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A STUDY OF DIBORANE DIHYDRATE AND X-RAY PHOTOELECTRON
SPECTROSCOPY OF INORGANIC COMPOUNDS

Patricia Ann Finn
(Ph. D. thesis)

November 1971

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Table of Contents

Abstract	v
Part I. A Study of Diborane Dihydrate	1
I. Introduction	2
II. Experimental	3
III. Results and Discussion	8
IV. References	18
Part II. X-ray Photoelectron Spectroscopy of Inorganic Compounds .	23
I. Paper: Chemical Shifts in Core Electron Binding Energies for Some Gaseous Nitrogen Compounds	24
A. Abstract	24
B. Introduction	24
C. Experimental Section	26
D. Results and Discussion	27
E. Conclusions	33
F. References	35
G. Appendix	42
II. Paper: Chemical Shifts in Boron 1s Binding Energies of Some Gaseous Compounds	43
A. Abstract	43
B. Introduction	44
C. Experimental	44
D. Results and Discussion	45
E. References	51

III. Paper: The Nitrogen 1s Binding Energies of Transition	
Metal Nitrosyls	55
A. Introduction	55
B. Experimental	55
C. Results and Discussion	56
D. References	62
IV. Paper: Nitrogen 1s Binding Energies of Some Azide,	
Dinitrogen and Nitride Complexes of Transition	
Metals	65
A. Introduction	65
B. Experimental	65
C. Results	66
D. References	70
Acknowledgements	72

A Study of Diborane Dihydrate and X-ray Photoelectron Spectroscopy
of Inorganic Compounds

Patricia Ann Finn

ABSTRACT

The dihydrate and diethanolate of diborane have been prepared at -130° and their compositions have been established by stoichiometric measurements. The dihydrate is assigned the structure $\text{BH}_2(\text{H}_2\text{O})_2^+\text{BH}_4^-$ on the basis of low-temperature infrared spectra of the deuterated and nondeuterated species. A study of the evolution of hydrogen from the reaction of diborane with a solution of HCl in a water-methanol mixture at -78° has provided further evidence for the asymmetric cleavage of diborane by water and alcohol.

Chemical shifts in core electron binding energies for gaseous nitrogen compounds and gaseous boron compounds are compared to their respective atomic charges estimated by Pauling, CNDO, and extended Hückel methods. The best linear correlation for both sets of compounds is found with the extended Hückel charges. A comparison between the experimental chemical shifts and the shifts estimated by the application of the thermodynamic method (based on the approximation that $\Delta E = 0$ for the interchange of equally-charged atomic cores between two different species) shows better agreement than the atomic charge methods.

The nitrogen 1s core binding energies of a series of transition metal nitrosyls are correlated with their structures, their electronic features, and their N-O stretching frequencies.

The nitrogen is binding energies of azide, dinitrogen and nitride transition metal complexes are interpreted in terms of interaction of the ligands with the metal atoms.

PART I. A STUDY OF DIBORANE DIHYDRATE

ABSTRACT

The dihydrate and diethanolate of diborane have been prepared at -130° and their compositions have been established by stoichiometric measurements. The dihydrate is assigned the structure $\text{BH}_2(\text{H}_2\text{O})_2^+\text{BH}_4^-$ on the basis of low-temperature infrared spectra of the deuterated and nondeuterated species. A study of the evolution of hydrogen from the reaction of diborane with a solution of HCl in a water-methanol mixture at -78° has provided further evidence for the asymmetric cleavage of diborane by water and alcohol.

I. INTRODUCTION

The cleavage of the bridging hydrogen bonds in diborane by a Lewis base, X, can be either symmetric, to give BH_3X , or asymmetric, to give BH_2X_2^+ and BH_4^- . In the reaction of ammonia with diborane, both types of cleavage have been observed.^{1,2} With increasing methyl substitution in the methyl amine series ($(\text{CH}_3)_{3-x}\text{NH}_x$), there is an increasing tendency to produce symmetric cleavage.³⁻⁵ For various ethers, symmetric cleavage of the diborane molecules has been observed.⁶ Young and Shore⁷ have discussed some of the factors which may affect the course of cleavage reactions; it appears that it is not yet possible to predict the course of such reactions with certainty.

In studies of the reaction of diborane with water⁸ and alcohols⁹ at room temperature, no intermediate cleavage products have been isolated because complete hydrolysis occurs rapidly.

Davis and Gottbrath¹⁰ were able to isolate sodium hydroborate from the reaction of diborane with aqueous sodium hydroxide at 0° , and Jolly and Schmitt¹¹ prepared potassium hydroborate by the reaction of diborane with powdered potassium hydroxide at -30° . These results suggest that the reaction occurs by asymmetrical cleavage of diborane and prompted a further study of this type reaction. This paper details the preparation and characterization of the diborane-water reaction product.

II. EXPERIMENTAL

General Information.- Diborane was prepared by the addition of KBH_4 to H_3PO_4 ,¹² and deuteriodiborane was prepared by the addition of BF_3 etherate to LiAlD_4 in diethyl ether.¹³ Helium was used as the carrier gas to collect the deuteriodiborane. The purity of both compounds was verified by vapor pressure measurements¹⁴ and infrared spectroscopy.¹⁵ LiAlD_4 (deuterium content 99%) was obtained from Bio-Rad Laboratories, Richmond, California and deuterium oxide (deuterium content 98.8%) from International Chemical and Nuclear Corp. Chemical and Radioisotope Division, Irvine, California. All other chemicals were of reagent grade. Ideal gas behavior was assumed for vapors and gases when making calculations from PVT data. Small pressures of water, ethanol and methanol were used to ensure the ideality of their vapors.

Stoichiometric Studies.- The glass reaction vessel was 20 cm long with all three connections (one for evacuation) located at the top. Two 1/8" metal tubes, joined to the glass vessel with Swagelock fittings, were freely suspended next to each other with their ends located 1 cm from the base of the vessel. Nupro metering valves were attached to the tubes to control the flow of the gases. The tubes were heated during deposition by heating tape which was wound around the portions above the reaction vessel.

A hundredfold excess of diborane and either water, ethanol, or methanol were cocondensed as an intimate solid mixture by allowing the vapors to separately but simultaneously effuse into the vessel which

was cooled to -196° . The mixtures were then warmed to -130° (-112° for the methanol mixture). When the reaction was judged complete (2-3 hours for water, 1 hour for ethanol, 2-4 hours for methanol), the excess diborane was removed by pumping. A large excess of water was condensed into the vessel and each sample was then warmed to room temperature to effect complete hydrolysis. The amount of diborane which had reacted was calculated by measuring the evolved hydrogen, which had been Toepler-pumped into a gas buret. It was assumed that each mole of diborane consumed in hydrolysis at room temperature produces six moles of hydrogen.¹⁶

The reaction between excess water (280 mmol) and diborane (0.20-0.25 mmol) was studied at -130° to determine the percent of diborane that reacted as a function of time. Within fifteen minutes, 86% had reacted; after two hours, 98% had reacted.

Acid Hydrolysis.- Approximately 25 ml of ~ 0.5 M HCl in 88% by volume methanol and 12% by volume water was pipetted into a 70-ml flat-bottomed flask containing a stirring bar. The vessel was cooled to -78° using a Dry Ice-acetone bath and then was evacuated while the solution was stirred and the glass walls were heated. The heating eliminates droplets which cause excessive decomposition. Diborane (0.05-0.10 mmol) was introduced by diffusion into the reaction vessel by momentarily opening a stopcock which connected the vessel with a chamber containing diborane gas at -130° . All unreacted diborane in the entry line was then removed by pumping. The pressure of the evolved hydrogen was measured after 40-90 seconds in a constant volume

system consisting of the reaction vessel and an adjustable manometer. The hydrogen pressures for four different runs were 0.30, 0.43, 0.64 and 0.78 cm. These pressures were corrected for the hydrogen evolved by the hydrolysis of any $\text{BH}_3 \cdot \text{H}_2\text{O}$ species in solution. This was done using the first order rate law $a = a_0 e^{-kt}$ where $k = 2.3 \times 10^{-3} \text{ sec}^{-1}$ at -78° in 0.5 M HCl .¹⁷ The corrected hydrogen pressures (P_{H_0}) were 0.27, 0.39, 0.58 and 0.67 cm, assuming that the diborane reacted immediately as follows, $\text{B}_2\text{H}_6 + 3\text{H}_2\text{O} = \text{BH}_2(\text{H}_2\text{O})_2^+ + \text{BH}_3 \cdot \text{H}_2\text{O} + \text{H}_2$.

After approximately forty minutes, the total pressure of evolved hydrogen was measured. The hydrogen pressures $P_{\text{H}_{2400}}$ were 0.80, 1.11, 1.41, and 1.45 cm, respectively. The reaction vessel was then isolated from the system and warmed to room temperature to complete hydrolysis. The total pressure of evolved hydrogen was measured in the constant volume system after the reaction vessel was cooled to -78° . Typical hydrogen pressures ($P_{\text{H}_{\infty}}$) were 1.71, 2.41, 2.96 and 3.44 cm. Because the external temperature varied less than 1° and because care was taken to keep the level of the -78° bath around the reaction vessel from varying, the hydrogen pressure measurements were used to determine the ratio of moles of hydrogen initially evolved (corrected) to moles of diborane consumed (assumed to be equal to $1/6$ of the total pressure of evolved hydrogen). These ratios were: 0.97, 0.98, 1.18, and 1.18.

Infrared Measurements.- The metal low-temperature infrared-cell¹⁸ used for the experiments consisted of an outer shell with CsI windows perpendicular to the optical axis and an inner part which contained the refrigerant (liquid nitrogen). From the inner part was suspended a copper block in which was mounted the CsBr plate upon which the samples

were codeposited. The inner part could be rotated relative to the outer shell during the course of the experiment, allowing the CsBr plate to be oriented normal either to the gas inlet system or to the optical axis. The spectra were recorded on a Perkin-Elmer 221 spectrophotometer calibrated with polystyrene.

Because a thermocouple was not inserted into the CsBr plate, its temperature was not known accurately. The approximate temperature of the plate was obtained by measuring the vapor pressure (4 cm at -130°)¹⁴ of the excess diborane at various time intervals during warmup after first removing the liquid nitrogen. It takes an hour of warming for reaction to occur ($\sim -140^{\circ}$) and the product remains stable for another hour of warming (~ -100).

Gaseous diborane and water vapor were introduced through Nupro metering valves and cocondensed on the CsBr plate cooled to -196° . For different runs, the deposition rate of diborane was 1-2 mmol/hr and that of water was 3-4 mmol/hr. The deposition time was 60-90 minutes. Longer deposition times produced a thick film on the CsBr plate which stopped light transmittance. The ratios used ($1 \text{ B}_2\text{H}_6 : 2\text{H}_2\text{O}$) are not typical ratios for matrix isolation systems (1:100); they were, however, the only ones which produced useful spectra.

After deposition, an initial spectrum was taken at -196° . The refrigerant was then removed and the infrared cell was allowed to warm in order that the gaseous diborane could react with the porous, reactive water. Spectra of the $3000\text{-}2000 \text{ cm}^{-1}$ region were recorded at 5-10 minute intervals during warmup to follow the reaction. The

-7-

diffused diborane was collected in a -196° trap before each spectrum was run and afterwards returned to the system. Within an hour, the system was warmed to approximately -140° . The unreacted diborane (80-90%) was removed by pumping leaving a final ratio of $B_2H_6 \cdot 2H_2O : 18 H_2O$. The reaction was quenched by the introduction of liquid nitrogen and a spectrum of the $4000-500 \text{ cm}^{-1}$ region was then recorded at -196° . The refrigerant was removed and the infrared cell was allowed to warm gradually. Spectra of the $3000-2000 \text{ cm}^{-1}$ region were again taken at 5-10 minute intervals while continuously pumping. The peaks diminished with increasing temperature; their complete disappearance coincided with the evolution of a large amount of hydrogen. A final spectra was run. Reported frequencies are accurate to $\pm 10 \text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

Stoichiometric Studies.- Because the diborane hydrate and diborane alcoholates decompose when the temperature is high enough to volatilize water, ethanol, or methanol, it was not possible to determine the amount of these reagents that reacted with diborane when they were in excess. Therefore stoichiometric studies were possible only when using excess diborane, which is volatile even at -140° . The results of these studies are summarized in Table I. Diborane was present in at least a hundred-fold excess in most of the experiments.

