opposite to those of Chatt and Williams inasmuch as they show a weakened acidity for the organometallic derivatives. This can be attributed to electron release from the silicon or germanium to the pyridyl ring. They reason that electron donation predominates over dative backbonding in this system because the greater electronegativity of nitrogen compared to carbon makes release of electron density from the pyridyl ring to empty d-orbitals on the substituent group less favored than in phenyl systems.

TABLE I

Dissociation Constants for 4-substituted Benzoic Acids[2]

Substituent	Ka
H	1.05×10^{-6}
t-Butyl	0.70×10^{-6}
$Si(CH_3)_3$	1.11×10^{-6}
$Ge(CH_3)_3$	1.07×10^{-6}

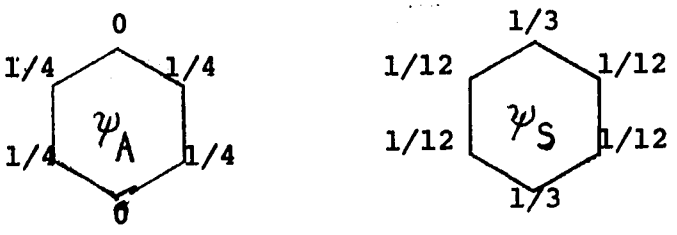
TABLE II

pKa values of Substituted Pyridines[3]

Substituent	pKa	
	3-position	4-position
H	5.21	5.21
Me	5.65	6.03
t-Butyl	5.82	5.99
Me_3Si	5.57	5.57
Ph_3Si		5.10

Other experimenters have found evidence of p-d π bonding in silicon and germanium substituted aryl systems. Bedford et al.[4], reported the results of an EPR investigation of the phenyltrimethylsilyl and -germyl radical anions. Based on observations of the hyperfine splitting constants, they found that the unpaired electron on the organometallic substituted phenyl anion goes into the symmetric molecular orbital, while the extra electron in the t-butylbenzene anion goes into the antisymmetric orbital. They conclude that the silicon and germanium substituents are electron withdrawing, and the t-butyl group is electron releasing. The rationale for this conclusion is based on the electron densities at each carbon for the two orbitals. (Figure I). If the substituent group is electron repelling, the extra electron occupies the antisymmetric orbital, since its density at the substituent site is zero.

FIGURE I[4]



ANTISYMMETRIC SYMMETRIC

A recent review article[5] describes various other studies which were done to measure the extent of backbonding into the d-orbitals of Group IV substituents in aryl systems. While backbonding is a generally accepted phenomenon in such systems, whether it can predominate over the σ electron releasing inductive effect is open to question.

In an article subtitled "A Re-evaluation of the Results of the Chatt and Williams Experiment", Wilson, Zuckerman, et al.[6], disputed Chatt and Williams' interpretation of their data in terms of p-d π interaction between the silicon and phenyl ring. They stated rather that the results follow in a straightforward manner from the known properties of the silicon atom (electron release relative to carbon). This statement is based on experiments to determine pKa values of t-butyl- and (trimethylsilyl)benzoic acids in the range 288.15-313.15°K. From the variation of -log K with temperature, $\Delta G°$, $\Delta H°$, and $\Delta S°$ are calculated. The results are listed in Table III. They deem the relatively high acid strength of (trimethylsilyl)benzoic acid as anomalous and attribute it to a remarkably high value of $\Delta S°$. The high entropy value is explained by assuming the trimethylsilyl group to be hydrophobic, i.e., the large group prohibits the solvent molecules from orienting themselves around the acid anion in

a high degree of orderliness. The high $\Delta H°$ value is in line with electron release from silicon along the σ framework of the molecule. The conclusion drawn from this study is that pKa values cannot be used to interpret internal acid strengths.

TABLE III

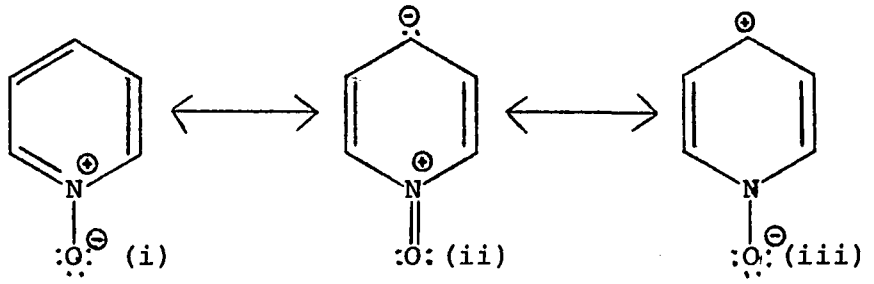
Thermodynamic Data for para-Substituted Benzoic Acids.[6]

Acid	$\Delta G°$	$\Delta H°$	$\Delta S°$
	(cal $mole^{-1}$)		(cal $mole^{-1}deg^{-1}$)
Benzoic	+5735	+150	-18.7
p-t-Butylbenzoic	+5988	+2900	-10.4
p-Trimethylsilyl-benzoic	+5719	+3060	-8.9

In order to shed further light on this subject, a system which would lend itself readily to experiments designed to clearly show electron withdrawing or donating effects of substituent groups had to be found. The system chosen for this study was pyridine N-oxide. Several reasonance forms can be written for pyridine N-oxide.

FIGURE II

(FIGURE II A)



(FIGURE II B)

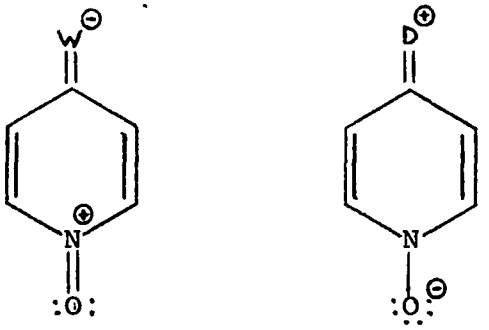


Figure II B shows that reasonance form (ii) would predominate when an electron withdrawing group is in the 4-position and reasonance form (iii) would predominate when an electron donating substituent is in the 4-position.

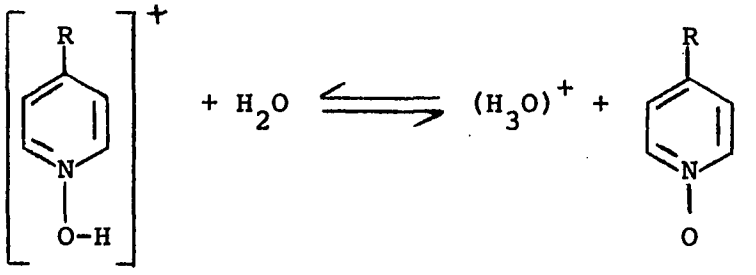
Jaffe and Doak[7] measured the basicities of 4-substituted pyridine N-oxides and found the pKa values to be linearly related to Hammett σ constants for the substituents. Their results showed that the pKa values of pyridine N-oxides substituted with electron donating groups (e.g., NH_2, OH, CH_3) are larger than that of unsubstituted pyridine N-oxide. (Table IV).

TABLE IV

The Basicities of Substituted Pyridine N-Oxides[7]

Substituent	σ	pK
4-NH_2	-0.660	3.65
4-OH	-0.357	2.36
4-CH_3	-0.170	1.29
H	0	0.79
4-COOH	0.728	-0.48
4-NO_2	1.270	-1.7

The Ka is for the equilibrium:

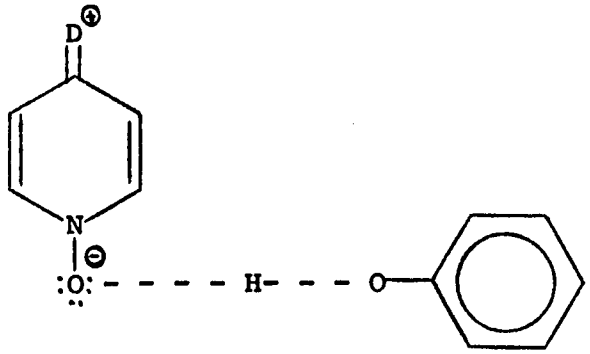


(1)

When R is a donating group there is a greater electron density at the oxygen atom. The O-H bond in the N-hydroxypyridinium ion would be stronger and the equilibrium would lie more towards the left than when R is a withdrawing group. The hydroxypyridinium ion would be a weaker acid and the conjugate base, the pyridine N-oxide, would be a stronger base. Thus it seems that in substituted pyridine N-oxides, the pKa of the conjugate acid is a measure of the electronic behavior of the substituent group.

Drago et al.[8], showed that when substituted pyridine N-oxides hydrogen-bond with phenol, the shifts in the O-H stretching frequency of phenol can be correlated to Hammett substituent constants (σ^+) and are linearly related to the enthalpy of hydrogen-bond interaction. Electron donating substituents have the effect of increasing the extent of hydrogen bonding. (Figure III)

FIGURE III



Furthermore, Shindo[9] showed that the N-O stretching frequency in 4-substituted pyridine N-oxides is dependent on the nature of the substituent. The N-O stretching frequency is greater when the substituent is electron withdrawing, indicating more double bond character in the N-O bond, as shown in Figure II B.

In view of the interest in the p-d π bonding abilities of silicon and germanium, Weiner[10] measured the stretching frequencies of 4-substituted pyridine N-oxides. He found the values of the N-O stretching frequency to increase in the order: t-butyl-<unsubstituted-<organometallic substituted pyridine N-oxide. He interpreted these results in terms of backbonding from the ring π orbitals into available d-orbitals on the organometallic substituents.

The present report details basicity studies on organosilicon and organogermanium substituted pyridine N-oxides.

TABLE V

Frequency Shifts for C_6H_5OH-4-Z-C_5H_4NO Interactions in Carbon Tetrachloride[8]

Z	$\Delta\nu$(O-H) (cm^{-1})	σ	-ΔH(kcal/mole)
NO_2	220	0.778	4.1
Cl	435	0.227	7.6
H	468		8.1
CH_3	468	-0.170	8.8
OCH_3	>530	-0.268	>9.0

TABLE VI

N-O Stretching Frequencies of 4-Substituted Pyridine N-Oxides[9,10]

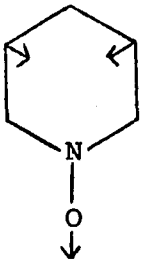
Substituent	N-O Stretching Frequency (cm^{-1}) (2% CS_2 solution)
NO	1303
CN	1301
$COCH_3$	1258
Br	1271
Cl	1269
H	1265
CH_3	1260
$(CH_3)_3C$	1259
OCH_3	1240
$(CH_3)_3Si$	1275
$(CH_3)_3Ge$	1270
$(CH_3)_3Sn$	1268

RESULTS AND DISCUSSION

The objective of this study was to compare the basicities of organosilicon and organogermanium substituted pyridine N-oxides to the unsubstituted and t-butyl pyridine N-oxides. The desired aim was to obtain consistent results in a series of experiments which would show evidence of backbonding from the ring π system to the empty d-orbitals of silicon and germanium. Electron donation from the 2p π orbital on oxygen into the π system of the ring increases the π electron density at the 2- and 4-positions. These positions are therefore particularly sensitive to substituent effects attributed to π bonding. The 3- position is insensitive to O→ring backbonding and substituent effects would be relatively small. For comparison with the 4-substituted compounds, 3-substituted pyridine N-oxides were prepared and basicity studies were done. Attempts to determine the N-O bond order of the 3-substituted compounds by measuring the N-O stretching frequencies were not successful as this peak could not be isolated. It has been shown that it is coupled with other vibrational modes.[11] (Figure IV) However, the 3-substituted compounds caused no special difficulties in the pKa determinations, or in the IR or NMR studies of hydrogen bond strength.

(14)

FIGURE IV



The values of pKa for the substituted pyridine N-oxides in aqueous solution were determined spectrophotometrically. The experiment was tested by comparing the result obtained for unsubstituted pyridine N-oxide to that reported by Jaffe and Doak.[7] The value of 0.82 pKa units compares favorably with 0.79 obtained by Jaffe and Doak. The values reported in Table VII show that the 4-substituted organometallic hydroxypyridinium cations are stronger acids than the t-butyl analog and stronger also than the unsubstituted hydroxypyridinium cation. It seems unlikely that the organosilicon and -germanium groups could withdraw electron density from the positively charged hydroxypyridinium ring. It follows then that the smaller pKa values are a result of the weakened basicity of the organometallic substituted pyridine N-oxide. Electron withdrawal <u>via</u> p-d π bonding from the 4-position stabilizes the basic form over the acid form, and the equilibrium (1) lies more towards the right.

TABLE VII

pKa VALUES OF SUBSTITUTED PYRIDINE N-OXIDES

Substituent	pKa	
	4-position	3-position
H	0.82	0.82
$(CH_3)_3C$	1.16	0.84
$(CH_3)_3Si$	0.60	0.85
$(CH_3)_3Ge$	0.60	0.86

As expected, no significant variation in pKa is seen among the 3-substituted compounds.

Zuckerman, et al.[6], claimed that low pKa values obtained for silicon and germanium substituted aryl systems are caused by high solvation energies of the acid ions. They argued that the large organometallic groups do not allow the solvent molecules to orient themselves around the ion in a high degree of orderliness. This contributes to a high value of $\Delta S°$. According to these authors, it is the high $\Delta S°$, rather than any significant trend in $\Delta H°$ or base-proton bond strength, that causes the low free energy values. In order to show, then, that the organometallic groups do withdraw electron density and lower the base-proton bond strengths, it was necessary to have experiments which

would not be affected by solvation energies. The strength of hydrogen bonds formed between pyridine N-oxides and suitable acids would not be affected by solvation effects at the other end of the molecule. The hydrogen bonding acids chosen were phenol and methanol.