The diborane hydrate is fairly stable; only 3% decomposition¹⁹ occurred in one hour at -112° . Both alcoholates, however, are very unstable. In one hour at -130° 25% decomposition¹⁹ of the ethanolate occurs. Decomposition is negligible at -160° ; however studies were not conducted at this temperature because excess diborane cannot be removed by pumping. In the case of the diborane methanolate, 50% decomposition¹⁹ occurs in two to four hours at -112° . Studies were not conducted at -130° .

For both diborane-water and the diborane-ethanol reactions, approximately 2:1 molar ratio was found at -130° for $H_2O:B_2H_6$ and $C_2H_5OH:B_2H_6$. The ratio was low, 1.7:1, for the methanol-diborane system. We have no explanation for this low result, except the fact that the system was studied at a relatively high temperature.

Hydrolysis Study.- The stepwise hydrolysis of hydroborate in acidic solution at -78° has been followed kinetically.¹⁷ In the first step, one mole of hydroborate reacts essentially instantaneously to produce $BH_3 \cdot H_2O$ and a mole of hydrogen.

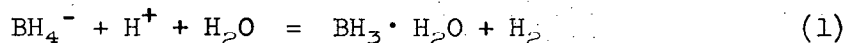
Table I

Stoichiometric Studies of the Reaction of Diborane and
Water, Ethanol or Methanol at -130°

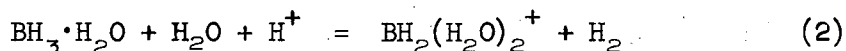
Reactant	mmol	Diborane Introduced mmol	Diborane Consumed ^a mmol	$\frac{\text{mmol H}_2\text{O or ROH}}{\text{mmol B}_2\text{H}_6 \text{ consumed}}$
Water	0.010	3.926	0.0052	1.9
	0.017	4.050	0.0080	2.1
	0.019	3.986	0.0082	2.3
Ethanol	0.055	2.770	0.0243	2.3
	0.069	2.692	0.0307	2.2
	0.027	3.218	0.0143	1.9
	0.032	3.215	0.0150	2.1
	0.023	2.872	0.0123	1.9
	0.026	2.494	0.0150	1.7
Methanol ^b	0.060	2.617	0.035	1.7
	0.100	3.311	0.062	1.6

^a Calculated from the evolved hydrogen upon complete hydrolysis.

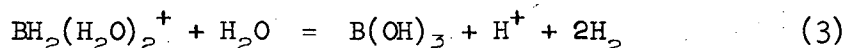
^b The reaction was studied at -112° .



The second step proceeds more slowly (half-time approximately five minutes at -78° in 0.5 M acid) and produces a second mole of hydrogen and $\text{BH}_2(\text{H}_2\text{O})_2^+$.



The species $\text{BH}_2(\text{H}_2\text{O})_2^+$ is relatively stable in acidic solution (the greater the acidity, the more stable), and further hydrolysis occurs only when the temperature is increased or during prolonged standing (three to four hours).



We observed the reaction of diborane with 0.5 M HCl in 88% by volume methanol and 12% by volume water. If $\text{BH}_3 \cdot \text{H}_2\text{O}$ were the initial product, hydrogen evolution would be gradual; in forty minutes (about eight half-times) almost two moles of hydrogen would be produced per mole of diborane. If $\text{BH}_2(\text{H}_2\text{O})_2^+$ and BH_4^- were the initial reaction products, one mole of hydrogen per mole of diborane would be evolved instantaneously (Eq. 1), followed by the evolution of a second mole of hydrogen, essentially complete in thirty minutes (Eq. 2).

We found that one mole of hydrogen was evolved instantaneously, followed by the evolution of a second mole of hydrogen, complete in forty minutes. Therefore the initial reaction products are $\text{BH}_2(\text{H}_2\text{O})_2^+$ and BH_4^- .

Spectra.- Initially at -196° , the spectrum of the diborane-water mixture appears as the superimposed spectra of diborane and water. While warming the mixture, the diborane gradually disappears as the reaction product forms, as seen by the increased intensity of the product peaks and the decreased intensity of the diborane peaks. After the unreacted diborane was removed from the system by pumping and the refrigerant reintroduced, a clean (no unreacted diborane) spectrum of the product was obtained at -196° . When the system was again warmed, this time for a longer period, the compound gradually decomposed. The final spectrum was that of boric acid.²⁰ No other species were observed.

In Figure 1 are presented the initial spectrum of the reactants, the spectrum of diborane dihydrate plus excess water, and the final spectrum of boric acid and water.

Similar spectra were obtained for the deuteriodiborane-deuterium oxide system using the same experimental procedure. The initial spectrum of the reactants, the spectrum of $B_2D_6 \cdot 2D_2O$ plus excess deuterium oxide, and the final spectrum of deuterated boric acid and deuterium oxide are presented in Figure 2.

The two boron-hydrogen stretching frequencies characteristic of BH_3X species are located in the region $2450-2200\text{ cm}^{-1}$.²¹⁻²³ For known $BH_2X_2^+$ salts, a doublet is observed in the region $2600-2400\text{ cm}^{-1}$.²⁴⁻²⁶ corresponding to the boron-hydrogen stretching frequencies. The spectra of lithium, sodium, and potassium hydroborate contain one peak with two shoulders located in the region $2400-2200\text{ cm}^{-1}$.²⁷ For $NaBH_4$ in a Nujol mull, Waddington²⁸ observed splitting of the band at 2300 cm^{-1} .

(2390, 2290 and 2210 cm^{-1}) which he attributed to the failure of BH_4^- to rotate freely in the crystal lattice. Each of the three species BH_3X , BH_2X_2^+ and BH_4^- has a single band assigned to the HBH bending mode located in the 1200-1100 cm^{-1} region. The spectrum of diborane dihydrate has two stretching bands in the 2400-2200 cm^{-1} region and a third near 2700 cm^{-1} . Two deformation bands are located in the 1200-1100 cm^{-1} region. Because our spectra contain different types of boron-hydrogen stretching bands and more than one deformation band, we compared them with the spectra of various hydroborates and of known BH_2X_2^+ compounds.

The major infrared absorption frequencies for the dihydrate of diborane are listed in Table II with their respective assignments. Table III contains the major bands for the deuterated species, with the assignments listed.

The spectrum of hydroborate is sensitive to various solid state effects. Schutte recorded the spectrum of thin films of NaBH_4 at 25° and -182°. ²⁹ He observed four bands (three stretching, one bending deformation) at 25°. These became sharp at -182°: a weak band at 2404 cm^{-1} , a strong band at 2305 cm^{-1} , a strong doublet at 2223 and 2238 cm^{-1} and a strong band at 1123 cm^{-1} . He correlated the observed spectral changes (splitting of the stretching mode) with the phase transition observed in NaBH_4 . Coker and Hofer ³⁰ have observed hydroborate in various solid lattices. They found a lattice-dependent frequency shift. In a CsBr lattice, the observed frequencies are: ν_3 (2340), $\nu_2 + \nu_4$ (2278), $2\nu_4$ (2167), ν_4 (1090). In a KCl lattice,

Table II

Infrared Absorption Frequencies of the Dihydrate of Diborane

cm^{-1}	Intensity	Assignment
3200	v.st.	OH stretch
2750, 2720	st.	BH stretch (BH_2X_2^+)
2420	st.	BH stretch (BH_4^-)
2320	st.	BH stretch (BH_4^-)
1605	m.	OH deformation
1400	st.	BO stretch
1185	st.	BH deformation (BH_4^-)
1155	st.	BH deformation (BH_2X_2^+)

Table III

Infrared Absorption Frequencies of the Deuterated Dihydrate
of Deuteriodiborane

cm^{-1}	Intensity	Assignment
3250	st.	OH stretch
2400	v.st.	OD stretch
1845	st.	BD stretch (BD_2X_2^+)
1745	m.	BD stretch (BD_4^-)
1700	m.	BD stretch (BD_4^-)
1350	v.st.	BO stretch
1085	st.	OD deformation
885	st. shoulder	BD deformation (BD_4^-)
855	st.	BD deformation (BD_4^-)
745	m.	BD deformation (BD_2X_2^+)

the frequencies are: $\nu_2 + \nu_4$ (2425), ν_3 (2321), $2\nu_4$ (2256), ν_4 (1142).

Much of the diborane originally codeposited had diffused from the solid mixture. The excess water present in the form of ice functioned as a solid lattice that acted as a perturbation on the vibrational levels. Comparing our data to Coker and Hofer's we assign three of the frequencies of diborane dihydrate, 2420, 2320 and 1185³¹ cm^{-1} to hydroborate.

Coker and Hofer³⁰ also observed the spectrum of deuterioborate in various solid lattices. In a CsBr lattice, the observed frequencies are: ν_3 (1748), $\nu_2 + \nu_4$ (1694), $2\nu_4$ (1653) and ν_4 (835). In a KCl lattice the frequencies are: $\nu_2 + \nu_4$ (1775), $2\nu_4$ (1739), ν_3 (1696) and ν_4 (863). The deuterated product which we studied has peaks located at 1745, 1700, and 855 cm^{-1} which are assigned to the BD_4^- species.

For BH_2X_2^+ salts, a doublet is observed in the region 2600-2400 cm^{-1} ,²⁴⁻²⁶ which corresponds to the boron-hydrogen stretching frequencies. The deformation frequency is found as an intense band near 1160 cm^{-1} .²⁴⁻²⁶ A doublet was observed for the dihydrate of diborane in the 2700 region and a deformation band is found at 1155 cm^{-1} .³¹ These frequencies are assigned to the $\text{BH}_2(\text{H}_2\text{O})_2^+$ species. The large frequency shift (100 cm^{-1}) for the doublet is possibly due to a coupling between the boron-hydrogen stretching mode and the oxygen-hydrogen stretching mode. Also oxygen atoms have a greater electronegativity than nitrogen atoms. Therefore a B-O bond has more p character and less s character than a B-H bond. A shift to higher frequency is then expected for the B-H bond in

$\text{BH}_2(\text{H}_2\text{O})_2^+$ because it would have greater s character than would a B-H bond in $\text{BH}_2(\text{NH}_3)_2^+$. Water is a much weaker base than ammonia; therefore we can consider $\text{BH}_2(\text{H}_2\text{O})_2^+$ to be essentially BH_2^+ . The bonding is then sp rather than sp^3 . The presence of a higher B-H stretching frequency is consistent with this assumption.

The absorption bands at 1845 and 745 cm^{-1} in the $\text{B}_2\text{D}_6(\text{D}_2\text{O})_2$ spectrum are assigned respectively to the boron-deuterium stretching mode and the boron-deuterium deformation mode of $\text{BD}_2(\text{D}_2\text{O})_2^+$.

The $\nu_{\text{H}}/\nu_{\text{D}}$ ratios for the two $\text{BH}_2(\text{H}_2\text{O})_2^+$ bands are 1.48 and 1.55. The $\nu_{\text{H}}/\nu_{\text{D}}$ ratio for the DOD deformation is 1.48. The $\nu_{\text{H}}/\nu_{\text{D}}$ ratios for the hydroborate species are 1.39, 1.36, and 1.39. The boron-oxygen stretching frequency is not noticeably affected by deuteration.

An infrared study of the deuteriodiborane-water system was also done. Because of the broad HOH deformation band in the 1700-1600 cm^{-1} region, no boron-deuterium bands were visible for the BD_4^- species. A boron-deuterium stretch at 1850 cm^{-1} assigned to $\text{BD}_2(\text{H}_2\text{O})_2^+$ was observed as was a small band in the 2700 cm^{-1} region. To account for the presence of this latter band, we have assumed that proton exchange has occurred between the hydrogen of the excess water and some of the deuterium of deuteriodiborane.