Phenol did not prove to be a practical acid for determining $\Delta\nu$(O-H) (the shift in the O-H stretching frequency between the free phenol and the frequency in the hydrogen bonded complex). The shifts were large and the resultant peaks were asymmetric due to interference from the C-H stretching frequencies in the 3000 cm^{-1} region. Methanol, however, is a weaker acid than phenol and the $\Delta\nu$(O-H) values are smaller. The resultant peak is in an uncluttered region and the center of the peak is easily read to $\pm$ 5 cm^{-1}. In order to avoid intermolecular methanol-methanol hydrogen bonding, it was necessary to use dilute solutions (0.04M in CCl_4). Suitably strong absorptions were observed at this low concentration as a 6 mm pathlength cell was used. The results (Table VIII) show that the organometallic substituted pyridine N-oxides have smaller $\Delta\nu$(O-H) values than the t-butylpyridine N-oxide when the substituent group is on the 4-position. There is not much difference between the organometallic

substituted and unsubstituted values. In line with previous studies[8] that have shown linear relationships between $\Delta\nu$(O-H) and ΔH of base-alcohol hydrogen-bonding interactions, these results show that the organometallic substituted pyridine N-oxides are weaker hydrogen bonding bases than the t-butyl analog. There is no significant variation in base strength between the organometallic substituted and unsubstituted pyridine N-oxides. It is reasonable to assume that while backbonding into the d-orbitals of silicon and germanium is taking place, the extent of it is diminished because of the presence of the hydrogen-bond. The oxygen electrons are tied up somewhat by the hydrogen-bond, so that the ability of oxygen to send electron density into the ring is lessened and therefore, the amount of electron density which can be withdrawn by silicon and germanium is also lessened.

TABLE VIII

$\Delta\nu$(O-H) VALUES FOR METHANOL-SUBSTITUTED PYRIDINE N-OXIDE HYDROGEN-BOND COMPLEXES

Substituent	$\Delta\nu$(O-H) (cm^{-1}) 4-position	3-position
H	280	280
$(CH_3)_3C$	310	290
$(CH_3)_3Si$	270	285
$(CH_3)_3Ge$	280	285

The ν(O-H) for unassociated methanol in CCl_4 is 3640 cm^{-1}.

In order to corroborate these results, phenol was used as a hydrogen-bonding acid in a subsequent experiment. As mentioned previously, the $\Delta\nu$(O-H) values of phenol were too large to allow precise readings. However, Eyman and Drago[12] have shown a linear relationship between $\Delta\nu$(O-H) and the proton magnetic resonance chemical shift of the hydroxy hydrogen in phenol-base hydrogen bonded complexes. The proton resonance due to the acid hydrogen is always shifted downfield in the hydrogen-bonded complex as compared to the free acid. This is because the electron donor molecule polarizes the O-H bond of phenol and alters the screening of the proton. The greater the extent of hydrogen-bonding, the greater is the downfield shift. Although no work was previously reported using pyridine N-oxide as a base, in the present study chemical shifts of the hydroxy proton of phenol obtained using pyridine N-oxide, and 4-methyl, 4-methoxy, and 4-acetylpyridine N-oxides as bases correlated well with literature values of $\Delta\nu$(O-H). Complete complexation occured at a molar ratio (pyridine N-oxide/phenol) of 10:1. The chemical shifts changed upon changing the concentration ratio below 10:1; however, above this ratio no appreciable changes were seen. Phenol is in a monomeric state at about 0.1M, so the experiment required concentrations of 1M for

pyridine N-oxide and 0.1M for phenol in methylene chloride. The results using phenol as a hydrogen-bonding acid (Table IX) are consistent with those of methanol, inasmuch as the $(CH_3)_3Si$- and $(CH_3)_3Ge$-substituted compounds showed less hydrogen-bond strength than the $(CH_3)_3C$ derivative, but an increase in hydrogen-bond strength over the unsubstituted pyridine N-oxide. The latter result was not found when methanol was the hydrogen-bonding acid. This can be explained by realizing that phenol, a stronger acid than methanol, ties up the oxygen electrons on pyridine N-oxide to a greater extent. The electron density at the 4-position is not as enhanced and there is that much less backbonding into the substituent d-orbitals. The net effect is apparent electron donation by the silyl and germyl groups.

TABLE IX

Chemical Shifts for Phenol Adducts with Substituted Pyridine N-Oxides

Substituent	δ(ppm)	
	4-position	3-position
H	10.10	10.10
$(CH_3)_3C$	10.51	10.26
$(CH_3)_3Si$	10.15	10.25
$(CH_3)_3Ge$	10.20	10.21
CH_3O	11.02	
CH_3	10.54	
$CO(CH_3)$	8.96	

The conclusion that can be drawn from the results of these studies is that the electronic distribution in the pyridine N-oxide system depends upon the experimental conditions as well as upon the nature and position of substituent groups. It was shown that the ability of the empty d-orbitals on silicon and germanium to withdraw electron density from the pyridine ring is a function of the availability of the oxygen π electrons to backbond into the ring. In each study the 4-substituted pyridine N-oxides were shown to be the weaker bases when the substituent was

trimethylsilyl or trimethylgermyl, than when it was t-butyl. However, the organometallic substituted pyridine N-oxides were either as strong or stronger bases (depending on the strength of the acid) than the unsubstituted pyridine N-oxide, when in the hydrogen-bonded complex state. Clearly there are two opposite forces in effect here; namely, the positive inductive effect of silicon and germanium opposed by backbonding via the π system. This can be further seen by examining the data for the 3-substituted pyridine N-oxides. The 3-position does not obtain the enhanced electron density, due to O→ring backbonding, and the positive inductive effect predominates. The pyridine N-oxides with the organometallic groups in the 3-position are therefore stronger bases than the analogous compounds substituted in the 4-position. However, even when on the 3-position, the organometallic groups do not donate electron density to a greater extent than the t-butyl group as would be predicted by the electronegativity scales. This indicates that there is still some backbonding taking place at the 3-position. It is also of interest to note that the electron donation by the t-butyl group to the oxygen atom decreases considerably in going from the 4- to the 3-position. (3-t-Butyl pyridine N-oxide is a weaker base than 4-t-butyl-pyridine N-oxide) This is in line with the hyperconjugative

mechanism for electron donation from alkyl groups. These experiments also show no significant variations in base strength in going from silyl to germyl substituents. This indicates a similar degree of overlap of the ring π orbitals with the 3d or 4d orbitals.

EXPERIMENTAL

4-(Trimethylsilyl)- and 4-(trimethylgermyl)pyridine N-oxide were prepared by Weiner[10] and used in this study. 4-t-Butyl and 4-acetylpyridine N-oxide were prepared from the corresponding commercially available pyridines by the method of Ochiai.[13] 4-Picoline N-oxide and 4-methoxypyridine were commercially available and were purified by crystallization from ethanol/ether. Pyridine N-oxide, also commercially available, was sublimed under vacuum before use. All the compounds were dried by pumping for several hours in the presence of P_2O_5. The solvents used were all spectroquality. Carbon tetrachloride and methylene chloride were stored for several days over Linde 4-A molecular sieves, which had been baked overnight. Methanol was stored over Drierite. Phenol was sublimed under vacuum. Ether, used as a solvent in the preparation of the organolithium reagent, was distilled over $LiAlH_4$ immediately before each use. Handling of the organolithium reagent and the preparations of the organometallic substituted pyridine compounds were carried out under an inert atmosphere. All NMR spectra were taken on a Varian Associates A-60 spectrometer and the reported

chemical shifts are downfield from tetramethylsilane. Analyses were done by Schwartzkopf Microanalytical Laboratories.

Preparation of n-Butyllithium. n-Butyllithium was prepared from n-butyl bromide and lithium wire in ether at -30° by the method of Gilman[14] et al. The product was titrated against a standard acid.

Preparation of 3-(Trimethylsilyl)pyridine. A three-necked flask equipped with a nitrogen inlet tube, stirrer, and addition funnel was charged with 300ml (0.29 moles) of 0.96M n-butyllithium in ether. The solution was cooled to -40° in a dry ice-acetone bath, and 3-bromopyridine (36g, 0.23 moles) in 250 ml of ether was added slowly to it. A yellow white precipitate formed. Some decomposition of the 3-pyridyllithium did occur as evidenced by some orange-brown coloration. The suspension was stirred vigorously for 10-15 minutes, and trimethylchlorosilane (29 g, 0.26 moles) was added dropwise. The mixture was refluxed for 2 hours and then hydrolyzed over an ammonia-ice slurry. The ether layer was separated, washed several times and dried over Na_2SO_4. The ether was stripped off under vacuum and fractional distillation of the residue gave 12 g (31%) of

3-trimethylsilylpyridine, b.p. 60°/5mm. (Reported[15] b.p. 94°/30 mm)

NMR: ($CDCl_3$): τ10.8 (s, 9, Me_3Si), 3.18 (m, 1, H_γ) 2.60 (m, 1, H_β), 1.70 (m, 2, H_α)

Preparation of 3-(Trimethylsilyl) pyridine N-oxide.

To a round bottom flask fitted with a condenser was added 3-(trimethylsilyl)pyridine (3 g, 0.018 moles), 15 ml of glacial acetic acid, and 2 ml of 30% H_2O_2. The solution was heated on a water bath to 75°. After 3 hours of heating, an additional 1 ml of H_2O_2 was added and the solution was heated overnight. The solution was then concentrated to 10 ml, an equal volume of water was added, and the solution was again concentrated to 10 ml. Anhydrous K_2CO_3 was added to neutralize the acetic acid and to absorb much of the water. The product was extracted into chloroform and dried over Na_2SO_4. The chloroform was stripped off under vacuum and fractional distillation of the residue gave 1.3 g (40%) of 3-trimethylsilylpyridine N-oxide, b.p. 117°/0.4 mm. (Reported[15] b.p. 146°/6mm)

NMR: ($CDCl_3$): τ9.71 (s, 9, Me_3Si), 2.51(m, 2, $H_{\beta,\gamma}$), 1.65 (m, 2, H_α).

Anal. Calculated for $C_8H_{13}NOSi$: C, 57.64; H, 7.83; N, 8.78.

Found: C, 57.64; H, 8.11; N, 8.46%

Preparation of 3-(Trimethylgermyl)pyridine and its N-oxide. These compounds were prepared for the first time in a manner identical to the analogous silicon compounds. Reaction of 3-bromopyridine (11g, 0.070 moles), trimethylbromogermane (15g, 0.078 moles), and 60 ml of 1.4M n-butyllithium (0.084 moles) gave 4.0 gm of 3-(trimethylgermyl)pyridine (29%), b.p. 73°/5mm.

NMR: τ9.75 (s, 9, Me_3Ge), 3.00 (m, 1, H_γ), 2.40 (m,1, H_β) 1.55 (m, 2, H_α).

Anal: Calculated for $C_8H_{13}NGe$: C, 49.07; H, 6.69

Found: C, 49.15; H, 6.70%

The product was oxidized with hydrogen peroxide in acetic acid. 3-(Trimethylgermyl)pyridine (2.9g, 0.015 moles) gave upon oxidation 0.9g (28%) of 3-(Trimethylgermyl-pyridine N-oxide, b.p. 125°/5 mm.

NMR: ($CDCl_3$): τ9.56 (s, 9, Me_3Ge), 2.51 (m, 2, $H_{\beta,\gamma}$) 1.65 (m, 2, H_α).

Anal: Calculated for $C_8H_{13}NOGe$: C, 45.37; H, 6.19; N, 6.62. Found: C, 45.16; H, 5.97; N, 6.56%

Preparation of 3-t-butylpyridine. 3-t-butylpyridine was prepared by the methylation of 3-ethylpyridine by the method of Essery and Schofield[16]. Liquid ammonia (400 ml)

was introduced into a three-necked round bottom flask equipped with a mercury seal stirrer and a dry ice condenser. Sodium (23 gm, 1.0 mole), which had been cut up into small pieces, was added piece by piece to the stirred liquid ammonia, into which 0.05 gm of $Fe(NO_3)_3$ had been added. 3-Ethylpyridine (106 gm, 1.0 mole) was then added to the sodium amide solution over a period of 5 minutes. Methyl chloride (50 gm, 1.0 mole) was then introduced through the condenser over a period of 4 hours. The ammonia was allowed to evaporate overnight. The residual liquid was decanted off and the solid was extracted with ether. The ether extracts were combined with the liquid. The ether was removed <u>in vacuo</u> and the residue was distilled over a range of 165-178° through a heated column packed with helices. Examination of the NMR spectrum showed that much starting material was in this cut. A second distillation was done, and the material collected at 178-180° (23.4 g) was found to be 90% isopropylpyridine. The 90% isopropylpyridine was added to a mixture of 31 gm of potassium in 350 ml of liquid ammonia. Methyl bromide (75 g) was added dropwise over 4 hours. The mixture was worked up as described above and distilled on a spinning band column to yield 4.3 g of 3-t-butylpyridine, b.p. 194-195°. (Reported value was 190-192°.)[16] The NMR

spectrum showed no peaks due to isopropyl hydrogens.

Preparation of 3-t-butylpyridine N-oxide.

The 3-t-butylpyridine was oxidized in the same manner as the trimethylsilyl and trimethylgermyl derivatives. 3-t-Butylpyridine (3 gm, 0.022 moles) yielded 1.5 gm (45%) of 3-t-butylpyridine N-oxide, b.p. 123-124°/0.5 mm. (Reported value was 132-134°/1mm.)[16] The methyl to pyridyl hydrogen integrated ratio in the NMR spectrum was 9:4 and no isopropyl hydrogens were seen.

pKa Determinations. The pKa values were determined spectrophotometrically. All spectra were taken on a Cary Model 14 Spectrophotometer, using matched 1 cm cells. The aqueous solutions were approximately 10^{-5}M. The spectra were taken in the temperature range of 24-28° and showed no variation in the limits of this range. The values for pKa were calculated using the formula:

$$pK = pH + \log (e_b - e_i / e_i - e_a)$$

were e is the extinction coefficient at 256 nanometers; a refers to the solution containing only the acid form generated with 50% (v/v) H_2SO_4; b refers to the neutral solution (Pyridine N-oxide exists as a free base in water);

i refers to solutions containing both acid and base forms generated by adding successive amounts of sulfuric acid to the neutral solution. At least three solutions of varying acid-base form ratios were used in each determination. The results were reproducible to within ± 0.04 pKa units. The pH values were determined by titration against standardized NaOH. Table X lists the data used in pKa calculations.

Determination of $\Delta\nu$(O-H).

Measurements were carried out with a Perkin-Elmer 621 infrared spectrophotometer, using a 6 mm cell. Before each determination, the spectrum of the stock solution of methanol in carbon tetrachloride was obtained in order to check for the presence of water, which results in a broad band at 3300-3500 cm^{-1}. An acceptable methanol solution showed only a base line in the region in which the hydrogen-bonded ν(O-H) would appear. The pyridine N-oxide was then added to the methanol solution and the spectrum obtained. All manipulations of the pyridine N-oxides and the methanol solutions were carried out in a nitrogen-filled glove bag. The pyridine N-oxide concentrations were ca. 0.015 M, while the concentration of the methanol

TABLE X

Spectrophotometric Data in the Determination of pKa Values of Substituted Pyridine N-Oxides

Substituent	$e_a x10^{-4}$	$e_b x10^{-4}$	$e_i x10^{-4}$	pH	pKa
4-$(CH_3)_3C$	0.331	1.64	0.880	0.991	1.13
			1.03	1.19	1.14
			0.604	0.616	1.20
4-$(CH_3)_3Si$	0.340	1.73	1.23	0.863	0.611
			1.13	0.678	0.559
			0.992	0.562	0.615
4-$(CH_3)_3Ge$	0.470	1.75	1.52	1.13	0.567
			0.885	0.313	0.623
			0.905	0.317	0.592
3-$(CH_3)_3Si$	0.505	1.26	0.854	0.777	0.845
			1.03	1.25	0.892
			0.824	0.661	0.798
3-$(CH_3)_3Ge$	0.226	1.17	0.625	0.604	0.800
			0.695	0.824	0.887
			0.875	1.20	0.884
3-$(CH_3)_3C$	0.246	1.14	0.615	0.680	0.826
			0.580	0.575	0.805
			0.600	0.703	0.891

solutions were 0.04 M. A brief study on 4-t-butylpyridine N-oxide in which the methanol/base molar ratio was varied between 3/1 and 1/3 yielded no appreciable change in results. The measurements were carried out at a room temperature of ca. 25°.

Determination of chemical shifts. The NMR spectra were obtained within a Varian Associates A-60 spectrometer. The temperature (29 ± 1°) was determined using a methanol solution and calibration data supplied by Varian Associates. The chemical shifts were all recorded relative to the internal standard tetramethylsilane and were readable to within ± 0.02 ppm. The pyridine N-oxides were weighed in NMR tubes and enough stock solution of phenol in methylene chloride was added to make the solutions 1M in pyridine N-oxide. The phenol concentration was 0.1M as it has been shown[12] that phenol is monomeric at this concentration.

PART II

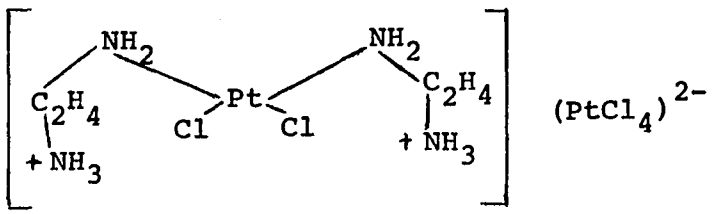
ORGANOPHOSPHONIUM SUBSTITUTED PYRIDINE AS A LIGAND IN TRANSITION METAL COMPLEXES

In the pyridine N-oxide molecule it was observed that the pyridine ring donates charge to the oxygen or withdraws charge from the oxygen, depending upon the nature of substituent groups on the ring. The next step in this study was to determine the effectiveness of the pyridine ring as a transmitter of π effects in transition metal complexes. A substituent group which would alter the electronic distribution in the pyridine ring most significantly (by withdrawing electronic charge most effectively) would be one which is positively charged. For these reasons, phosphonium substituted pyridines were used as ligands in this study. Previous workers have investigated transition metal complexes containing cationic ligands and have obtained interesting results.

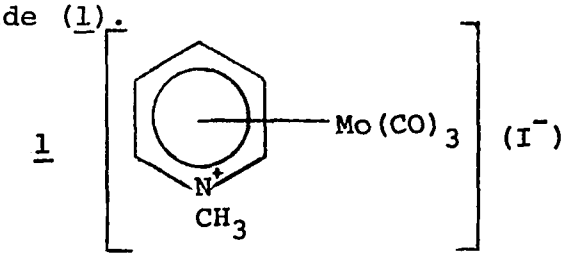
In the next section, the various systems previously studied will be discussed.

HISTORICAL

The first reported cationic ligands were prepared by Drew in 1932[17]. He found that monoprotonated ethylene diamine acts as a ligand toward the platinum ion in the salt:



Moore and Wilkinson[18] synthesized π type complexes by reacting metal carbonyls with the iodide salts of N-methylated heterocycles. For example, refluxing molybdenum hexacarbonyl with 1-methylpyridinium iodide in THF gave tricarbonyl-π-1 methylpyridinemolybdenum iodide (1).

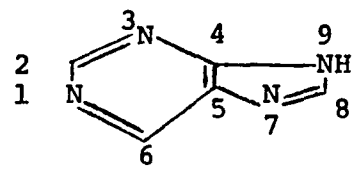


1

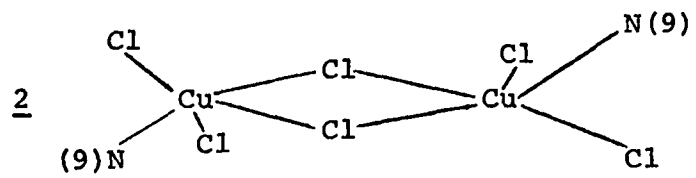
It was assumed that the positive charge originally on the nitrogen atom is delocalized in the complex.

Metal complexes containing protonated purine derivatives (adeninium and guaninium ions) have been prepared. Price[19] prepared dibromodiadeniniumcopper (II) dibromide.

It has been shown[20] that this complex takes the form of a compressed tetrahedron with the coordination almost halfway between tetrahedral and square planar. Adenine is protonated at N(1) and coordinates via N(9). The atoms in a purine system are numbered as follows:



Villa[21] reported the results of a spectral study of trichloroguaniniumcopper (II) monohydrate (2).



This complex exists as a chloride bridged dimer of D_{3H} symmetry with the three chloride ions in the equatorial plane and one chloride ion and the guaninium ion in the axial position. The guaninium ion is protonated at N(3) and N(7) and is coordinated via N(9). He showed that there is somewhat weaker bonding on the axial position, probably caused by the presence of the positively charged guaninium ion.

The first systematic study of the coordinating

ability of cationic ligands was reported by Quagliano and coworkers in 1964[22]. They prepared metal complexes with monomethylated diamines acting as ligands. They compared the electronic spectrum of the octahedral complex formed between Ni(II) and the β-aminoethyltrimethylammonium cation. (abbreviated as β-L^+) with the Ni(II) complex of the γ- aminopropyltrimethylammonium cation (abbreviated as γ-L^+). (3)

3 $\left[Ni(II)(CH_3)_3N^+(CH_2)_3NH_2)_6\right]^{+8}(8ClO_4^-)$

The spectra showed an appreciable shift to lower frequencies for the complexes of γ-L^+ compared to those of β-L^+. The Ni(II) complex of γ-L^+ absorbed at 27,000, 17,000 and 10,000 cm^{-1}, whereas the β-L^+ complex absorbed at 26,000, 16,500 and 10,100 cm^{-1}. Similar shifts to lower frequencies by the β-L^+ complexes were also observed in the octahedral Co(II) complexes as well as the tetrahedral Cu(II) complexes. Absorptions at lower frequencies indicate that the ligand produces a weaker field. Basicity studies of the two cationic ligands paralleled the spectral measurements. That is to say, the ligand which produced the weaker field (β-L^+) was the weaker base. The spectral measurements placed the γ-L^+ ligand very close to methylamine in the

spectrochemical series, while the β-L^+ ligand was placed towards the weaker field end, about halfway between methylamine and water. This study showed that a positive charge three methylene groups removed from the donor site does not effect the donor ability of the ligand, whereas a positive charge two methylene groups from the donor site does reduce the donor ability.

In a continuation of the study of the effect of positive charge on the donor ability of ligands, these same workers prepared complexes with the 1,1,1-trimethylhydrazinium cation, acting as a ligand.[23] In these complexes the site of positive charge is immediately adjacent to the nitrogen donor atom. They found that slow evaporation of an aqueous solution of a nickel (II) halide and the corresponding trimethylhydrazinium halide in a molar ratio of 1:2 gave yellow crystals of the complex $\left[NiX_4\left((CH_3)_3N^+NH_2\right)_2\right]$. The d-d electronic spectra of these complexes indicated a tetragonally distorted octahedral stereochemistry, with the cationic ligands in the axial position. The spectra were virtually superimposable with those of the complexes $\left[NiX_4(H_2O)_2\right]^{2-}$, indicating that the field strength of the trimethylhydrazinium cation must be very similar to that of water, and much lower than that of uncharged primary amines.

Thus a positive charge adjacent to the donor atom in a ligand considerably lowers the donor ability of the ligand. The trimethylhydrazinium cation has, of course, an extremely low basicity (-2.9 pKa units) and it is interesting that it would form complexes at all. In fact, only complexes of nickel were isolable and at temperatures near 100° they transformed to the blue complex salts $\left[NiX_4^{2-}\right]\left(2(CH_3)_3N^+NH_2\right)$, containing the tetrahedral tetrahalonickelate (II) anion.

Quagliano and Vallarino[24] extended their study of the donor properties of positively charged ligands to include phosporus donors. They reacted the halide salts of some mono-benzylated ditertiary phosphines:

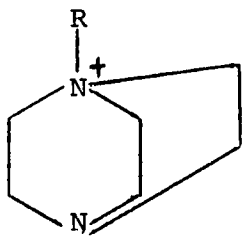
4 $(C_6H_5)_2PCH_2CH_2P^+(C_6H_5)_2(CH_2C_6H_5)$

5 $(C_6H_5)_2PCH_2P^+(C_6H_5)_2(CH_2C_6H_5)$

with the cobalt(II) and nickel(II) halides under anhydrous conditions. Blue crystalline compounds of stoichiometry $MX_3^-(L^+)$ were formed. On the basis of the d-d spectra, and magnetic porperties, these compounds were formulated as high spin four coordinate complexes $\left[MX_3L\right]$. The d-d electronic spectra showed the same pattern of absorption as the pseudotetrahedral anions $\left[MX_3(C_6H_5)_3P\right]^-$ and on this basis the complexes were assigned a C_{3V} symmetry. The magnetic moments

of the Ni(II) and Co(II) complexes were in the range usually observed for tetrahedrally coordinated Co(II) and Ni(II). (A detailed description of the electronic spectra and magnetic properties of d^7 and d^8 C_{3V} complexes is found in the Results and Discussion Section.) The complexes were considered to have a zwitterionic structure in which the positive charge on the quaternized phosphorous atom of the ligand is separated from the center of negative charge on the (MX_3^-) moiety. A comparison of the spectra of the complexes containing ligands 4 and 5 showed them to be superimposable even though in ligand 4 the site of positive charge is separated from the phosphorous donor atom by only one CH_2 group. The conclusion drawn from this result is that in complexes of C_{3V} symmetry the presence of a positive site on the ligand does not affect the position of the donor in the spectrochemical and nephelauxetic series. This conclusion is similar to the one arrived at by these authors in studying a different series of complexes.[25] They prepared complexes containing the monoquaternized diamine 1,4-diazabicyclo [2.2.2] octane (6) (referred to as "dabco").

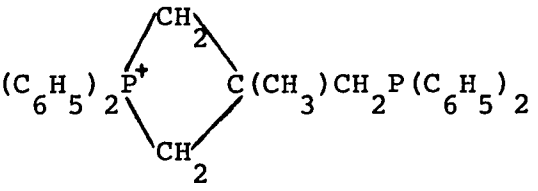
6



The donor atom in these ligands is a tertiary nitrogen of very low basicity (pKa = 2.90) and they would be expected to behave as poor ligands. However, reaction of the "dabconium" halide (5) with the halides of first row divalent transition metals (Mn(II) to Zn(II)) produced stable complexes of C_{3V} symmetry. While it is generally assumed that for essentially σ - bonding ligands basicity measurements are a good indication of donor properties toward transition metal ions, the d-d electronic spectra in the solid state were virtually superimposable with those of the corresponding $[MLX_3]^-$ complexes, where L is a much stronger nitrogen donor base, e.g. pyridine (pKa = 5.1). These authors suggest that the large field produced by this cationic ligand can be explained by assuming a highly ordered crystal lattice with the positive and negative sites arranged head-to-tail. The positive charge of the quaternized nitrogen which in aqueous solution reduces the basicity of the unquaternized nitrogen considerably (by approximately 6 pKa units) is effectively neutralized by electron interaction with the neighboring MX_3^- group

in the solid state.

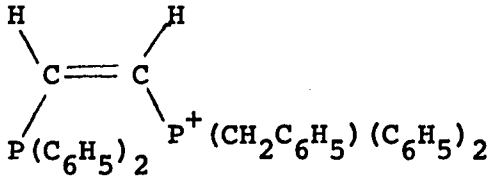
Berglund and Meek[26] prepared complexes containing the cationic ligand:

7 

Gold, platinum, and palladium complexes, formed from the salt of 7 and the metal chloride in a 1:1 molar ratio, were found to be of square planar symmetry. Nickel and cobalt complexes were characterized by their electronic spectra as pseudotetrahedral (C_{3V}). The spectra were very similar to the triphenylphosphine complexes, $\left[MP(C_6H_5)_3X_3\right]^-$, and the authors comclude that the complex functions essentially as a triphenylphosphine complex, and the presence of the cationic group three carbon atoms away does not appreciably influence the coordination properties of the phosphino ligand.

Kolodny, Morris, and Taylor[27] reported the results of a study of complexes with cationic ligands in which the effect of the positive site is transmitted to the donor site via an unsaturated organic bridge. They

prepared Co(II) zwitterionic complexes of C_{3V} symmetry with the cationic ligands:

8 

9 $(C_6H_5)_2P\text{-}C{\equiv}C\text{-}P^+(C_6H_5)_2(CH_2C_6H_5)$

A comparison of the d-d spectra of these complexes with complexes of the analogous neutral ligands led these authors to the conclusion that the positive site makes a negligible contribution to the donor capabilities of the unquaternized phosphorus atom. Table XI lists some of the results obtained.