The infrared spectra of the diborane-ethanol system and of the diborane-methanol system were not recorded because the carbon-hydrogen stretching frequencies would interfere with the boron-hydrogen stretching frequencies. Therefore we cannot assign structures to these two species.

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31. The 1185 cm^{-1} band was assigned to BH_4^- and the 1155 cm^{-1} band to $BH_2X_2^+$ in order to obtain the best product rule ratio ν_H/ν_D .

Figure Captions

Figure 1. The initial spectrum of the reactants. The spectrum of diborane dihydrate plus excess water. The final spectrum, of boric acid and water.

Figure 2. The initial spectrum of the reactants. The spectrum of $B_2D_6(D_2O)_2$ plus excess deuterium oxide. (A is the spectrum of the same sample as B but at increased gain.) The final spectrum, of deuterated boric acid and deuterium oxide.

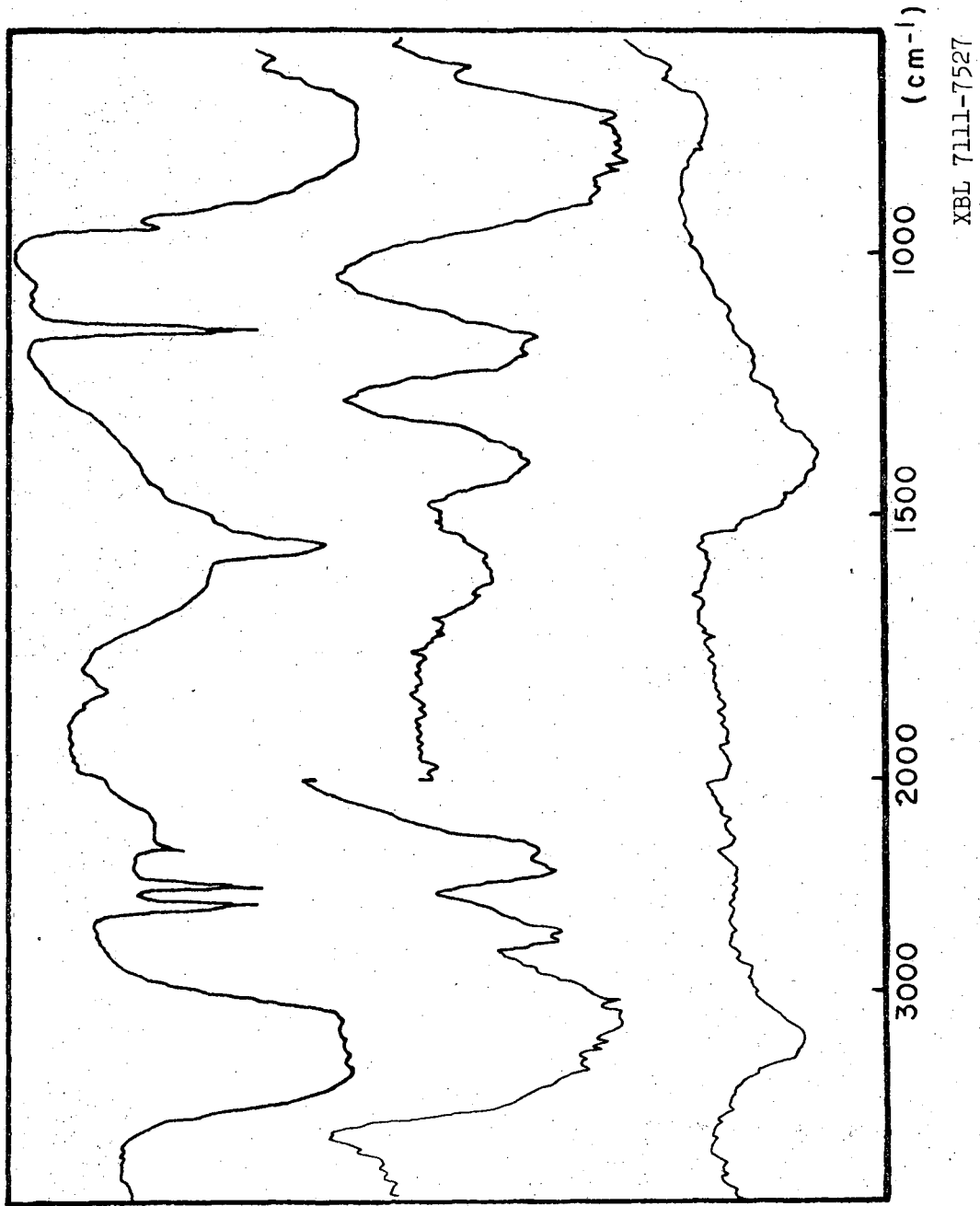


Figure 1

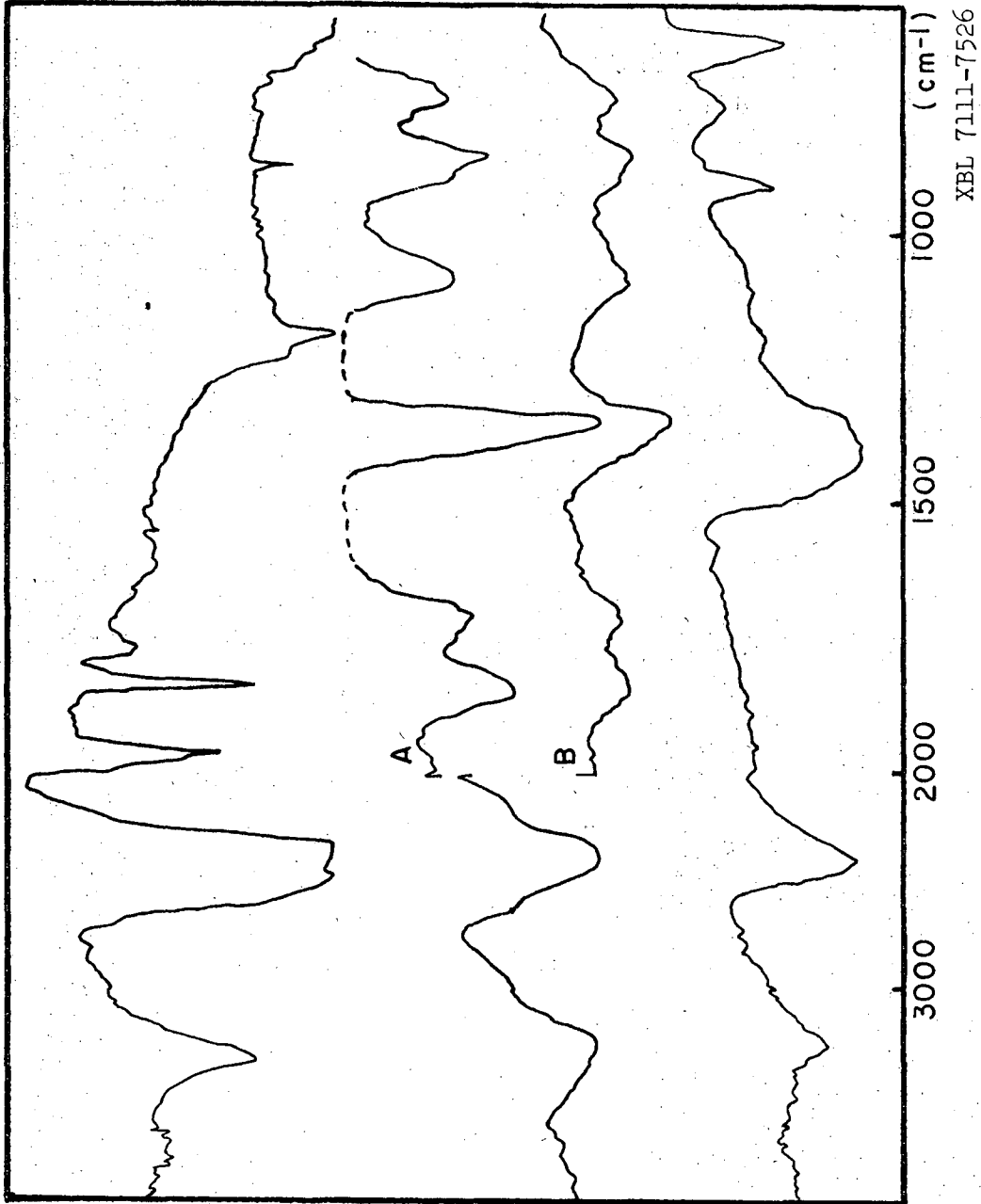


Figure 2

XBL 7111-7526

PART II. X-RAY PHOTOELECTRON SPECTROSCOPY
OF INORGANIC COMPOUNDS

ABSTRACT

Chemical shifts in core electron binding energies for gaseous nitrogen compounds and gaseous boron compounds are compared to their respective atomic charges estimated by Pauling, CNDO, and extended Hückel methods. The best linear correlation for both sets of compounds is found with the extended Hückel charges. A comparison between the experimental chemical shifts and the shifts estimated by the application of the thermodynamic method (based on the approximation that $\Delta E = 0$ for the interchange of equally-charged atomic cores between two different species) shows better agreement than the atomic charge methods.

The nitrogen 1s core binding energies of a series of transition metal nitrosyls are correlated with their structures, their electronic features, and their N-O stretching frequencies.

The nitrogen 1s binding energies of azide, dinitrogen and nitride transition metal complexes are interpreted in terms of interaction of the ligands with the metal atoms.

I. Paper: Chemical Shifts in Core Electron Binding Energies for Some Gaseous Nitrogen Compounds

(By Patricia Finn, Richard K. Pearson, Jack M. Hollander, and William L. Jolly; Inorganic Chemistry, 10, 378 (1971))

A. Abstract

Chemical shifts in core electron binding energies for gaseous nitrogen compounds are compared with values estimated by various theoretical and empirical methods. The relative merits of these methods are discussed.

B. Introduction

X-ray photoelectron spectroscopy is of great interest to chemists because the measured core electron binding energies are a function of the chemical environment of the atoms--that is, the binding energies show chemical shifts. Experimental binding energies for compounds of a given element can be estimated from (1) correlations with calculated atomic charges,¹⁻⁶ (2) thermodynamic data based on the approximation that the energy of core electron capture by a nucleus is independent of chemical environment,⁷⁻⁹ (3) empirical parameters characteristic of the directly bonded groups,⁸ and (4) molecular orbital calculated binding energies.^{6,10-12}

In order to appraise the relative usefulness of the various methods of estimating chemical shifts, it is important to have chemical shifts that span a wide energy range. We chose to study compounds of nitrogen because of the wide variety of bonding types that they possess and the probability that they would yield a wide range of chemical shifts. We found that the estimation methods that were most readily tested with our data were the atomic charge correlation method and the thermodynamic method. The empirical group parameter method could only be partially tested with our data because, in the set of compounds we studied, many of the groups bonded to nitrogen atoms are unique to those nitrogen compounds. Molecular orbital calculated binding energies are available for only a few of the compounds we studied; however, we hope that the availability of the experimental data will encourage others to make the further calculations required for a complete comparison.

In this paper we report data only for gaseous nitrogen compounds. Although many successful correlations and estimations have been made by using chemical shift data for solid compounds, there are both experimental and theoretical reasons for preferring the study of gaseous compounds. For example, by use of gaseous mixtures, it is a simple matter to measure chemical shifts between compounds of the same element from a single spectrum. Chemical shifts for gaseous compounds do not suffer from uncertainties of work functions which arise in the case of solid compounds.¹ Both theoretical and empirical calculations of core electron binding energies are much simpler for gaseous molecules than for solid compounds.