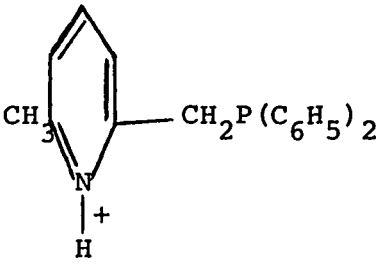
TABLE XI

Absorption Maxima of some Phosphorous Donor Complexes of Co(II)[27]

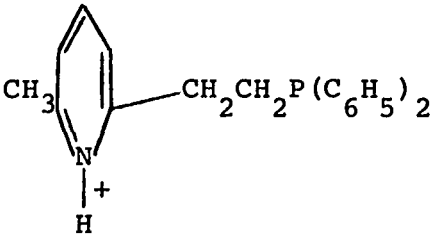
Complex	Electronic Absorption Maxima (cm^{-1})
$\left[Ph_2PC_2H_2P^+Ph_2(CH_2Ph)CoBr_3^-\right]$	14,910 15,260 16,270
$(Et_4N^+)\left[CoBr_3^-Ph_2PC_2H_2PPh_2\right]$	14,990 15,100 16,210
$\left[Ph_2PC_2P^+Ph_2(CH_2Ph)CoBr_3^-\right]$	14,650 15,000 15,200
$(Et_4N^+)\left[CoBr_3^-Ph_2C_2PPh_2\right]$	14,560 14,950 16,150

Nelson and coworkers[28] prepared Co(II) and Ni(II) complexes of the positively charged ligands:

10 (PN'H)



11 (PN"H)



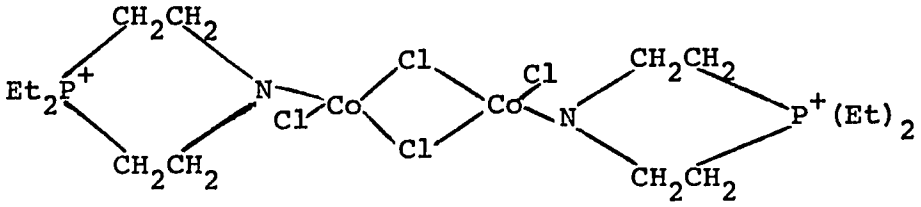
The complexes formed between the halide salts of these cations and Co(II) and Ni(II) halides were found to be 1:1 zwitterionic complexes of C_{3V} symmetry. A comparison between the d-d spectra of the complexes of 10 and 11 showed that the ligand in which the positive charge is closer to the donor phosphorus atom produced a slightly higher average field. (Table XII) These authors concluded that the higher field is a result of a greater degree of metal to phosphorus π bonding in complexes of 10. The cationic site withdraws electron density from the phosphorus atom to a greater extent in the ligand where the two sites were closer and complex of this ligand would show a greater degree of M$\longrightarrow$P backbonding.

TABLE XII

Absorption Maxima of some Phosphorus Donor Complexes of Co(II) and Ni(II)[28]

Complex	Absorption Maxima (cm^{-1})
Co (PN'H)Cl_3	18,300
	16,500
	14,700
	8,200
	4,500
Co (PN"H)Cl_3	18,000
	16,400
	14,000
	8,000
	4,500
Ni (PN'H)Br_3	16,300
	9,500
	8,600
	5,800
Ni (PN"H)Br_3	16,000
	9,600
	8,800
	5,600

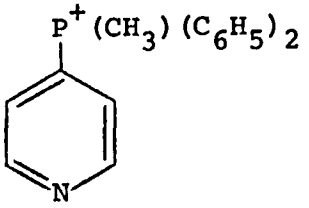
All of the complexes containing one positively charged ligand and three halide ligands that have so far been discussed were shown to be zwitterions of C_{3V} symmetry. Yoke and coworkers[29] have suggested a bridged dinuclear structure for a 1:1 complex formed between Co(II) chloride and hexahydro 1,4,4-triethyl-1,4-aza-phosphorinium chloride (12).

12 

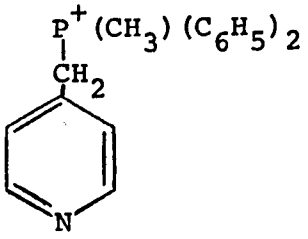
The magnetic moment and the d-d ligand field spectrum showed this complex to be pseudotetrahedrally coordinated. Conductance measurements, however, showed that the complex is highly conducting in absolute ethanol. The molar conductance was calculated to be 157 $ohm^{-1}cm^{-2}mol^{-1}$ which is well in excess for values of 1:1 electrolytes. Zwitterions are non-conducting but show a small degree of electrolytic behavior in polar solvents due to partial solvolysis.

The present report describes the preparation of the methyldiphenyl-4-pyridylphosphonium ligand (13) in which the positive charge is conjugated to the donor nitrogen atom via the π orbitals of the pyridine ring; and the methyldiplenyl-4-picolylphosphonium ligand (14) in which a CH_2 group is inserted between the ring and the phosphonium moiety. The formation of complexes of these ligands with Co(II) and Ni(II) bromides and characterization of these complexes by spectral, magnetic, and conductance measurements is discussed.

13



14

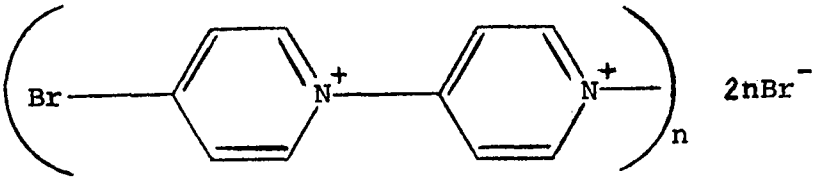


RESULTS AND DISCUSSION

Preparation of the Ligands

Two methods were used in preparing the phosphonium halides. Methyldiphenyl-4-pyridylphosphonium iodide was prepared by methylation of diphenyl-4-pyridylphosphine with methyl iodide. The diphenyl-4-pyridylphosphine; prepared from 4-bromopyridine, n-butyllithium and chlorodiphenylphosphine was first reacted with HI to form diphenyl-4-pyridylphosphine hydroiodide. This step protects the nitrogen atom and leaves the phosphino group available for quaternization with the methyl iodide, thus avoiding a mixture of products. (See Reaction Scheme I of Figure V for the chemical equations involved in this synthesis.) Following reaction of the pyridinium iodide with methyl iodide, the HI is removed with aqueous ammonia to form the product. The corresponding bromide, methyldiphenyl-4-pyridylphosphonium bromide was obtained in the same manner. Since handling methyl bromide proved to be somewhat troublesome, a different route was also taken to form the phosphonium bromide. Direct quaternization of methyldiphenylphosphine (formed from the reaction of methyllithium and chlorodiphenylphosphine) with 4-bromopyridine produced

methyldiphenyl-4-pyridylphosphonium bromide (Reaction Scheme II). The yield in this reaction is poor because 4-bromopyridine self-quaternizes to form the polymeric species:[30]



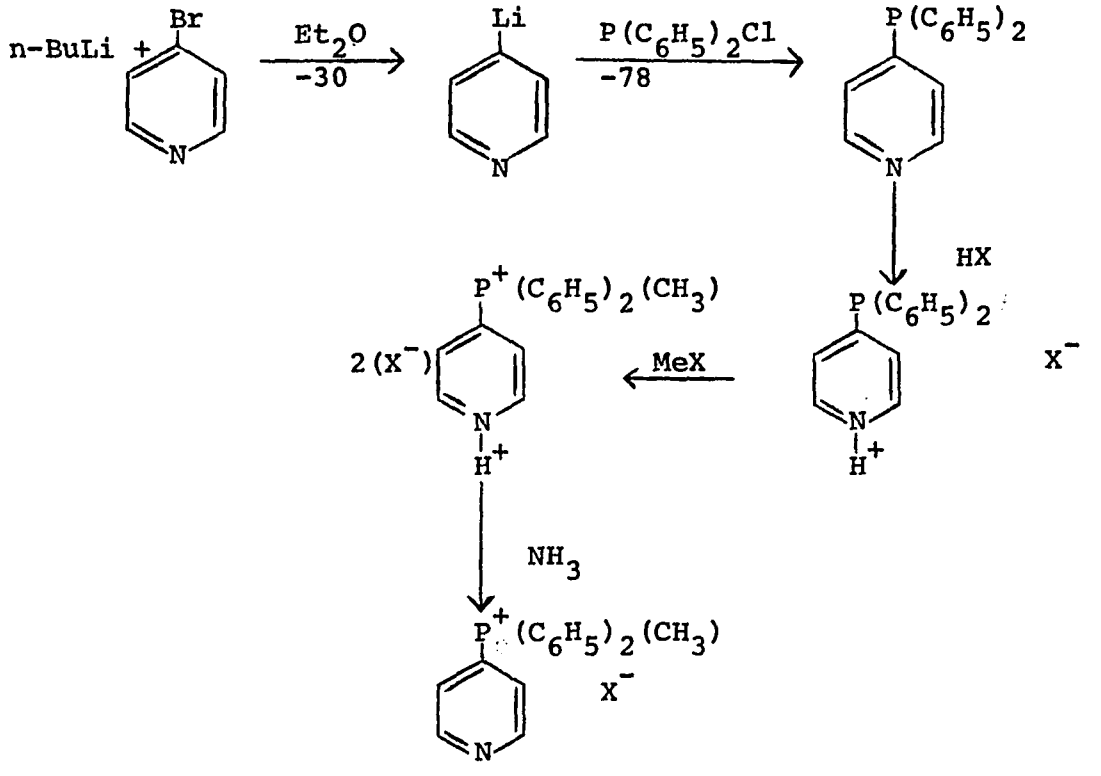
The unwanted side product is of deep purple hue and imparts its color to the product. The only successful method to separate this highly colored material from the white phosphonium bromide was found to be column chromatography. The purple color remained on the column and the phosphonium bromide was eluted, but the recovery of product in this process is poor.

The preparation of methyldiphenyl-4-picolyphosphonium bromide followed in a similar manner. The reaction however was much faster, product forming almost immediately upon the addition of 4-bromopicoline to methyldipenylphosphine, (The preparation of the pyridyl analog required overnight stirring.) An orange color, attributed to a self-quaternization product of 4-bromopicoline, formed and was separated on a chromatography column while the desired phosphonium

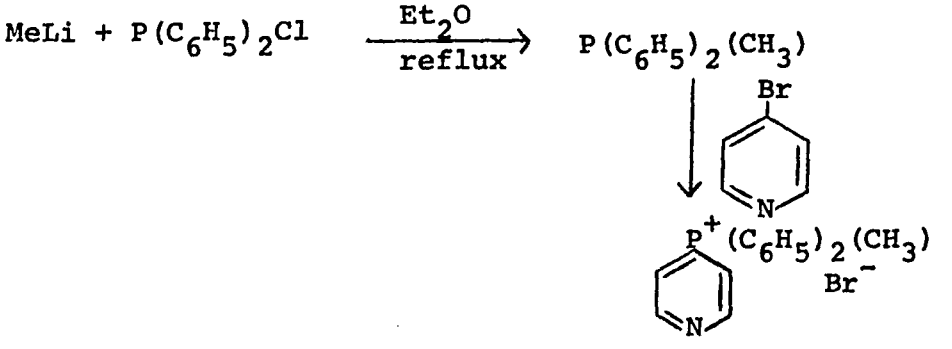
FIGURE V

Reaction Schemes in the Preparation of Phosphonium Substituted Pyridines

Reaction Scheme I:



Reaction Scheme II:



bromide was eluted. The details of these syntheses are described in the Experimental section.

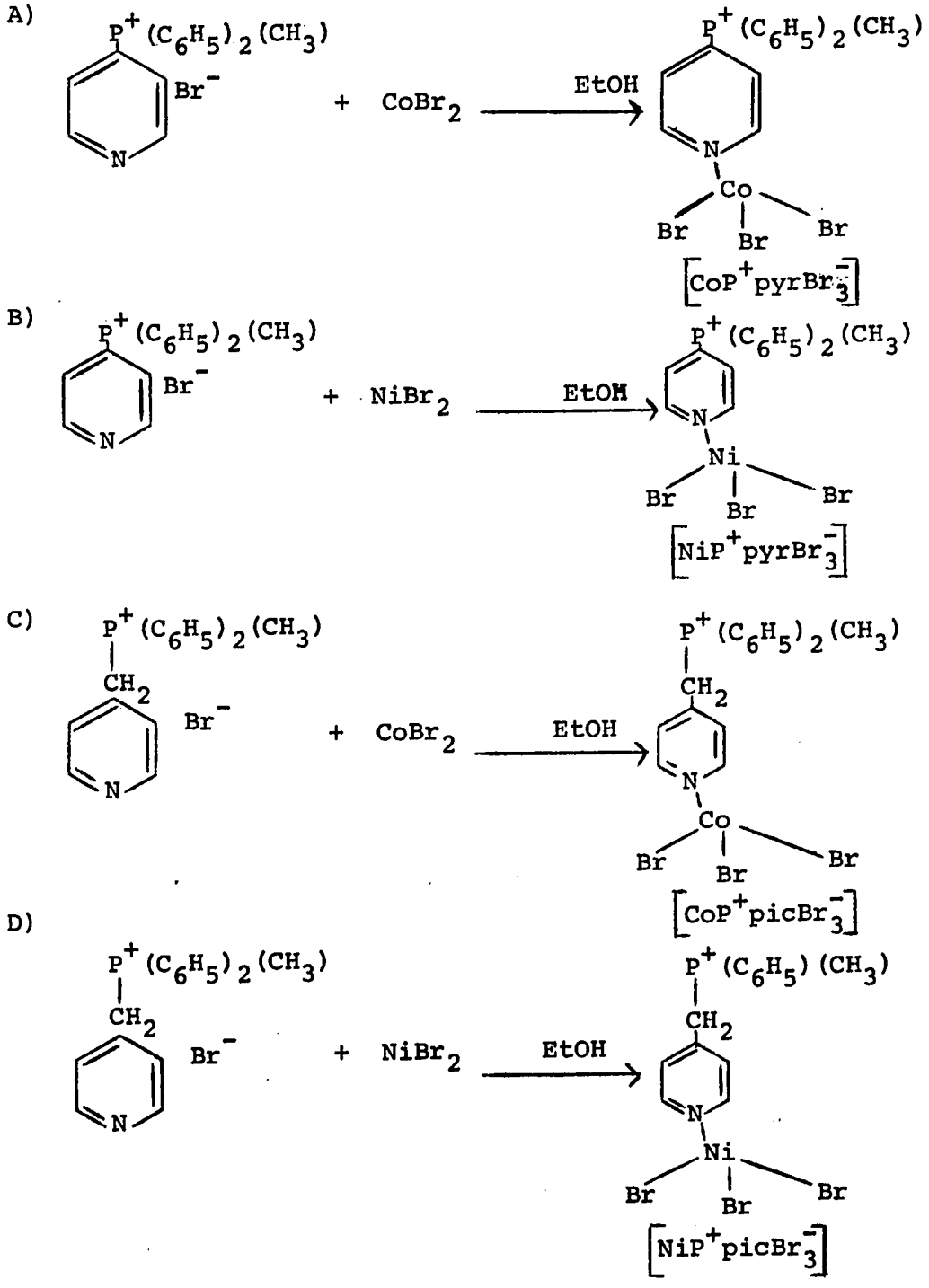
Preparation of the Complexes

The complexes were prepared by reacting ethanol solutions of the metal halide with solutions of the appropriate ligand in a 1:1 molar ratio. After a few minutes of refluxing, the blue colored complexes crystallized out of solution. Anhydrous conditions were maintained throughout. This was especially necessary for the complexes of nickel(II) which would not form unless anhydrous conditions were rigorously maintained. The complex of Ni(II) iodide could not be isolated under the strictest conditions, and no further work was done with iodide complexes.

For comparison purposes, a complex which does not contain a cationic ligand was prepared. The complex $(Et_4N^+)\left[Co(II)\ Br_3(C_5H_5N)\right]^-$ was prepared from cobalt bromide, tetraethylammonium bromide and pyridine. The analogous nickel(II) complex could not be prepared. Instead of blue crystals, characteristic of tetrahedral symmetry, yellow crystals were formed, probably containing a complex of

FIGURE VI

Formation of the Complexes



octahedral symmetry. Figure VI shows the formation of the complexes that were studied and the abbreviations used to identify the complexes throughout this discussion.

Characterization of the Complexes

Measurements of magnetic moments, molar conductances, and spectra were used to characterize these complexes as zwitterions of C_{3V} symmetry.

A. Magnetic Measurements

Magnetic measurements yield important information in determining the structure of a complex. The experimental magnetic moment is indicative of a particular stereochemistry. The magnetic moment of the Co(II) complexes fall within the 4.4-4.8 B.M. range usually observed for a d^7 ion in tetrahedral symmetry[31]. The ground state of Co(II) in T_d symmetry is an orbital singlet ($^4A_2$), so that reducing the symmetry to C_{3V} does not split the ground state and the effect on the magnetic moment is small. The magnetic moments of the Ni(II) complexes are somewhat below 3.9-4.2 range found for a d^8 ion in environments having nearly rigorous T_d symmetry, but are very similar to values found for a d^8 ion in pseudo-

tetrahedral environments.[32] The ground state of Ni(II) in T_d symmetry is an orbital triplet. This state is split by the low symmetry component and the orbital contribution to the magnetic moment is thereby reduced. The fact that the magnetic moments for the C_{3V} complexes are higher than those of similar complexes of C_{2v} symmetry is evidence that the ground state is ^3E.[33] (See Figure IX.)

Table XIII lists the magnetic moments for the complexes under study, calculated from the magnetic susceptibility by the formula:

$$\mu_{eff} = (3kT\chi'_M/N\beta^2)^{\frac{1}{2}}$$

where χ'_M is the molar susceptibility corrected for diamagnetic contributions of the ligands, k is the Boltzmann constant, T is the absolute temperature, N is Avogadro's number, and β is the Bohr magneton. (See the experimental section for the data used in the calculations of magnetic susceptibility.)

TABLE XIII

Magnetic Moments

Complex	Magnetic Moment (Bohr Magnetons)
$[CoP^{+}pyrBr_3^{-}]$	4.74
$[CoP^{+}picBr_3^{-}]$	4.70
$(Et_4N^{+})[CopyrBr_3]^{-}$ [40]	4.65
$[NiP^{+}pyrBr_3^{-}]$	3.8
$[NiP^{+}picBr_3^{-}]$	3.7

B.) Conductance Measurements

Conductance measurements were done to distinguish between a zwitterionic and a bridged structure as formulated by Yoke and coworkers[29] (vide supra). A zwitterionic complex should show no conductance while a bridged complex would show conductance greater than that of a 1:1 electrolyte. In fact, conductance measurements in acetonitrile and nitromethane yielded values somewhat less than those of a 1:1 electrolyte. This is indicative of a zwitterionic species in which partial solvolysis is taking place. The electronic spectra of the complexes in solution and in the solid state showed noticeable spectral shifts, indicating that the species in solution and in the solid state are probably not the same. The solvent appears to replace the pyridyl ligands to some extent in the coordination sphere of the metal. Table XIV lists the values obtained for the molar conductances of the complexes under study, calculated using the formula:

$$\Lambda_M = 1000\ k/M$$

where k is the conductivity determined by dividing the cell constant by the resistance.

(See the Experimental Section for further details, and data used in calculating the values for molar conductance.)

TABLE XIV

Molar Conductance Values

Complex	(Solvent)	Molar Conductance ($ohm^{-1}cm^{2}mol^{-1}$)
$(Et_4N^+)[CopyrBr_3I^-]$	(CH_3NO_2)	75.5
$[Cop^+picBr_3^-]$	(CH_3NO_2)	23.8
$[NiP^+pyrBr_3^-]$	(CH_3NO_2)	56
$[NiP^+picBr_3^-]$	(CH_3NO_2)	57
$(Et_4N^+)[CopyrBr_3]^-$	(CH_3CN)	95.5
$[CoP^+pyrBr_3^-]$	(CH_3CN)	84
$[CoP^+picBr_3^-]$	(CH_3CN)	65.5

C.) Measurements and Interpretation of Electronic Spectra

All spectra were taken in the solid state as Nujol mulls spread on filter paper. Table XV lists the absorption maxima obtained for the d-d transitions. The pattern of the spectra is very typical of a pseudo-tetrahedral geometry.

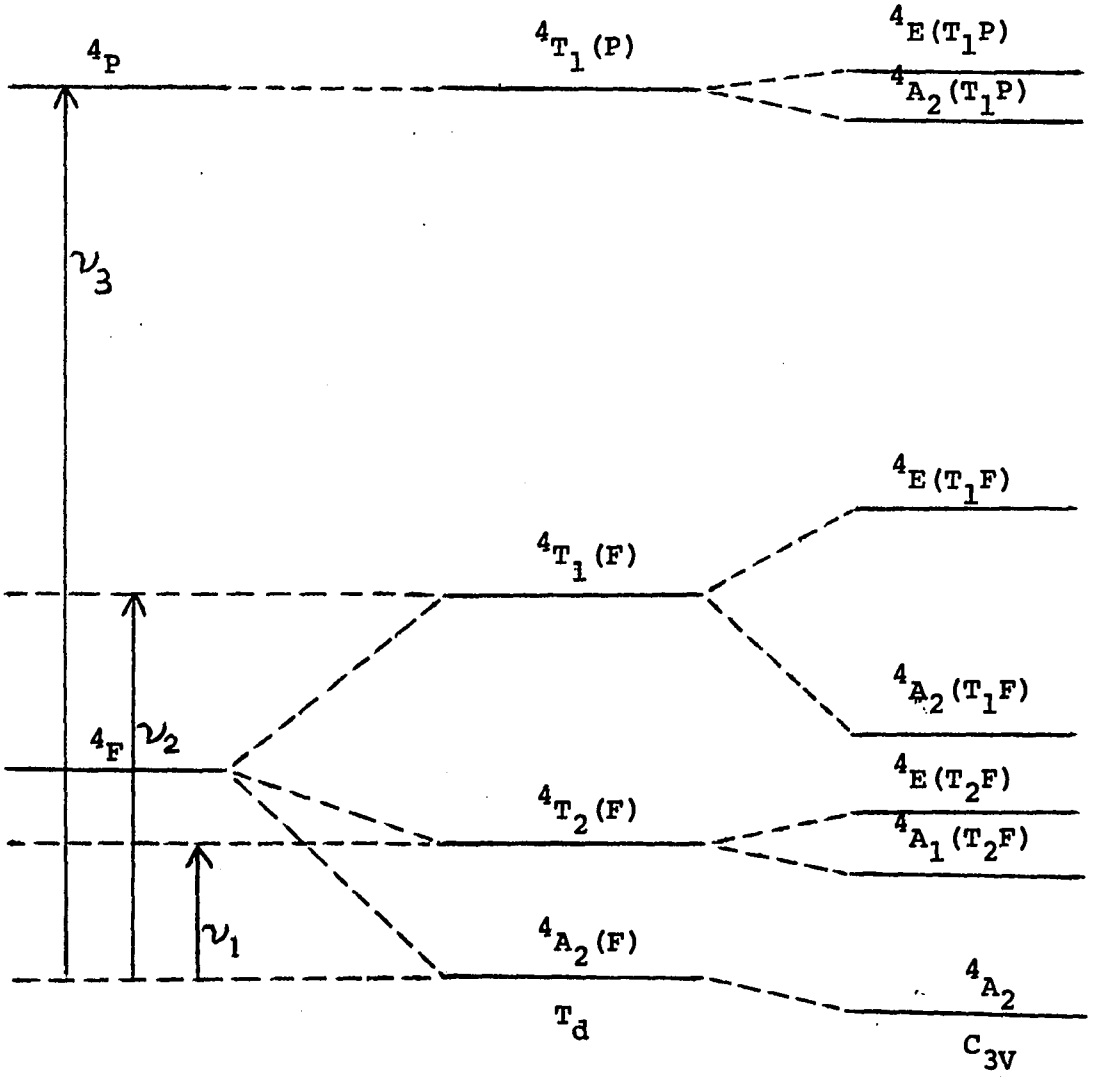
TABLE XV

Absorption Maxima for C_{3V} Complexes of Co(II) and Ni(II) Containing a Pyridine ligand.

Complex	Absorption Maxima (cm^{-1})
$[CoP^+pyrBr_3^-]$	4,720 (w) 7,520 14,700 15,300 (sh) 16,100 (sh)
$[CoP^+picBr_3^-]$	4,720 (w) 7,400 14,550 15,200 (sh) 16,200 (sh)
$(Et_4N^+)[CopyrBr_3]^-$	4,720 (w) 7,250 14,600 15,300 (sh) 16,200 (sh)
$[NiP^+pyrBr_3^-]$	8,850 (w) 15,500
$[NiP^+picBr_3^-]$	8,770 (w) 15,400

Figure VII shows a term diagram for a d^7 metal ion in a field of C_{3V} symmetry.

FIGURE VII



In a tetrahedral d^7 ion there are three spin allowed transitions: $^4T_2(F) \leftarrow {}^4A_2$ (ν_1), $^4T_1(F) \leftarrow {}^4A_2$ (ν_2), and $^4T_1(P) \leftarrow {}^4A_2$ (ν_3). The first transition in CoL_4 derivatives is electronically forbidden and would be expected to be extremely weak.[34] In complexes of lower symmetry this transition does become allowed but appears in the infrared region of the spectrum and becomes obscured by vibrational transitions. In the complexes under consideration ν_1 is not observed. The lowest energy peak, at around 4700 cm^{-1}, is assigned to a transition from the ground state to the $^4A_2$ state in C_{3V} symmetry. (The group theoretical term T_1 in T_d symmetry splits into E and A_2 in C_{3V}.) This peak is weak and at first difficult to observe. Only under amplification of ten times the normal absorbance was it seen. The band in the 7,000 cm^{-1} region is assigned to the transition ^4E $(T_1F) \leftarrow {}^4A_2$ in C_{3V} symmetry. This peak is broader and shows a greater absorbance than the lower energy peak. In order for the center of gravity to be maintained, in moving from a tetrahedral to a pseudotetrahedral environment, it is assumed that an average value for ν_2 (Figure VII) is arrived at by summing 2/3 of the $^4E \leftarrow {}^4A_2$ transition energy and 1/3 of the $^4A_2(T_1F) \leftarrow {}^4A_2$ transition energy. Under this assumption the values for ν_2 are:

6590 cm^{-1} for $\left[CoP^{+}pyr\ Br_3^{-}\right]$; 6500 cm^{-1} for $\left[CoP^{+}picBr_3^{-}\right]$; and 6400 cm^{-1} for $(Et_4N^{+})\ \left[CopyrBr_3\right]^{-}$.

As can be seen from Figure VIII, the ν_3 transition ($^4T_1(P) \longleftarrow {}^4A_2$) results in a multicomponent absorption in the visible region of the spectrum. The shoulder on the high energy side is probably the result of a spin forbidden transition. The value for ν_3 is obtained by measuring the halfwidth of the multicomponent band, excluding the highest energy shoulder.[34] Using this procedure the values for ν_3 are 15,000 cm^{-1} for $\left[CoP^{+}pyrBr_3^{-}\right]$; 14,900 for $\left[CoP^{+}picBr_3^{-}\right]$ and 14,880 for $(Et_4N^{+})\ \left[CopyrBr_3\right]^{-}$. Once the values for ν_2 and ν_3 are obtained, values for the crystal field splitting parameter Dq and the interelectronic repulsion parameter B can be calculated.[35] Using the Td equations:

$$E(\nu_2) = 7.5B + 15Dq - \tfrac{1}{2}(225B^2 + 100Dq^2 - 180\ DqB)^{\frac{1}{2}}$$

$$E(\nu_3) = 7.5B + 15Dq + \tfrac{1}{2}(225B^2 + 100Dq^2 - 180\ DqB)^{\frac{1}{2}}$$