C. Experimental Section

Photoionization was accomplished with magnesium $K\alpha$ X-radiation (1253.6 eV). An iron-free double-focusing magnetic spectrometer^{13,14} was used to determine the kinetic energies of the photoelectrons. The gases were introduced from a metal vacuum line into a 200-ml source chamber. During each run, the pressure within this chamber was held constant (to $\pm 20\%$) in the range 10-40 μ . First the pure compound was studied in order to determine the approximate magnitude of the photoelectron kinetic energy. Then an approximately 1:1 mixture of the compound and some convenient reference compound was studied. Nitrogen gas was the first choice as a reference because of its low reactivity, but other gases were used when the chemical shift was less than 2 eV from that of nitrogen gas. (Siegbahn, et al.,⁶ have reported an absolute binding energy of 409.9 eV for N_2 .) The width of each channel in the spectrum was 0.27 eV; the counting times were such that at least 1000 counts were recorded in the channel nearest the signal peak. The signal-to-noise ratios were in the range 4.0-8.7, and the widths of the photoelectron lines at half-height were in the range 1.0-1.5 eV. Most samples were run twice; we never observed a change in the chemical shift greater than 0.1 eV in different runs of the same compound. The spectrometer pressure was maintained at less than 10^{-4} μ .

Most of the gases were taken from commercial cylinders. Except for N_2 , NO, N_2O , and NF_3 , samples were purified by vacuum distillation. The purity of each sample was checked by mass spectrometry and by comparison

of the infrared spectrum with the literature.¹⁵⁻¹⁷ Hydrogen cyanide was prepared by the addition of potassium cyanide to phosphoric acid in a closed system. Its mass and infrared spectra agreed with the literature.¹⁵⁻¹⁷ Dr. William Fox of Allied Chemical Co kindly provided us with a sample of ONF₃.

D. Results and Discussion

The measured nitrogen 1s binding energies, relative to molecular nitrogen, are given in Table I. The values span a total range of 12.3 eV. In the following paragraphs we discuss these values in terms of the various methods of estimating chemical shifts in binding energies.

Atomic Charge Method.- Previous studies of the relation between binding energies of solids and calculated atomic charges have shown improvement in the correlations when more sophisticated methods for calculating atomic charges were used.²⁻⁵ The present binding energies for gaseous molecules should permit a more meaningful comparison of the correlating abilities of atomic charges calculated by different methods. Therefore in this study we have used both the Pauling and CNDO methods for calculating atomic charges.

The Pauling method is based on the relation between the ionic character of a bond and the difference in the electronegativities of the atoms.¹⁸ We used Pauling's technique¹⁹ for estimating the electronegativities of charged atoms and iterated the calculations until

Table I. Nitrogen 1s Binding Energies for Some Gaseous Compounds

No.	Molecule	Relative Binding Energy, eV	Pauling Atomic Change	CNDO Atomic Change	Thermo. Estimated Rel. Binding Energy, eV
1	ONF ₃	7.1	1.24	0.70	
2	NF ₃	4.3	0.45	0.30	
3	NO ₂	3.0 ^a	0.53	0.41	3.3 ^{c,d}
4	*NNO	2.6 ^a	0.51	0.52	
5	N ₂ F ₄	2.4	0.32	0.23	2.8 ^{d,e,f}
6	ONCl	1.5	0.05	0.17	
7	NO	0.8 ^{a,b}	-0.37	0.05	0.9 ^{c,d}
8	N ₂	0.0	0.00	0.00	0.0
9	*NNO	-1.3 ^a	-0.34	-0.24	-0.9 ^{c,d}
10	HCN	-3.1	-0.06	-0.10	-2.6 ^{c,d,g}
11	N ₂ H ₄	-3.8	-0.26	-0.14	
12	NH ₃	-4.3 ^a	-0.39	-0.26	-3.5 ^{c,d,h,i}
13	CH ₃ NH ₂	-4.8	-0.32	-0.21	-3.9 ^{c,d,i}
14	(CH ₃) ₂ NH	-5.0	-0.23	-0.17	-4.2 ^{c,d,j}
15	(CH ₃) ₃ N	-5.2	-0.15	-0.14	

^aThe following values were obtained by Siegbahn et al (Ref.6): NO₂, 2.99; NNO, 2.6; NO, 0.4; *NNO, -1.4; NH₃, -4.3.

^bWeighted average of two peaks caused by spin of molecule.

^cU.S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D.C., 1952.

^dNational Standard Reference Data System, U.S. National Bureau of Standards, Washington, D.C., NSRDS-NBS 26, June 1969.

(notes to Table I, continued)

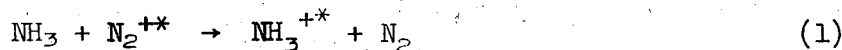
- ^e A. Kennedy and C. B. Colburn, J. Chem. Phys., 35, 1892 (1961).
- ^f Calculated for the reaction $\text{NF}_2 + \text{NO}^+ \rightarrow \text{OF}_2^+ + \text{N}_2$. In view of the low dissociation energy of N_2F_4 , this approximation is reasonable.
- ^g H. Pritchard and A. G. Harrison, J. Chem. Phys., 48, 2827 (1968).
- ^h M. A. Haney and J. L. Franklin, J. Chem. Phys., 50, 2028 (1969);
J. L. Beauchamp and S. E. Buttrill, J. Chem. Phys., 48, 1783 (1968).
- ⁱ V. L. Tal'roze, Pure Appl. Chem., 5, 455 (1962).
- ^j The proton affinity of $(\text{CH}_3)_2\text{O}$ was estimated to be 190 kcal/mole on the basis of data given by M. S. B. Munson, J. Am. Chem. Soc., 87, 2332 (1965).

consistent sets of charges and electronegativities were obtained. For NO and NO₂, Linnett structures were used to establish the initial formal charges.²⁰ For N₂O, we used the average charges calculated from the initial structures N⁻=N⁺=O and N=N⁺-O⁻. The calculated Pauling charges are listed in the fourth column of Table I, and Figure 1 is a plot of binding energy vs. calculated charge. The least-squares-fitted straight line, $E_B = 7.45q - 0.87$, fits the points rather poorly, with an average error of ± 1.62 eV.

The CNDO molecular orbital calculations were made with a CDC 6400 computer using a Fortran IV program.²¹ Cartesian coordinates were obtained from program PROXYZ²² coupled with literature values of the molecular parameters.²³⁻²⁵ The calculated CNDO charges are listed in the fifth column of Table I, and Figure 2 is a plot of binding energy vs. calculated charge. The least-squares-fitted straight line, $E_B = 11.83q - 1.27$, fits the points slightly better than the line in Figure 1, with an average error of ± 1.26 eV.

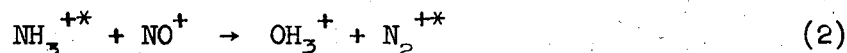
van der Avoird²⁶ has pointed out that the linear relationship between binding energies and atomic charges can be improved if the interatomic Madelung potential, M, is taken into account. We have confirmed this improvement. Using the Pauling charges, the least-squares line is $E_B - M = 18.08q - 0.95$, with an average deviation of ± 1.40 eV. Using the CNDO charges, the least-squares line is $E_B - M = 23.97q - 1.62$, with an average deviation of ± 0.99 eV.

Thermodynamic Method.- The difference in the nitrogen 1s binding energies of NH₃ and N₂ is the energy of the reaction



$$\Delta E = E_B(\text{NH}_3) - E_B(\text{N}_2)$$

(The asterisks indicate 1s electron vacancies.) If we make the approximation that $\Delta E = 0$ for any process in which an N^{6+} core in one species is interchanged with an O^{6+} core in another species, we may write



$$\Delta E = 0$$

Then, by adding reactions 1 and 2, we obtain



$$\Delta E = E_B(\text{NH}_3) - E_B(\text{N}_2)$$

Thus the shift in binding energy is, to the accuracy of our approximation, equal to the energy of Eq. 3 -- a quantity which can be evaluated from available thermodynamic data. Similarly, most of the other chemical shifts in Table I can be approximated by thermodynamic data. The thermodynamically estimated chemical shifts are listed in the sixth column of Table I. The average discrepancy between the experimental and estimated values is ± 0.52 eV. The latter value is artificially high because of the choice of N_2 as the reference compound. The overall average discrepancy is only 0.3 eV. Figure 3 is a plot of the experimental binding energy shifts vs. the estimated shifts.

Empirical Parameter Method.- It has been shown that chemical shifts in binding energy can be approximated by the sum of empirically evaluated parameters characteristic of the attached atoms or groups.⁸ This additivity rule can be checked with a few of the binding energy data in Table I.

When all three hydrogen atoms of ammonia are replaced with methyl groups, the binding energy decreases by 0.9 eV. In the case of monomethylamine, the decrease would be expected to be one-third as much, 0.3 eV, whereas it is actually 0.5 eV. In the case of dimethylamine the predicted and actual decreases are 0.6 and 0.7 eV, respectively.

The addition of an oxygen atom to the nitrogen atom of NF_3 causes the binding energy to increase by 2.8 eV. (This is the chemical shift between NF_3 and ONF_3 .) A similar change would be expected on adding an oxygen atom to molecular nitrogen. Indeed, the binding energy for the middle atom of N_2O is 2.6 eV greater than that of the atoms in N_2 .

The binding energy of NF_3 is 8.6 eV greater than that of NH_3 . We would expect the difference between N_2F_4 and N_2H_4 to be a little more than two-thirds as great, i.e., a little greater than 5.73 eV. Indeed, the observed chemical shift between N_2F_4 and N_2H_4 , 6.2 eV, is in agreement with this expectation. From the few comparisons made above, we tentatively conclude that the empirical parameter method is capable of predicting chemical shifts to about ± 0.2 eV.

Computational Method.- Basch and Snyder¹³ have obtained nitrogen 1s orbital energies for some of the compounds in Table I from SCF-MO calculations using a double- ζ basis of gaussian functions. According

to Koopmans' theorem, these energies may be taken as equal to binding energies. Their calculated values, relative to N_2 , are as follows (in eV): NNO , 3.9; NNO^* , 0.7; HCN , -2.4; N_2H_4 , -3.8; NH_3 , -5.4. The average deviation of these values from the experimental values is ± 1.0 eV.

E. Conclusions

The Pauling atomic charge method, although it gives very rough correlations with binding energy, has the advantage that it can be applied to any set of molecules for which complete octet structures can be written. In the case of resonating molecules, ambiguity arises as to the relative weights of the resonance structures.²⁷ In these cases the experimental data can be used to establish the relative weights. Barber and Clark¹² cited the essentially equal carbon 1s binding energies of acetonitrile as evidence for the inadequacy of atomic charge-binding energy correlations. It is true, that by use of only the $H_3CC\equiv N$ structure, the CN carbon atom would be expected to have a significantly greater binding energy than the CH_3 carbon atom.²⁸ However contribution from the hyperconjugated $H^+H_2C=C=N^-$ structure (which cannot be ignored, in view of the observed acidity²⁹ of acetonitrile) would bring the carbon atom charges closer together, and thus the binding energy data are consistent with such hyperconjugation. Although the CNDO atomic charge method gives a slightly better correlation than the Pauling method, many chemists may consider

this advantage to be outweighed by the relative difficulty and expense of the CNDO calculations.

The thermodynamic method gives more accurate predictions than the atomic charge method, and it is completely nonempirical, at least with respect to binding energies. However it is applicable only when the appropriate heats of formation are known or can be estimated.

The empirical parameter method has not yet been adequately tested with accurate gas-phase binding energy data. However, the few comparisons which we have been able to make indicate that, with the availability of appropriate sets of empirical data, the method should yield very accurate predictions.

Relatively few comparisons have been made between experimental and highly refined molecular orbital calculated binding energies. The available results show agreement to ± 1 eV and suggest that the error due to the assumption of Koopmans' theorem is approximately the same for all molecules.¹¹

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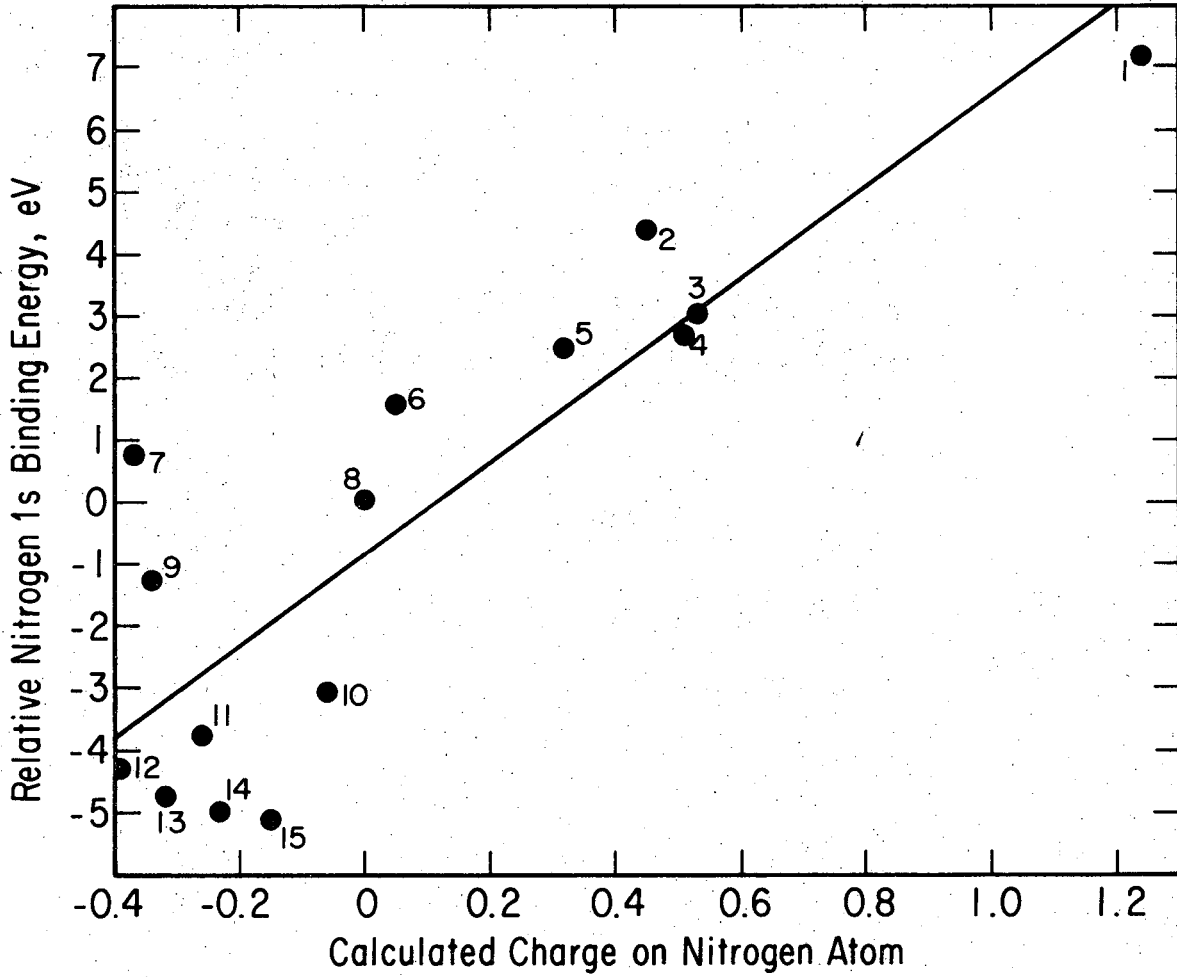
28. The chemical shifts between HCN and C_2H_6 is 2.8 eV.¹¹
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Figure Captions

Figure 1. Correlation of binding energy with atomic charge calculated by the Pauling method. Numbers refer to the compounds in Table I.

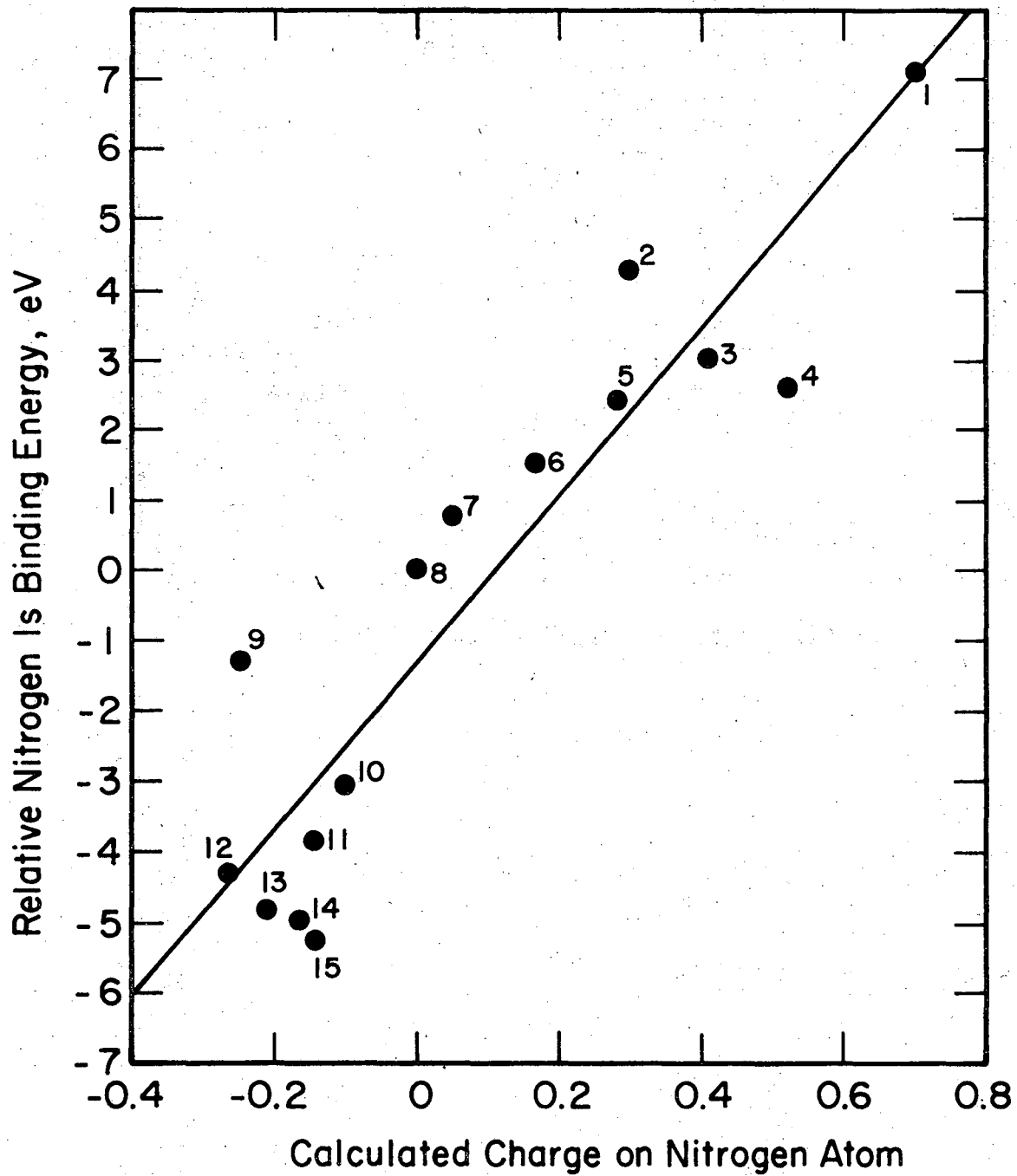
Figure 2. Correlation of binding energy with atomic charge calculated by the CNDO method. Numbers refer to the compounds in Table I.

Figure 3. Comparison of experimental and thermodynamically estimated binding energies. The line has a slope of unity and passes through the origin. The numbers refer to the compounds in Table I. The line would fit the points much more closely if point 9 or 10 (rather than 8) had been arbitrarily placed at the origin. It is significant that most of the points fit a line of unit slope.



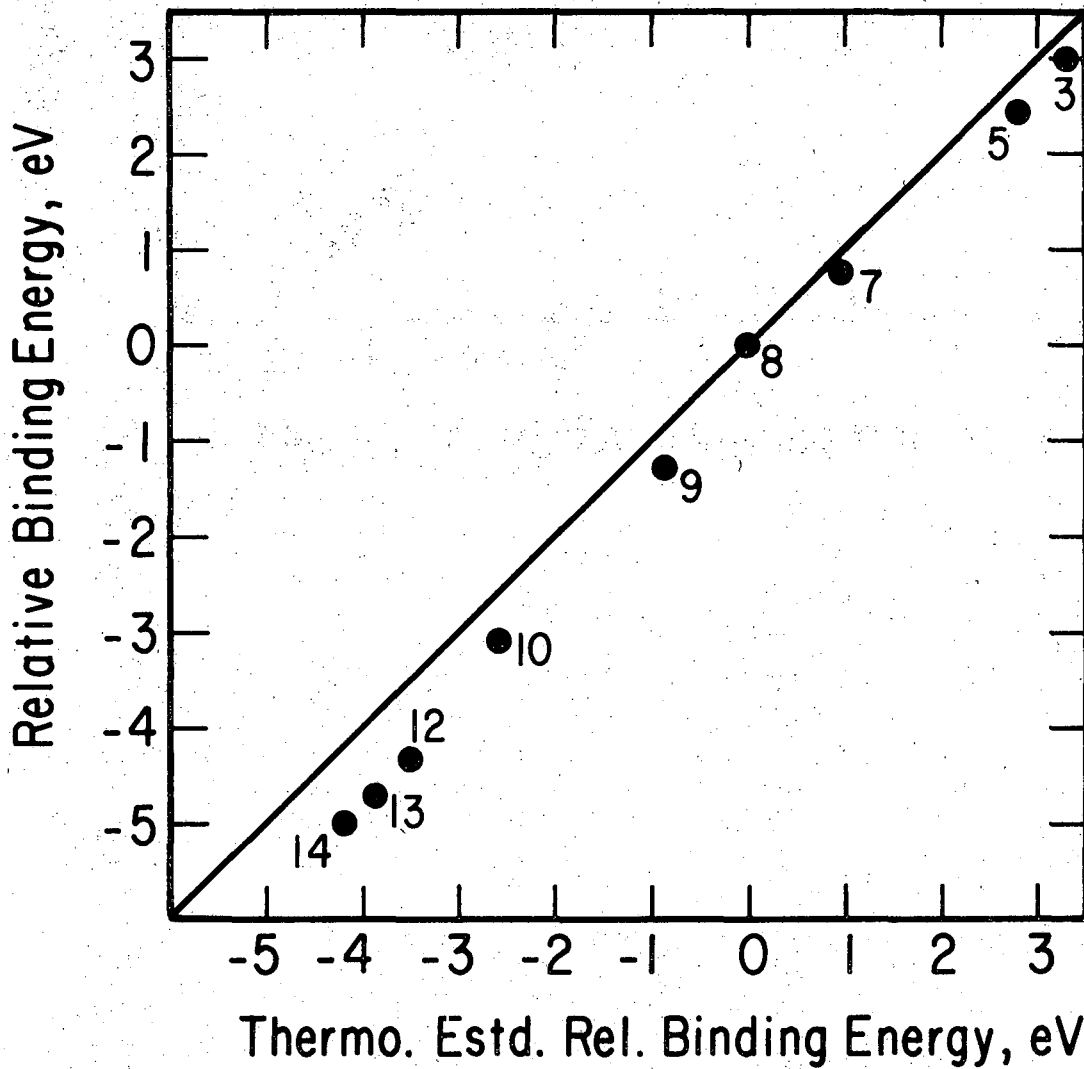
XBL 706-1097

Figure 1



XBL 709-6494

Figure 2



XBL 706-1096

Figure 3

G. Appendix

Extended Hückel calculations were made with a CDC 6600 computer using a Fortran IV program (R. Hoffman, J. Chem. Phys., 39, 1397 (1963)). The calculated nitrogen atomic charges for the gaseous nitrogen compounds are: ONF_3 (1.57), NF_3 (0.95), NO_2 (0.76), $\overset{*}{\text{NNO}}$ (0.66), N_2F_4 (0.70), ONCl (0.40), NO (0.22), N_2 (0.0), $\overset{*}{\text{NNO}}$ (-0.11), HCN (-0.52), N_2H_4 (-0.71), NH_3 (-1.00), CH_3NH_2 (-0.88), $(\text{CH}_3)_2\text{NH}$ (-0.72), and $(\text{CH}_3)_3\text{N}$ (-0.55). The least squares fitted straight line relation, $E_B = 4.93q - 0.635$ is the best fit between binding energy and atomic charge with an average error ± 0.39 . When the interatomic, "Madelung potential," M (A. van der Avoird, Chem. Comm., 727 (1970)) is included in the binding energy, no improvement is noted, $E_B = 14.78q - 1.09$, average error ± 1.86 .