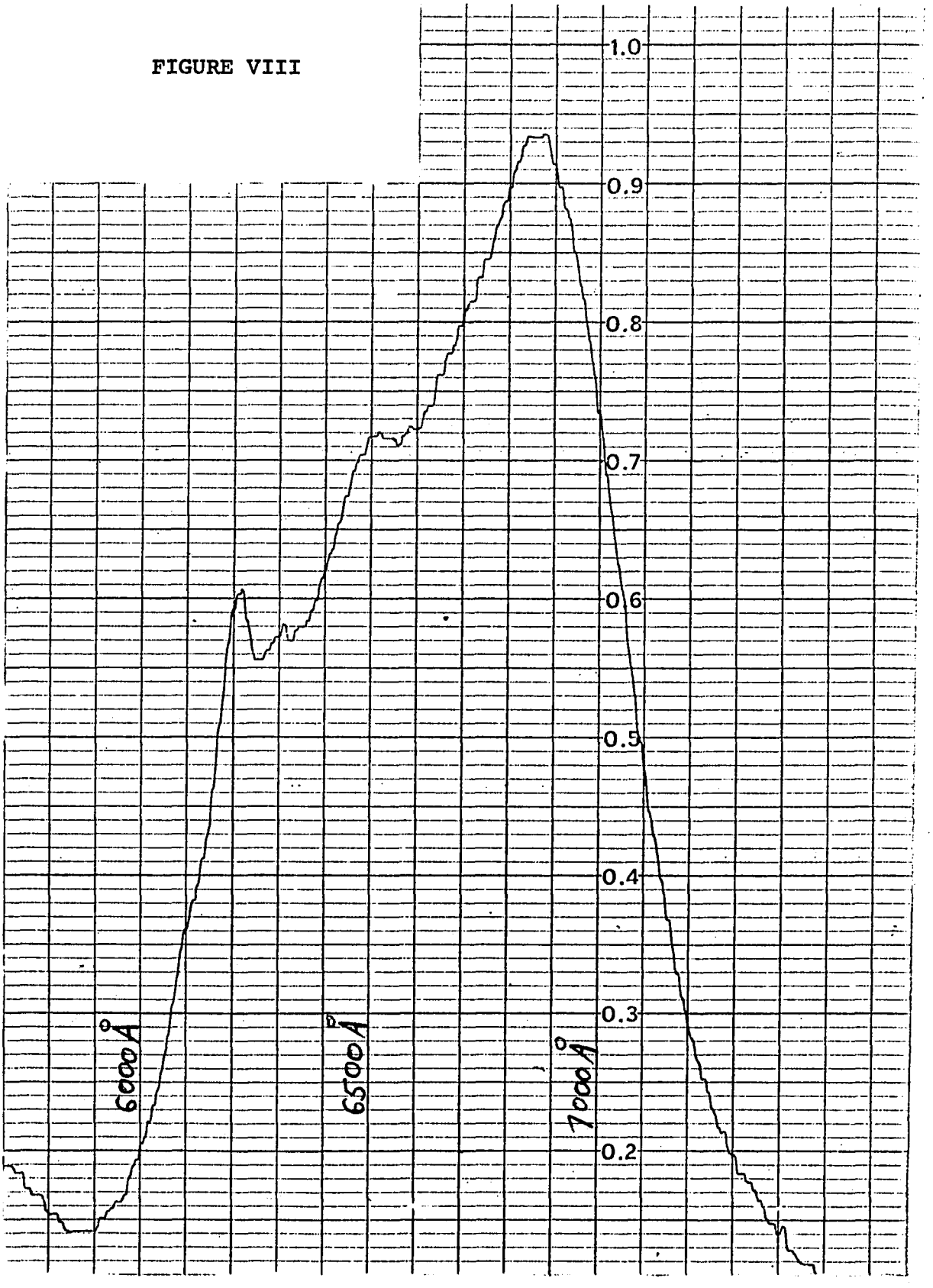
and the appropriate Tanabe-Sugano diagram for the variation of Dq/B with E/B , values for Dq and B are obtained. Table XVI lists these values as well as the value for Δ, the magnitude of the splitting of the ν_2 transition (<u>vide infra</u>).

TABLE XVI

Spectral Parameters for Co(II) Complexes

Complex	Dq($\pm$5 cm^{-1})	B($\pm$2 cm^{-1})	Δ($\pm$ 100 cm^{-1})
$[CoP^{+}pyrBr_3^{-}]$	380	672	2800
$[CoP^{+}picBr_3^{-}]$	375	676	2680
$(Et_4N^{+})[CopyrBr_3]^{-}$	370	680	2530
$[Copyr_2Br_2]$[36,37]	445	650	
$[CoBr_4]^{2-}$	285	715	

FIGURE VIII



The values of Dq and B obtained for the mono-pyridyl complexes are between the literature values for the complexes $\left[Copyr_2Br_2\right]$ [36] and $\left[CoBr_4\right]^{2-}$ [37]. This is reasonable on the basis of an average ligand field environment.[38] The complexes thus show an increasing ligand field and an increasing M-L bond covalency (as reflected by lower B values) in the order:

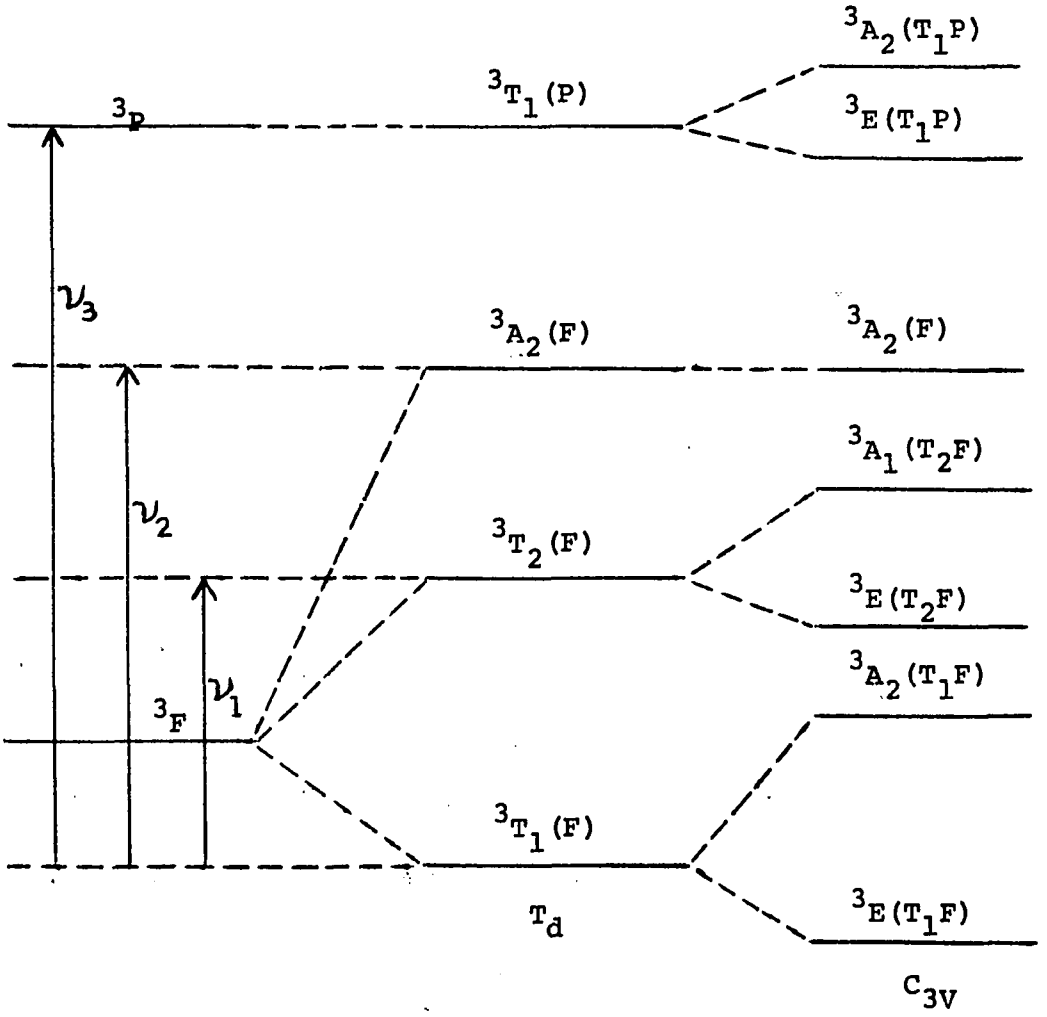
$$\left[CoBr_4\right]^{2-} < \left[CopyrBr_3\right]^{-} < \left[CoP^{+}picBr_3^{-}\right] < \left[CoP^{+}pyrBr_3^{-}\right] < \left[Co\ pyr_2Br_2\right]$$

Another indication of the ligand field strength of the pyridyl ligand in a d^7 complex of C_{3V} symmetry is the splitting of the ν_2 band. As previously mentioned, the T_1 state in T_d symmetry splits into A_2 and E states in C_{3V} symmetry. The extent of this splitting is a function of the difference in ligand field strengths between the two types of ligands present in the complex. Using this criterion, the values for Δ listed in Table XVI again show a ligand field increasing in the order:

$$pyr < P^{+}pic < P^{+}pyr$$

Figure IX is the term diagram for a d^8 complex in C_{3V} symmetry. As in the Co(II) complexes, there are three spin allowed transitions in tetrahedral Ni(II) complexes: $^3T_2 \leftarrow {}^3T_1(F)\,(\nu_1)$; $^3A_2 \leftarrow {}^3T_1(F)\,(\nu_2)$; $^3T_1(P) \leftarrow {}^3T_1(F)\,(\nu_3)$. The low energy transition is usually not isolable but using the

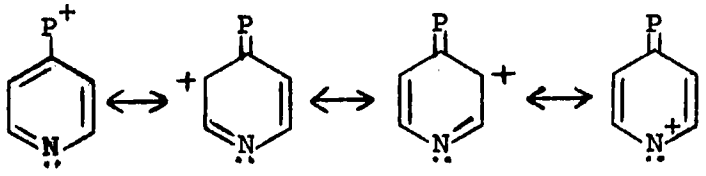
FIGURE IX


$^3A_2(T_1P)$
$^3T_1(P)$
^3P
$^3E(T_1P)$
ν_3
$^3A_2(F)$
$^3A_2(F)$
$^3A_1(T_2F)$
ν_2
$^3T_2(F)$
$^3E(T_2F)$
$^3A_2(T_1F)$
^3F
ν_1
$^3T_1(F)$
T_d
$^3E(T_1F)$
C_{3V}

equations for $E(\nu_2)$ and $E(\nu_3)$ and the proper Tanabe-Sugano diagram, Dq and B can be calculated. Upon lowering the symmetry from T_d to C_{3V}, the $^3T_1(F)$ ground state is split into $^3A_2$ and ^3E states. This lowering of the ground state, the extent of which is dependent upon the field strength of the odd ligand, renders direct calculation of the crystal field and Racah parameters unfeasible. However, the absorption energies in the near infrared region of the spectrum (see Table XV) do show that the cationic pyridyl ligand produces larger transition energies and therefore a somewhat larger field than the cationic picolyl ligand. This is consistent with the results of the study of the cobalt complexes.

The results of spectral measurements can be explained in terms of an increase in π backbonding from the metal to the ring in complexes of the cationic pyridines. As shown in Figure X, the positive charge on phosphorus can be delocalized into the π orbitals of the pyridine ring.

FIGURE X



Such resonance formulations are not possible in the picoline ligand because the positive charge on the phosphorus atom is insulated from the ring by a CH_2 group. Thus the cationic pyridine becomes a better π- acceptor than either the unsubstituted pyridine or the cationic picoline.

The resulting increased field strength can be explained with the aid of a molecular orbital diagram. Figure XI is the M. O. diagram for a tetrahedral complex with ligands that contain filled π bonding orbitals and empty π^* orbitals which can act as π acceptors. Assuming that the e orbitals are affected to a greater extent than the t_2 orbitals by $M \rightarrow L$ π bonding in tetrahedral systems (the t_2 orbitals are used in σ bonding), an increase in the acceptor nature of the pyridine π^* orbitals tends to increase the energy difference between the e and t_2 levels, leading to a larger resultant field. Experimental evidence for the increased acceptor ability or stabilization of the π^* orbitals in P^+pyr, as compared to P^+pic and the unsubstituted pyridine, is shown by examining the ultraviolet region of the spectra.

Three types of charge transfer transitions are seen in the UV. These are in order of increasing energy: $M(d) \rightarrow L(\pi^*)$, $L(\pi) \rightarrow M(d\pi)$, and $L(\pi) \rightarrow L(\pi^*)$. Figure XII shows the ultraviolet spectra of the three complexes under