II. Paper: Chemical Shifts in Boron 1s Binding Energies of Some
Gaseous Compounds

(By Patricia Finn and William L. Jolly)

A. Abstract

Chemical shifts in boron 1s electron binding energies for gaseous BF_3 , BCl_3 , $\text{B}(\text{OCH}_3)_3$, B_2H_6 , $\text{B}(\text{CH}_3)_3$, BH_3CO , and $\text{H}_3\text{BN}(\text{CH}_3)_3$ are shown to be linearly related to boron atom charges estimated by Pauling, CNDO, and extended Hückel methods. The best correlation is found with the extended Hückel charges, with inclusion of the interatomic "Madelung potential" (average deviation from straight-line relation, ± 0.83 eV). By application of the thermodynamic method (based on the approximation that $\Delta E = 0$ for the interchange of a pair of equally-charged atomic cores between two different chemical species), the chemical shifts are estimated with an average error of ± 0.57 eV. There is no obvious correlation between the 1s binding energy chemical shifts and published boron-11 nmr chemical shifts.

B. Introduction

Recently we reported¹ the nitrogen 1s electron binding energies for a series of gaseous nitrogen compounds and correlated the experimental values with calculated atomic charges and thermodynamic data. In this study we have measured the boron 1s electron binding energies of a series of gaseous boron compounds in order to provide data for further tests of the correlation of binding energies with atomic charges and thermodynamic data. We have also compared the boron 1s binding energies with boron-11 nuclear magnetic resonance chemical shifts.

C. Experimental

Magnesium K_{α} X-radiation was used for photoionization. Kinetic energies of the photoelectrons were measured with an iron-free, double-focusing magnetic spectrometer.² Each compound was first studied alone to determine the approximate magnitude of the photoelectron kinetic energy. Then an approximately 1:1 mixture of the compound and a reference compound, usually boron trifluoride, was studied. Because absolute binding energies were not determined, all the reported binding energies are relative. The width of each channel was 0.3 eV; the counting times were such that approximately 1000 counts were recorded in the channel nearest the signal peak. Signal-to-noise ratios were 2.0-4.0, and the widths of the photoelectron lines at half-height were 1.2-1.8 eV. Most samples were run twice; no peak position changed more than 0.1 eV.

Trimethyl borate was obtained from Alfa Inorganics, Inc., trimethylamine borane from Callery Chemical Co., and boron trifluoride and boron trichloride from the Matheson Co. Borane carbonyl,³ diborane,⁴ and boron trimethyl⁵ were prepared by literature procedures. The purity of the samples was checked by mass spectroscopy and by infrared spectroscopy.⁶⁻¹²

D. Results and Discussion

The measured boron 1s electron binding energies, relative to that of boron trifluoride, are listed in Table I.

Atomic Charge Method.- Pauling, CNDO, and extended Hückel methods were used for calculating boron atomic charges to permit a comparison of their correlations with experimental binding energies.

The Pauling method is based on a relation between the ionic character of a bond and the difference in the electronegativities of the atoms.¹³ Using Pauling's technique¹⁴ for estimating the electronegativities of charged atoms, the calculations were iterated until consistent sets of charges and electronegativities were obtained. The calculated charges are listed in column 4 of Table I. The least squares fitted straight line relation between binding energy and Pauling charge, $E_B = 4.35q - 4.39$ fits the data with an average error of ± 1.23 eV. A similar poor correlation with Pauling charges was found previously¹ for nitrogen compounds.

Using a Fortran IV program, the CNDO molecular orbital charge calculations¹⁵ were made with a CDC 6400 computer, using Cartesian coordinates obtained from program PROXYZ¹⁶ coupled with literature values for the molecular parameters.¹⁷ The calculated CNDO atomic charges are listed in column 5 of Table I. The least squares fitted straight line relation between binding energy and CNDO charge, $E_B = 7.58q - 6.37$, fits the points with an average error of ± 1.45 eV (worse than in the Pauling charge correlation).

Extended Hückel calculations were made with a CDC 6600 computer using a Fortran IV program.¹⁸ The Slater exponents used were 1.2, 2.6,

Table I

Boron 1s Chemical Shifts, Estimated Boron Charges, ^{11}B nmr Chemical Shifts, and

Thermochemically Estimated Chemical Shifts

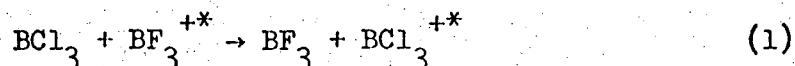
<u>Compound Number</u>	<u>Compound</u>	<u>Relative Binding Energy, eV</u>	<u>Pauling Charge</u>	<u>CNDO Charge</u>	<u>Extended Hückel Charge</u>	<u>^{11}B nmr Chemical Shifts, ppm.</u>	<u>Thermochemical Energy, eV</u>
1	BF_3	0	0.92	0.70	1.65	6.6	0
2	BCl_3	-2.3	-0.22	0.25	0.81	-29.2	-2.42
3	$\text{B}(\text{OCH}_3)_3$	-4.4	0.36	0.49	1.13	0.0	-3.02
4	B_2H_6	-6.3	-0.29	-0.03	-0.01	0.5	-5.42
5	$\text{B}(\text{CH}_3)_3$	-6.4	-0.62	0.13	0.31	-68.2	-6.86
6	BH_3CO	-7.6	-0.78	-0.43	0.15	-----	-8.03
7	$\text{BH}_3\text{N}(\text{CH}_3)_3$	-9.1	-0.60	-0.08	-0.19	24.9	-9.46

3.25, 3.9, 4.55, 5.2, and 4.5 for H, B, C, N, O, F, and Cl, respectively. Coulomb integrals were obtained from valence orbital ionization potentials.¹⁹ The calculated charges are listed in column 6 of Table I. The least squares fitted straight line relation, $E_B = 4.34q - 7.54$, provides the best fit of the three atomic charge methods with an average error ± 1.04 eV. For nitrogen compounds the extended Hückel method also gives the best fit.²⁰

By inclusion of the interatomic "Madelung potential", M ,²¹ the linear relationships between binding energy and atomic charge are improved. The improvement is negligible for the Pauling charges, yielding an average error ± 1.20 eV for the least squares fitted straight line $E_B - M = 4.98q - 4.37$. The average errors for the CNDO least squares fitted straight line $E_B - M = 8.29q - 6.04$, and the extended Hückel straight line $E_B - M = 5.15q - 7.48$, are significantly reduced, to ± 1.21 and ± 0.83 eV, respectively.

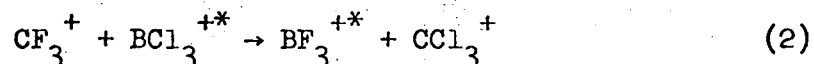
NMR Chemical Shifts.- The ^{11}B nmr chemical shifts reported by Phillips, Miller and Muettterties²² relative to methyl borate are listed in column 7 of Table I. There seems to be no correlation whatsoever between these data and the relative binding energies, even when considering the planar molecules alone.

Thermodynamic Method.- The difference in the boron 1s electron binding energies of boron trichloride and boron trifluoride is the energy of reaction 1. (An asterisk denotes removal of a core electron).

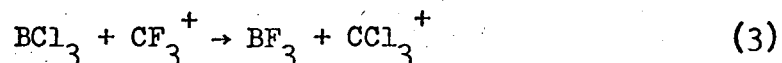


The basis of the thermodynamic method is the approximation that $\Delta E = 0$

for the interchange of a pair of equally-charged atomic cores between two different chemical species - specifically for the case in which one atomic core lacks one electron and the other has a complete set of electrons but has a nuclear charge one unit higher. Application of this approximation to the present set of data corresponds to the assumption that $\Delta E = 0$ for the interchange of B^{4+*} and C^{4+} cores between different species. Thus we take $\Delta E = 0$ for reaction 2.



The sum of reactions 1 and 2 is reaction 3, for which, to the accuracy of our approximation, ΔE is the chemical shift in binding energy between BF_3 and BCl_3 .

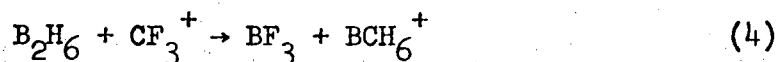


Reactions analogous to reaction 3 can be written for all the other boron compounds studied. The corresponding energies, calculated from literature data,²³⁻³⁰ are given in column 8 of Table I. A plot of the experimental relative binding energies vs the thermodynamically estimated relative binding energies is presented in Figure 1. The least squares fitted straight line drawn through the data, forced to have a slope of unity, corresponds to the relation $E_B(\text{exptl}) = E_B(\text{calcd}) - 0.13$. The average deviation between the experimental and calculated values is ± 0.57 eV.

Thermodynamic Calculations.- Most of the heats of formation used to calculate the relative binding energies were taken from the literature.²³⁻²⁵ However, not all the data required for diborane (B_2H_6) and trimethylamine

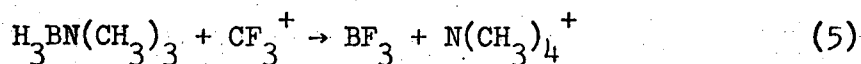
borane $[\text{H}_3\text{BN}(\text{CH}_3)_3]$ are available, and it was necessary to make further approximations in these cases.

The binding energy of B_2H_6 , relative to that of BF_3 , is taken to be the energy of reaction 4, where BCH_6^+ is the species formed by replacing

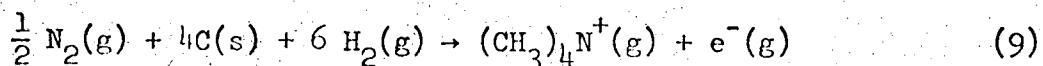
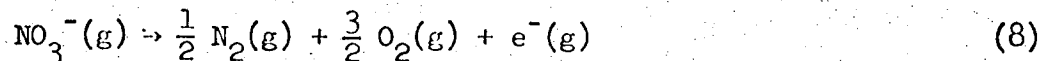
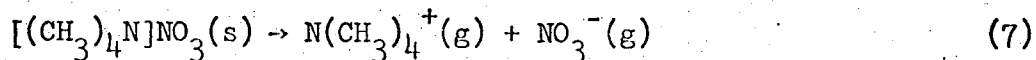
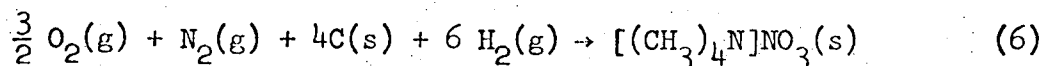


a boron atom in B_2H_6 with a C^+ ion. The heat of formation of this species is unknown. We have assumed that its heat of formation from BH_3 and CH_3^+ is equal to the heat of formation of the isoelectronic species, B_2H_6 , from two BH_3 molecules.

The binding energy of $\text{H}_3\text{BN}(\text{CH}_3)_3$, relative to that of BF_3 , is taken to be the energy of reaction 5.



Although the heat of the formation of the gaseous tetramethylammonium ion apparently has not been recorded, it can be estimated from a Born-Haber cycle for tetramethylammonium nitrate. The sum of reactions 6, 7, and 8 is reaction 9, for which ΔH° is the heat of formation of the gaseous



tetramethylammonium ion. Medard and Thomas²⁶ have determined ΔH_6° to be -80.8 kcal/mol. The value of ΔH_7° (117.2 kcal/mol) was estimated by the formula of Kapustinsky, which, for salts of univalent anions, is²⁷

$$U = 287.2 \left[\frac{n(n+1)}{(r_+ + r_-)} \right] \left[1 - \frac{0.345}{(r_+ + r_-)} \right]$$

where n is the charge on the cation and r_+ and r_- are the cationic and anionic radii. The radius of the tetramethylammonium ion (2.43 Å) was calculated from the lattice constants for the chloride, bromide, and iodide salts^{28,29} and the halide ionic radii.³⁰ The nitrate ion radius was taken as 2.10 Å.²⁷ A previously calculated value of ΔH_8° (89.0 kcal/mol²⁷) was used. The resulting value for the heat of formation of $(\text{CH}_3)_4\text{N}^+(\text{g})$ is 125.4 kcal/mol.

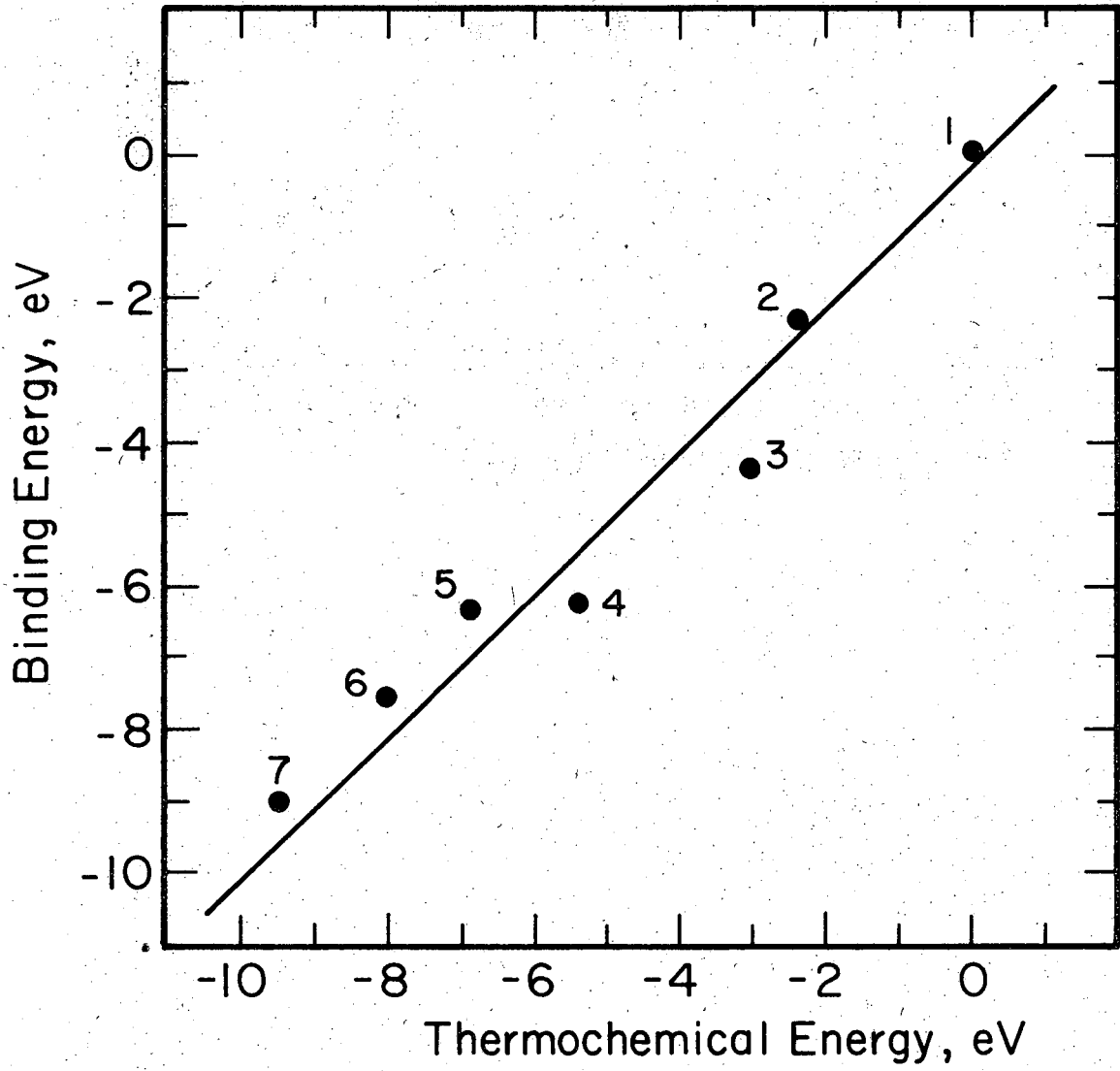
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Figure Caption

Figure 1.- Plot of boron 1s binding energies vs thermodynamically estimated binding energies.



XBL716-6854

Figure 1

III. Paper: The Nitrogen 1s Binding Energies of Transition Metal Nitrosyls

(By Patricia Finn and William L. Jolly)

A. Introduction

The bonding and electronic structure of transition metal nitrosyls have been frequently studied in recent years.¹⁻⁶ Two limiting situations have been identified: linearly coordinated NO^+ groups and angularly coordinated ("bent") NO^- groups. We have investigated the X-ray photoelectron spectra⁷ of a series of these compounds to attempt correlations of the nitrogen 1s electron binding energy with structure,⁸⁻¹⁹ electronic features, and N-O stretching frequency.^{16,20-39}

B. Experimental

The compounds were kindly supplied by Philip G. Douglas and Robert D. Feltham of the University of Arizona, by G. Dolcetti, P. Farnham, and James P. Collman of Stanford University, and, in the case of $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$,⁴⁰ by Mark Iannone of this department.

The powdered samples were brushed onto double-faced conducting tape attached to an aluminum plate. The reproducibility was ± 0.2 eV. In each case the carbon 1s line (due to a film of pump oil on the samples) was recorded and used as a reference peak. Individual lines had widths at half-height of 1.2-2.8 eV; broader lines were due to decomposition or to the presence of a second peak.

The kinetic energy of the photoelectron, E_K , was measured in an iron-free double-focusing magnetic spectrometer⁴¹ in which the incident radiation, $E_{h\nu}$, was magnesium K_α X-radiation (1253.6 eV) and for which the work function, ϕ_s , was taken as 4.0 eV. The nitrogen 1s binding energy, E_B , (the difference between the Fermi level and the 1s atomic level energy) was calculated from the relation $E_B = E_{h\nu} - E_K - \phi_s$.

C. Results and Discussion

The data are presented in Table I. It was found advantageous to categorize the compounds in terms of the metal d electron configurations by making the arbitrary assumption that the nitrosyl groups were NO^+ ions. (Although this assumption is illogical for the few compounds that contain "bent" NO groups, we made the assumption to simplify the classification of the compounds.)

The first seven compounds in Table I are six-coordinate and formally have 5 or 6 d electrons. In compounds 1-4, the metal atoms are in "abnormally low" oxidation states (0, +1, and +1 for Mo, Cr, and Mn, respectively), whereas in compounds 5-7, the metal atoms are in "normal" oxidation states (+2 for Ru and Fe). As far as is known, the NO groups in these seven compounds are essentially linearly coordinated. The nitrogen 1s binding energies are all within ± 0.6 eV of 400.1 eV except for compounds 6 and 7, for which the binding energies are 402.9⁴² and 403.3 eV, respectively. The high values for the latter compounds are indicative of relatively high positive charges on the NO groups and may be rationalized by the fact that in these compounds the metal atoms are

Table I

Nitrogen 1s Binding Energies, N-O Stretching Frequencies, and M-N-O Bond Angles for some
Transition Metal Complexes

Compound Number	Compound	No. of d electrons ^a	Nitrogen 1s Binding Energy (eV)	Nitrosyl Stretching Frequency (cm ⁻¹)	Ref.	M-N-O angle (°)	Ref.
1	MoCl ₂ (NO) ₂ (diars)	6	399.6	1760, 1670	20		
2	<u>trans</u> -[CrCl(NO)(diars) ₂]ClO ₄	5	400.7	1690	20		
3	K ₃ [Cr(NO)(CN) ₅]	5	400.7 ^b	1645	21	176.0 ^c	8
4	[(C ₆ H ₅) ₄ P] ₃ [Mn(NO)(CN) ₅]·3H ₂ O	6	399.7	1725 ^d	22	174.3 ^d	9
5	<u>trans</u> -[RuCl(NO)(diars) ₂]Cl ₂	6	400.0	1883	23		
6	<u>trans</u> -[FeCl(NO)(diars) ₂](ClO ₄) ₂	6	402.9 ^e	1865	24		
7	Na ₂ [Fe(NO)(CN) ₅]·2H ₂ O	6	403.3	1939	25	178.3	10
8	[π -C ₅ H ₅ Cr(NO) ₂] ₂	7	400.7	1672, 1505	26		
9	RhI ₂ (NO)[P(CH ₃)(C ₆ H ₅) ₂] ₂	8	400.3	1628 ^f	27	120 ^g	11
10	RhCl ₂ (NO)[P(C ₆ H ₅) ₃] ₂	8	401.5	1630	28	123 ^h	12
11	CoCl ₂ (NO)(diphos)	8	400.7	1676	29		
12	<u>trans</u> -[FeCl(NO)(diars) ₂]ClO ₄	7	400.0	1620	30		
13	[Co(NO)(NH ₃) ₅]Cl ₂	8	400.7	1620	31	119.0	13
14	<u>trans</u> -[CoCl(NO)(diars) ₂]Cl	8	400.5	1562, 1548	32	124.4 ⁱ	14
15	[Co(NO)(diars) ₂](ClO ₄) ₂	8	402.3	1852	32	174 ^j	15

16	$\text{CoCl}_2(\text{NO})[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_2$	8	401.7, 399.6	1735, 1630	28		
17	$\text{CoCl}_2(\text{NO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	8	401.5, 399.7	1720, 1650	28		
18	$[\text{Fe}(\text{NO})(\text{diars})_2](\text{ClO}_4)_2$	7	401.2, 399.6	1760	30		
19	$(\text{RuCl}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2)\text{PF}_6$	8	402.6, 400.2	1845, 1687	16	179.5, 136.0	16
20	$(\text{Rh}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2)\text{PF}_6$	10	401.1	1730, 1720	33		
21	$(\text{Ir}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2)\text{PF}_6$	10	400.2	1760-1715	34	163.5	17
22	$\text{Co}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$	10	400.0	1738	35		
23	$\text{Co}(\text{NO})(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	10	400.8	1714	35		
24	$\text{Rh}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$	10	400.8	1650	36		
25	$\text{Ir}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	10	400.3	1615	37	180	18
26	$\text{Ir}(\text{NO})(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	10	399.6	1645	37		
27	$\text{Ru}_3(\text{NO})_2(\text{CO})_{10}$	10	400.4 ^k	1524, 1508	38		
28	$\text{NiCl}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	10	399.8	1735 ^l	39		
29	$\text{Ni}(\text{N}_3)(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	10	399.6	—		152.7	19

^a Based on the arbitrary assumption of NO^+ nitrosyl groups.

^b Reference 44.

^c The bond angle refers to the corresponding $\text{Co}(\text{en})_3^{3+}$

^d Both the stretching frequency and bond angle are for the corresponding potassium salt.

^e Reference 42.

^f The stretching frequency is for the compound containing the triphenylphosphine ligand.

^g The bond angle refers to the analogous iridium complex in which one CH_3 group has been replaced by an I atom.

^h The bond angle refers to the analogous iridium complex.