FIGURE XI

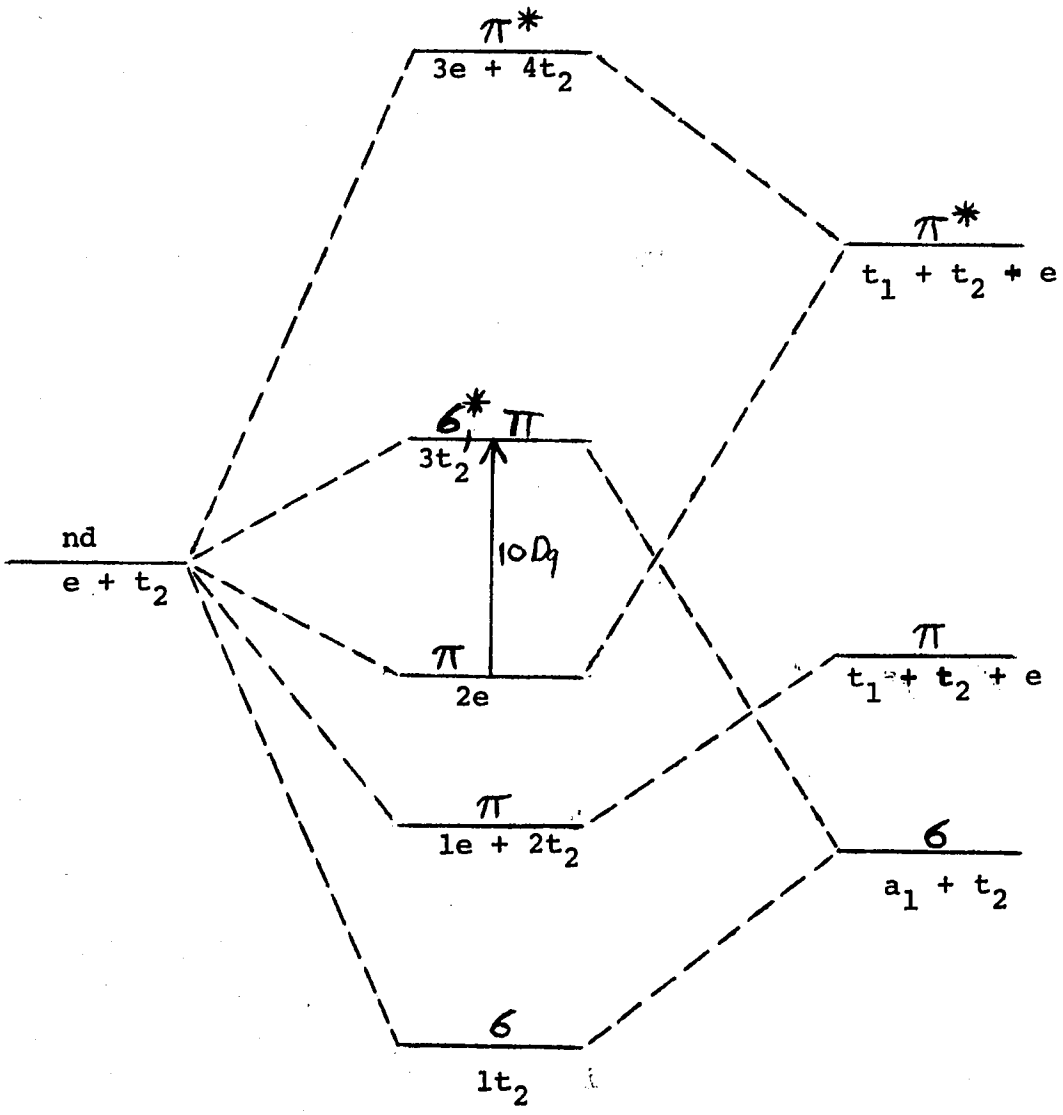
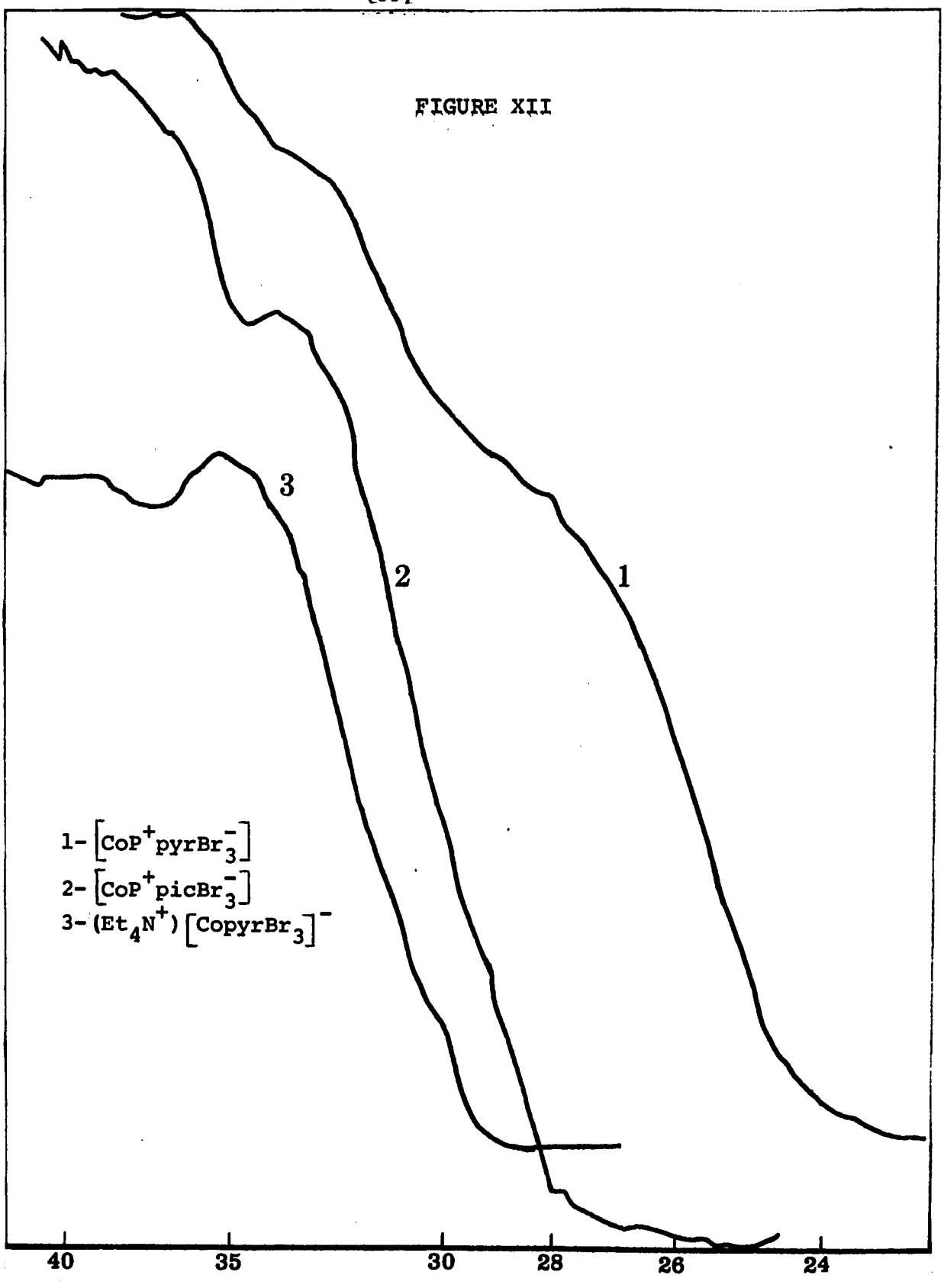

π*
3e + 4t2
π*
t1 + t2 + e
6*
3t2
π
10Dq
nd
e + t2
π
2e
π
t1 + t2 + e
π
1e + 2t2
6
a1 + t2
6
1t2

FIGURE XII


3
2
1
1- [CoP+pyrBr3-]
2- [CoP+picBr3-]
3- (Et4N+) [CopyrBr3]-
40
35
30
28
26
24
FREQUENCY, cm−1 x 10−3

consideration. It is seen that the complex containing the cationic pyridine has a shoulder at approximately 28,000 cm^{-1}. The complexes containing the cationic picoline and the unsubstituted pyridine do not absorb at all until a significantly higher energy. This shoulder in the spectrum of the cationic pyridine complex must be due to an electron transfer from the d orbitals on the cobalt to the π^* antibonding orbitals on pyridine. The ring antibonding orbitals in the other pyridines would be at higher energies, so that the M(d)→π (ring) transition would be at a higher energy and obscured by the L→M charge transfer transition.

Further proof of the assignment of this shoulder is seen in the solution spectra. In an approximately 10^{-4} M acetonitrile solution of $\left[Co^{+}pyrBr_3^{-}\right]$, the shoulder disappears, and both the substituted pyridine and picoline complexes have a single absorption peak at 33,000 cm^{-1}.

Conductance measurements indicate solvolysis is occuring in acetonitrile solutions of both complexes.

$$\left[CoBr_3^{-}L^{+}\right] + CH_3CN \rightleftharpoons \left[CoBr_3CH_3CN\right]^{-} \ (L^{+})$$

The peak at 33,000 cm^{-1} is therefore assigned to a transfer of an electron from a Br pπ orbital to the cobalt d(t_2) ($2t_2 \rightarrow 3t_2$ on Figure XI) orbitals. The shoulder which appears in the solid state but disappears in solution must then be

assigned to the M(d)$\rightarrow\pi^*$(ring)($3t_2\rightarrow 4t_2$) transfer. Absorbances at higher energies are probably due to intraligand $\pi\rightarrow\pi^*$ ($2t_2\rightarrow 4t_2$) transitions.

CONCLUSIONS

This is the first report of transition metal complexes with cationic ligands in which the positive charge on the ligand is transmitted to the donor atom *via* the π system of an aromatic (heterocyclic) ring. It was shown that while the sigma donor ability of nitrogen in phosphonium substituted pyridine ligands may be reduced, backbonding from the metal d-orbitals into the π system of the ring is enhanced. The net effect is an increased ligand field produced by the ligand in which the positive charge is directly conjugated to the ring system. Spectral, magnetic and conductance measurements confirmed the pseudotetrahedral (C_{3V}) symmetry of the complexes under consideration.

EXPERIMENTAL

Proton NMR spectra were obtained on a Varian A-60 spectrometer, Resonances are stated in parts per million downfield from tetramethylsilane used as an internal standard. Melting points were obtained with a Thomas-Hoover capillary apparatus. All reactions involving organophosphines were carried out under an atmosphere of argon or prepurified nitrogen. Dry ether was obtained by distillation over $LiAlH_4$. n.Butyllithium was prepared as in Part I. Methyllithium was prepared from methyl iodide and lithium wire. 4-Bromopyridine was obtained by adding aqueous KOH to a chilled solution of 4-bromopyridine hydrochloride, and extracting the product with ether.

The ether solution was then dried and the 4-bromopyridine could be obtained in suitable form by removing the ether under vacuum just before use. 4-Bromomethylpyridine was obtained from its hydrobromide in a similar manner. The preparation of 4-(bromomethylpyridine) hydrobromide from 4-pyridylcarbinol is described below. All compounds that are reported for the first time were analyzed by Galbraith Laboratories.

Preparation of Diphenyl-4-pyridylphosphine.

To 55 ml of a 1.00 M solution of n-butyllithium (0.055 mole) in dry ether at -78° was added dropwise 7.2 g of 4-bromopyridine (0.0455 mole) in 40 ml of ether. The resulting suspension of 4-pyridyllithium was stirred for 10-15 minutes at -78° and 11.0 g of chlorodiphenylphosphine (0.0495 mole) in 50 ml of ether was then added. The reaction mixture was allowed to warm to room temperature, refluxed for 1 hour, and was then poured into 15 ml of NH_3 mixed with 50 g of ice. The organic layer was separated, washed twice with water, and dried over Na_2SO_4. After the ether was removed under vacuum, the residual material was distilled without a column, and the material which distilled at 150-190° (0.2 mm) was collected. It solidified upon cooling, and the solid thus obtained was washed with a small amount of hexane and crystallized twice from hexane (under a nitrogen atmosphere), and dried in vacuo over P_2O_5 to give 9.5 g (75%) of diphenyl-4-pyridylphosphine, mp 69-70°

NMR ($CDCl_3$): δ 8.30-8.50 (m, 2, pyridyl H_α), 7.17-7.55 (m, 10, C_6H_5), 6.88-7.17 (m, 2, pyridyl H_β).

Anal. Calculated for $C_{17}H_{14}PN$: C, 77.56; H, 5.36.

Found: C, 77.44; H, 5.54.

Preparation of Methyldiphenyl-4-pyridylphosphonium Iodide. To a solution of 1.20 g of diphenyl-4-pyridylphosphine (4.6 mmole) in ether was added 1.2 ml of aqueous HI (6.6 mmole). A yellow precipitate, 4-diphenylphosphinopyridinium iodide, formed immediately. Most of the liquid phase was removed by decanting, and the remaining liquid was removed under vacuum. The yellow solid material was then suspended in 30 ml of methyl iodide and stirred overnight. An orange oil formed, indicative of reaction occurring. The excess methyl iodide was removed under vacuum and the residue was dissolved in water. Upon addition of ammonia (10-15 drops) to the solution, a white solid slowly precipitated. It was filtered , dried, and recrystallized from acetone to give 1.40 g (70%) of methyldiphenyl-4-pyridylphosphonium iodide, mp 220-221°.

NMR ($CDCl_3$): δ 8.84-9.11 (m, 2, pyridyl H_α), 7.57-8.15 (m, 12, C_6H_5 and pyridyl H_β), 3.34 (d, J_{HP} = 13 Hz, 3, CH_3).

Anal. Calculated for $C_{18}H_{17}PNI$: C, 53.35; H, 4.23 I, 31.32.

Found: C, 53.05; H, 4.37; I, 31.28.

Preparation of Methyldiphenylphosphine. To 100 ml of a 1.1M solution of methyllithium (0.110 moles) in dry ether was added dropwise 22 g of chlorodiphenylphosphine (0.100 mole) in 100 ml of ether. Refluxing occurred from the heat of reaction. The solution was then stirred for 2 hours. Water was added and the organic layer was separated, washed twice with water, and dried. The ether was removed under vacuum and fractional distillation of the residue gave 11 g (52%) of methyldiphenylphosphine, bp 130°/2 mm. (Reported bp, 110°/0.15mm)[39].

Preparation of Methyldiphenyl-4-pyridylphosphonium Bromide.

A) To a solution of 0.53 g of diphenyl-4-pyridylphosphine (2.0 mmole) in ether was added 0.50 g of an aqueous solution of HBr (2.9 mmole). The resulting precipitate was dissolved in ca.60 ml of methyl bromide and the solution was stirred for 3 days in a pressure bottle. During this time the adduct precipitated from the solution. The methyl bromide was allowed to evaporate, and the residue was dissolved in water and treated with ammonia. The solution was then saturated with Na_2SO_4 and the product was extracted into chloroform. The chloroform was removed under vacuum and the white residue was crystallized from ethanol-ether

and recrystallized from acetone to give 0.46 g (64%) of methyldiphenyl-4-pyridylphosphonium bromide, mp 269-270°.

NMR. ($CDCl_3$): δ 8.83-9.16 (m, 2, pyridyl H_α), 7.60-8.26 (m, 12, C_6H_5 and pyridyl H_β), 3.47 (d, J_{HP} =14 Hz, 3, CH_3).

Anal. Calculated for $C_{18}H_{17}PNBr$: C, 60.35; H, 4.78; Br; 22.31.

Found: C, 60.17; H, 4.94; Br, 22.20.

B) A mixture of 4.8 g of methyldiphenylphosphine (0.024 mole) and 3.8 g of 4-bromopyridine was stirred overnight at 40°. A deeply colored purple solid was formed. The unreacted starting materials were then dissolved in acetone and the undissolved residue was crystallized from ethanol-ether to give 3.0 g of crude product. The infrared spectrum of the purple solid indicated the presence of the phosphonium bromide. Attempts to clear up the purple color through recrystallization and through charcoal applications failed. A 1.7 g sample of the material was put on a column of 90 g of alumina (basic, activity I) and the product was eluted with 1 liter or chloroform. The purple color remained on the column. The chloroform was removed under vacuum and the residue was crystallized from acetone to give 0.40 g of methyldiphenyl-4-pyridylphosphonium bromide, mp 269-270°. The IR spectrum was identical to that of the product of preparation A.