ⁱ The bond angle refers to the analogous compound in which ethylenediamine groups have replaced the diarsine groups.

^j The bond angle refers to the analogous ruthenium complex in which two diphosphine groups have replaced the diarsine groups.

^k Very broad signal because of decomposition.

^l The stretching frequency is for the analogous bromo and iodo compounds.

in a "normal" oxidation state. It is noteworthy that the N-O stretching frequencies for compounds 6 and 7 are very high - a further indication of minimal electron donation into the π orbitals of the NO^+ groups. It is difficult to explain the low binding energy observed for compound 5, which contains ruthenium in a "normal" oxidation state and for which the N-O stretching frequency is very high. Perhaps the recorded binding energy corresponds to a decomposition product.⁴²

The second set of compounds in Table I formally have 7 or 8 d electrons and are either five- or six-coordinate.⁴³ Most of the binding energies lie within ± 0.4 eV of 400.3 eV; the two exceptions are compounds 10 and 15, with binding energies of 401.5 and 402.3 eV, respectively. It may be significant that both of the latter compounds are five-coordinate; one would expect a lower electron density on the metal and the attached nitrosyl group in a five-coordinate complex than in a six-coordinate complex. However, the low binding energies of the other two five-coordinate complexes, compounds 9 and 11, are then difficult to rationalize. In this set of eight compounds, compound 15 has both the highest binding energy and the highest N-O stretching frequency.

It is interesting that, although compound 8 contains both terminal and bridging NO groups,²⁶ only one nitrogen 1s peak was observed. Apparently, the NO groups are so similar in electron density that they are indistinguishable by X-ray photoelectron spectroscopy.

A binding energy of 402.0 eV was previously reported⁴⁴ for compound 13, $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$. We repeated this measurement several times with samples that were shown to be pure by magnetic susceptibility measurements,

and consistently observed one slightly broadened peak due to the NH_3 groups (at 400.2 eV) and the NO group. By computer fitting, we were unable to ascertain the position of the NO peak more precisely than 400.7 ± 1.3 eV.

It should be noted that, on going from compound 14 to compound 15, the complex ion changes only by the removal of a chloride ion - with the consequent change in coordination number from six to five. The increase in binding energy of 1.8 eV and the increase in the N-O stretching frequency of 300 cm^{-1} are the expected consequences of reduced electron donation into the NO^+ π orbitals.

The third set of compounds in Table I formally have 7 or 8 d electrons and show two separate nitrogen 1s peaks. For each of the cobalt compounds 16 and 17, two different coordination geometries are thought to be present: ²⁸ a trigonal bipyramidal structure with an equatorial linear nitrosyl and a square pyramidal structure with an apical bent nitrosyl. The two nitrogen 1s binding energies observed for both of these compounds are separated by about 2 eV. Presumably the bent nitrosyl corresponds to the lower binding energy and the linear nitrosyl corresponds to the higher binding energy in each case.

Two nitrogen 1s binding energies were observed for compound 18, $[\text{Fe}(\text{NO})(\text{diars})_2](\text{ClO}_4)_2$, although only one N-O stretching frequency has been reported. Three possible explanations come to mind. Perhaps different structural forms are present (as postulated for compounds 16 and 17), and the N-O stretching frequency of one form is of low intensity. Perhaps the spectral splitting is due to the paramagnetism of the sample.

Finally, it is not unlikely that the sample underwent decomposition in the X-ray beam and that the two peaks are due to the compound and its decomposition product.⁴⁵

In the ruthenium complex, compound 19, two different types of nitrosyl group are bonded to the same metal atom.¹⁶ This square pyramidal compound has an apical bent nitrosyl and a linear equatorial nitrosyl. Presumably, the higher binding energy (402.6 eV) and higher N-O frequency (1845 cm^{-1}) correspond to the linear nitrosyl, and the lower binding energy (400.2 eV) and lower N-O frequency (1687 cm^{-1}) correspond to the bent nitrosyl.

The fourth set of compounds in Table I (compounds 20-29) formally have ten d electrons and, except for compound 27, are four-coordinate. Probably because of the high electron densities on the metal atoms, the binding energies are low. The low N-O stretching frequencies are consistent with these results.

We draw the overall conclusion that there is a definite correlation between the nitrogen 1s binding energy of a nitrosyl group and the electron density on that group. Bent nitrosyls have low binding energies. Linear nitrosyls can have either low or high binding energies, depending on the extent of π back-bonding from the metal atom. The binding energies are at least roughly correlated with the N-O stretching frequencies: when one is high or low, so is the other.

Acknowledgments. - We are grateful to Professors R. D. Feltham and J. P. Collman for providing many of the samples and for helpful discussions. We thank Mr. Mark Iannone for preparing the $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$.

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- (42) Compound 6 underwent decomposition in the X-ray beam, as evidenced by a gradual decrease in the 402.9 eV peak and the simultaneous growth of a 400.0 eV peak. Although no similar evidence for decomposition was noticed in the case of compound 5, it is possible that such decomposition occurred before adequate counts for a decent spectrum were obtained.
- (43) Compound 8 may be considered six-coordinate if the π -cyclopentadienyl ion is considered to be tridentate.
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- (45) However, we were unable to observe any evidence of a shift in the relative intensities of the peaks with time of irradiation.

IV. Paper: Nitrogen 1s Binding Energies of Some Azide, Dinitrogen
and Nitride Complexes of Transition Metals

(By Patricia Finn and William L. Jolly)

A. Introduction

We have used X-ray photoelectron spectroscopy to determine the nitrogen 1s binding energies of azide, dinitrogen, and nitride complexes of several transition metals. Such data are of interest because the binding energy shifts can be interpreted in terms of the interaction of the ligands with the transition metal atoms.

B. Experimental

The compounds $\text{Ni}(\text{N}_3)(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$,¹ trans- $[\text{Ru}(\text{N}_3)\text{Cl}(\text{diars})_2]$,² trans- $[\text{Co}(\text{N}_3)_2(\text{diars})_2]\text{ClO}_4$,² trans- $[\text{Ru}(\text{N}_2)\text{Cl}(\text{diars})_2]$,² and $[\text{C}_6\text{H}_5(\text{N}_2)]\text{BF}_4$ ³ were kindly supplied by Philip G. Douglas and Robert D. Feltham of the University of Arizona. We prepared $\{\text{Cu}(\text{N}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}_2$,⁴ $[\text{Rh}(\text{N}_3)(\text{CO})_2]_2$,⁵ $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{N}_3)_5]$,⁶ $\text{K}_3[\text{Ru}_2\text{N}(\text{Cl})_8(\text{H}_2\text{O})_2]$,⁷ and $\text{ReN}(\text{Cl})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ⁸ by known procedures. The KBr pellet infrared spectra of these complexes were in good agreement with the literature data.

The powdered samples were brushed onto double-faced conducting tape attached to an aluminum plate. In each case, the carbon 1s line (due to a film of pump oil on the samples) was recorded and used as a reference peak. Individual lines had widths of 1.4-2.6 eV. The kinetic energy of the photoelectron, E_K , was measured in an iron-free, double-focusing magnetic spectrometer⁹ in which the incident radiation, $E_{h\nu}$, was magnesium K_α

X-radiation (1253.6 eV) and for which the work function, ϕ_s , was taken as 4.0 eV. The nitrogen 1s binding energy, E_B , (the difference between the Fermi energy and the 1s atomic energy) was calculated from the relation $E_B = E_{hv} - E_K - \phi_s$.

C. Results

The data are presented in Table I.

Azide Complexes.- The first group of compounds in Table I contain azide ions in various environments. It is noteworthy that sodium azide and the azide complexes have very similar spectra, with two peaks separated by 4.3 ± 0.4 eV. The peak at lower binding energy (corresponding to the two end atoms) has twice the intensity of the other peak (corresponding to the middle atom). These results indicate that the internal bonding of the azide ion is essentially unaffected by coordination to a transition metal atom; that is, the azide ion appears to be linked to the metal atom by an ionic bond with little polarization. The infrared spectra and X-ray diffraction structural data of such compounds are consistent with these conclusions. Thus the asymmetric stretching frequency and the bending frequency of the azide ion in complexes are almost unchanged from those of the azide ion in sodium azide.^{1,2,4-6} The N-N bond distances in azide complexes are within 0.02 \AA of that in sodium azide.¹⁰⁻¹²

Both peaks of $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{N}_3)_5]$, the only anionic azide complex considered, are appreciably shifted to lower binding energies (by 0.6 and 0.9 eV) from the peaks of sodium azide. Probably the -2 charge on the anion is responsible for the lower binding energies.

Table I

The Nitrogen 1s Binding Energies of Some Transition Metal Complexes

Compound	Nitrogen 1s Binding Energy (eV)	Intensity Ratio	Separation (eV)
NaN_3	403.7, 399.3 ^a	1:2	4.4
$\text{Ni}(\text{N}_3)(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	403.8, 399.6	1:2	4.2
<u>trans</u> - $[\text{Ru}(\text{N}_3)\text{Cl}(\text{diars})_2]$	403.9, 399.2	1:2	4.7
<u>trans</u> - $[\text{Co}(\text{N}_3)_2(\text{diars})_2]\text{ClO}_4$	403.2, 399.1	1:2	4.1
$(\text{Cu}(\text{N}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2)_2$	403.7, 399.2	1:2	4.5
$[\text{Rh}(\text{N}_3)(\text{CO})_2]_2$	403.2, 399.3	1:2	3.9
$[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{N}_3)_5]$	402.8, 398.7	1:2	4.1
<u>trans</u> - $[\text{Ru}(\text{N}_2)\text{Cl}(\text{diars})_2]$	402.3, 400.7	1:1	1.6
$\text{Re}(\text{N}_2)\text{Cl}(\text{diphos})_2$	399.9, 397.9 ^b	1:1	2.0
$[\text{C}_6\text{H}_5(\text{N}_2)]\text{BF}_4$	405.1, 403.8	1:1	1.3
$\text{K}_3[\text{Ru}_2\text{N}(\text{Cl})_8(\text{H}_2\text{O})_2]$	399.8		
$\text{ReN}(\text{Cl})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$	398.8		

^a D. Hendrickson, J. M. Hollander and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

^b See reference 19.

Dinitrogen Complexes.- The Ru-N bond length of 1.894 Å for the N₂ group in [Ru(N₃)(N₂)(en)₂]¹³ is significantly shorter than the Ru-N single bond distance of 2.144 Å in [Ru(NH₃)₆]¹⁴. Similar evidence for partial multiple bond character in metal-N₂ bonds is found for other transition metal complexes.¹⁵⁻¹⁸ Thus a dinitrogen complex can be considered to be a hybrid of two major resonance forms, M - $\overset{+}{N} = N$ and M = $\overset{+}{N} = \bar{N}$. Because the nitrogen atom directly attached to the metal atom has a formal positive charge in both forms, we expect decreased electron density on this nitrogen atom and a correspondingly higher binding energy. The nitrogen 1s spectrum of trans-[Ru(N₂)Cl(diars)₂] consists of two peaks; we assign the higher binding energy to the nitrogen atom directly attached to the ruthenium atom. Leigh et al.¹⁹ made a similar assignment for [Re(N₂)Cl(diphos)₂].

We found two nitrogen 1s peaks for [C₆H₅(N₂)]BF₄, with a peak separation of the same order of magnitude (1.3 eV) as found for the transition metal compounds. However, both peaks are at higher binding energy probably because of the +1 charge of the diazonium ion. For all resonance forms the nitrogen atom directly attached to the phenyl group has a formal positive charge; therefore the higher binding energy peak is assigned to this nitrogen atom.

Nitride Complexes.- The nitrogen 1s binding energies of K₃[Ru₂N(Cl)₈(H₂O)₂] and ReN(Cl)₂[P(C₆H₅)₃]₂ are of interest because these complexes contain nitride ion ligands which are bridging and non-bridging, respectively. In the former complex, two metal atoms compete for the electron density of the bridging nitride, therefore a higher binding energy is observed for this compound even though the complex has a -3 charge.

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