Preparation of 4-Bromomethylpyridine hydrobromide. To 125 ml of ice cooled acetic anhydride was added 30 ml of 48% HBr. 4-pyridylcarbinol (3 g, 0.027 mole) was then added and the solution refluxed at 100° for several hours. Acetic acid and excess hydrobromic acid were removed under vacuum. The yellow-white residue was triturated with ethyl acetate and filtered. The white solid was recrystallized from ethanol-ether to give 4.0 g (57%) of 4-bromomethylpyridine hydrobromide, mp 188-190°. (Reported mp 187°).[30]

Preparation of Methyldiphenyl-4-picolylphosphonium Bromide. Methyldiphenylphosphine (1.5 g, 7.2 mmole) was added to 1.1 g of 4-bromomethylpyridine (6.5 mmole) dissolved in 40 ml of ether. As the ether was being removed under vacuum, an orange-white semi-solid material started to form. The reaction vessel became warm to the touch from the heat of reaction. When it cooled to room temperature acetone was added to dissolve any unreacted phosphine. The undissolved residue was crystallized from methanol-ether to give 0.6 g of orange product. This material was put on a column of 30 g of alumina (basic, activity I) and the product was eluted with 200 ml of a chloroform/methanol (95/5) solution. The solvent was removed under vacuum and the residue was crystallized from acetone and recrystallized from ethanol-ether to

give 0.5 g (20%) of methyldiphenyl-4-picolylphosphonium bromide, mp 224-225°.

NMR (D_2O): δ 8.60-8.30 (m,2, pyridyl, H_α), 7.90-7.50 (m,10, C_6H_5), 7.20-6.80 (m, 2. H_β), 4.85-4.15 (m, 2, CH_2), 2.50 (d, J_{HP} = 13 Hz, 3, CH_3)

(Chemical shifts are reported downfield from sodium 2,2-dimethyl-2-silacyclopentane-5-sulfonate as internal standard.)

Anal. Calculated for $C_{19}H_{19}PNBr$: C, 61.31; H, 5.14, Br; 21.41. Found: C, 61.06; H, 5.11; Br, 21.47.

Preparation of the Complexes. The complexes were prepared by adding an ethanol solution of the anhydrous metal bromide to an ethanol solution containing an equimolar amount of the cationic ligand. The solution was refluxed for a few minutes and the complex precipitated. It was filtered, washed with hot ethanol, and dried in vacuo over P_2O_5. Anhydrous conditions were maintained during the preparation. Ethanol was dried over molecular sieves before being used as a solvent.

A). Cobalt bromide (100 mg) in a 2 ml of ethanol was added to 150 mg of diphenylmethyl-4-pyridylphosphonium bromide in 1 ml of ethanol to give 180 mg (74%) of $[CoP^+pyr\ Br_3^-]$.

Anal. Calculated for $C_{18}H_{17}PNCoBr_3$: C, 37.47, H, 2.97; Br, 41.55.

Found: C, 37.47; H, 3.10 Br; 41.42

B). Nickel bromide (100 mg) in 4 ml of ethanol was added to 150 mg of diphenylmethyl-4-pyridylphosphonium bromide in 3 ml of ethanol to give 150 mg (62%) of $[NiP^+pyr\ Br_3^-]$.

Anal. Calculated for $C_{18}H_{17}PNNiBr_3$: C, 37.49, H, 2.97 Br, 41.56.

Found: C, 37.30; H, 3.06; Br, 41.50.

C). Cobalt bromide (100 mg) in 2 ml of ethanol was added to 150 mg of diphenylmethyl-4-picolylphosphonium bromide in 5 ml of ethanol to give 240 mg (96%) of $[CoP^+picBr_3^-]$.

Anal. Calculated for $C_{19}H_{19}PNCoBr_3$: C, 38.61; H, 3.24; Br, 40.56.

Found: C, 38.41; H, 3.20; Br, 39.70.

D). Diphenylmethyl-4-picolylphosphonium bromide (150 mg dissolved in 5 ml of ethanol) was added to 200 mg of $NiBr_2$ in 10 ml of ethanol to give 200 mg (84%) of $[NiP^+pic\ Br_3^-]$.

Anal. Calculated for $C_{19}H_{19}PNNiBr_3$: C, 38.63; H, 3.24;

Br, 40.56.

Found: C, 38.45; H, 3.37; Br, 39.92.

E). $CoBr_2$ (1.10 gm in 5 ml of ethanol) was added to a solution of 1.00 g of tetraethylammonium bromide in 0.40 g of pyridine to give 2.00 g of $(Et_4N^+)[CopyrBr_3]^-$.[40]

mp, 138-139°.

Anal. Calculated for $C_{13}H_{25}N_2CoBr_3$: C, 30.74; H, 4.96;

Found: C, 30.66; H, 4.93.

Spectral Measurements. All spectra were taken on Nujol mulls spread on filter paper. The filter paper was mounted on a wooden block shaped to fit the dimensions of the sample chamber of a Cary Model 14 recording spectrophotometer. The samples were always referenced with Nujol on filter paper. The spectrophotometer was equipped with a 0-0.1 absorbance unit slide wire, which was used to detect peaks of very low intensity.

The spectral parameters Dq and B were calculated by assigning values for ν_2 and ν_3 as previously discussed. The assignments were made to within $\pm$ 50 cm^{-1}. The equations for the transition energies for a d^7 ion [35] in tetrahedral symmetry lead to the relationships:

1) $$\frac{E(\nu_2)}{E(\nu_3)} = \frac{7.5 + 15Dq/B - \frac{1}{2}(225 + 100(Dq/B)^2 - 180Dq/B)^{\frac{1}{2}}}{7.5 + 15Dq/B + \frac{1}{2}(225 + 100(Dq/B)^2 - 180Dq/B)^{\frac{1}{2}}}$$

2) $$\frac{E(\nu_2)}{B} = 7.5 + 15Dq/B - \tfrac{1}{2}(225 + 100(Dq/B)^2 - 180Dq/B)^{\frac{1}{2}}$$

3) $$\frac{E(\nu_3)}{B} = 7.5 + 15Dq/B + \tfrac{1}{2}(225 + 100(Dq/B)^2 - 180Dq/B)^{\frac{1}{2}}$$

The following sample calculation illustrates how values for Dq and B are determined. For the complex $\left[CoP^{+}pyr\ Br_3^{-}\right]$

ν_2 was found to be 6590 cm^{-1} and ν_3 was found to be 15000 cm^{-1} so that ν_2/ν_3 equals 0.439. Using the Tanabe-Sugano diagram to find an approximate value of Dq/B and then using a trial and error process with equation 1, Dq/B is found to equal 0.565. $E(\nu_2)/B$ then equals 9.83 and $E(\nu_3)/B$ equals 22.3 so that B equals 672 cm^{-1} and Dq equals 380 cm^{-1}. Using the same procedure at the upper and lower limits of ν_2 and ν_3 showed that B is determinable to $\pm$ 2 cm^{-1} and Dq is determinable to $\pm$ 5 cm^{-1}.

Magnetic Susceptibility Measurements.

Values for the magnetic susceptibility were determined with a Faraday balance. The sample bucket was weighed in the presence and absence of the magnetic field to give a change in weight δ. The powdered sample was introduced into the bucket and weighed with the field on and off. This procedure was repeated at least three times to get an average change in weight value Δ, precise to within $\pm$ 0.02 mg. The magnetic susceptibility is calculated from the formula:

$$\chi = \frac{\beta(\Delta-\delta)}{m}$$

Where m is the mass of the sample with the field off, and β is the calibration constant of the apparatus obtained

(with $HgCo(SCN)_4$ as a reference) from the formula:

$$\beta = \chi_{ref} \frac{m_{ref}}{(\Delta_{ref} - \delta)}$$

$\chi_{ref} = 16.44 \times 10^{-6}$ cgs units

$m_{ref} = 68.28$ mg

$(\Delta_{ref} - \delta) = 3.60$ mg

β then equals 312×10^{-6} cgs units.

Table XVII lists the experimental data and the calculated values for χ, χ'_m the molar magnetic susceptibility corrected for diamagnetic contributions of the ligands (obtained from Pascal Tables),[41] and μ, the magnetic moment calculated to within ± 0.04 Bohr magnetons.

TABLE XVII

Magnetic Data for the Complexes

Complex	$\Delta - \delta$	m	$\chi \times 10^6$	$\chi'_m \times 10^3$	μ
$CoP^+pyrBr_3^-$	0.63	12.56	15.7	9.28	4.7
$NiP^+pyr\ Br_3^-$	0.66	20.30	10.1	6.07	3.8
$CoP^+pyrBr_3^-$	1.27	26.30	15.1	9.19	4.70
$NiP^+picBr_3^-$	1.11	38.50	9.20	5.75	3.70

Conductance Measurements. Values for the molar conductances of the complexes were determined with a conductivity cell and a resistance bridge. The cell constant was determined by measuring the resistance, r, of a 0.20N KCl solution as calibrant. The cell constant is calculated using the formula:

$$k' = kr$$

where k equals 2.77×10^{-3} ohm^{-1} cm^{-1}, the known conductivity of the KCl solution, and r equals 0.38×10^{3} ohm, the measured resistance of the solution. The cell constant, k', then equals 1.05.

The resistance values of approximately 10^{-3} M solution in acetonitrile or nitromethane were measured and the molar conductances of the complexes were determined from the formula:

$$\Lambda_M = 1000\ k'/rM$$

Table XIX lists the experimental data and the calculated values of Λ_M.

TABLE XIX

Conductance Data for the Complexes

Complex	Molarity (Solvent)	Resistance (ohm)	Λ_M (ohm^{-1}cm^{2}mol^{-1})
(Et_4N^+) $CopyrBr_3^-$	0.85×10^{-3} (CH_3NO_2)	16.4×10^3	75.5
	1.62×10^{-3} (CH_3CN)	6.85×10^3	95.5
$CoP^+pyrBr_3^-$	0.31×10^{-3} (CH_3CN)	40.0×10^3	84
$CoP^+picBr_3^-$	1.05×10^{-3} (CH_3NO_2)	42.0×10^3	23.8
	0.63×10^{-3} (CH_3CN)	25.7×10^3	65.5
$NiP^+pyrBr_3^-$	0.94×10^{-3} (CH_3NO_2)	20.0×10^3	56
$NiP^+picBr_3^-$	0.36×10^{-3} (CH_3NO_2)	52×10^3	57

BIBLIOGRAPHY

1) L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York 1945 p64.

2) J. Chatt and A.A. Williams, J. Chem. Soc., 4403 (1954)

3) D.G. Anderson, J.R. Chipperfield, and D.E. Webster, J. Organometal. Chem, 12, 323 (1968

4) J. A. Bedford, J. R. Bolton, A. Carrington, and R. Prince, Trans. Faraday Soc. , 59, 323 (1963)

5) C.J. Attridge, Organometal Chem. Rev., Sect. A, 5, 323 (1970)

6) J. M. Wilson, A.G. Briggs, J.E. Sawbridge, P. Tickle, and J.J. Zuckerman, J. Chem. Soc. A, 1024 (1970

7) H.H.Jaffe and G.O.Doak, J. Amer. Chem. Soc., 77 4441 (1955)

8) D.W.Herlocker, R.S.Drago, and V.I. Meek, Inorg. Chem., 5, 2009 (1966)

9) H. Shindo, Chem. Pharm. Bull., 7, 791 (1959)

10) M.A. Weiner, J. Organometal. Chem., 23, C20 (1970)

11) E. Ochiai, Aromatic Amine Oxides, Elsevier, Amsterdam, 1967, p121

12) D.P. Eyeman and R.S. Drago, J. Amer. Chem. Soc., 88 1617 (1966)

13) E. Ochiai, J. Org. Chem., 18, 534 (1953

14) H.Gilman, J.A. Beel, C.G. Brannen, M.W. Bullock, G.E. Dunn, L.S. Miller, J.Chem. Soc., 1499 (1949)

15) Y. Sukata, K. Adachi, Y. Akahori, E. Hyashi, Yakugaku Zasshi, 87, 1374 (1967), Chem. Abstr., 68, 5969a (1968)

16) J.M. Essery and K. Schofield, J. Chem. Soc., 4953 (1960)

17) H.D.K. Drew, J. Chem. Soc., 2328 (1932)

18) B. Moore and G. Wilkinson, Proc. Chem. Soc., 61 (1959)

19) K. Price, Ph.D. Thesis, University of London, (1971)

20) P. DeMeester and A.C. Skapski, J. Chem. Soc, Dalton Trans, 1973 (424)

21) J. Villa, Inorg. Chem., 12, (1973)

22) J.V. Quagliano, J.T. Summers, S. Kida, and L.M. Vallarino, Inorg. Chem., 3, 1551 (1964)

23) V.L. Goedken, L.M. Vallarino, and J.V. Quagliano, Inorg. Chem., 10, 2682 (1971)

24) C. Ercolini, J.V. Quagliano, and L.M. Vallarino. Inorg. Chim. Acta., 3, 421 (1969)

25) J.V. Quagliano, A.K. Banaijee, V.L. Goedkin, and L.M. Vallarino, J. Amer. Chem. Soc., 92, 482 (1970)

26) D. Berglund and D.W. Meek, Inorg. Chem., 8, 2602 (1969)

27) R.A. Koloday, T.L. Morris, and R.C. Taylor, J. Chem. Soc., Dalton Trans., 328 (1973)

28) W.V. Dahloff, T.E. Dick, and S.M. Nelson, J. Chem. Soc. A, 2919 (1969)

29) R.N. Marvich and J. Yoke, Inorg. Chem., 12, 472 (1973)

30) F. Sorm and L. Sediuy, Coll. Czecki Chem. Comm., 13, 289 (1948)

31) R. Carlin, Transition Metal Chemistry, 1, 1 (1965)

32) R.A. Cotton, O.D. Faut, and D.M.L. Goodgame, J. Amer. Chem. Soc., 83, 344 (1961)

33) D.M.L. Goodgame and M. Goodgame, Inorg. Chem., 4, 139 (1965)

34) A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968, chapter 9

35) Ibid., Chapter 7.

36) A.B.P. Lever and S.M. Nelson, J. Chem. Soc. A., 859 (1966)

37) F.A. Cotton, D.M.L. Goodgame, and M. Goodgame, J. Amer. Chem. Soc., 83, 4690 (1961)

38) F.A. Cotton, D.M.L. Goodgame, M. Goodgame, and A. Sacco, J. Amer. Chem. Soc., 83, 4161 (1961)

39) D. Seyferth and D.E. Welch, J. Organometal Chem., 2, 1 (1964)

40) D.H. Brown, K.P. Forrest, R.H. Nuttall, and D.W.A. Sharp, J. Chem. Soc. A., 2146 (1968)

41) See for example, B.N. Figgis and J. Lewis in Techniques of Inorganic Chemistry, H. Jongssen and A. Weissberger

41) (cont.) (Ed.), Vol IV, Interscience, New York, 1965