of 30% enriched $^{15}NO_3Na$ contained in a coaxial 2-mm tube centered in a 10-mm sample tube.

The solvent effect on $\delta^{15}N$ did not exceed $\simeq 0.8$ ppm upfield when going from pure liquid (DMF (**1**)) to a 30% solution in $CHCl_3$, $CHCl_2CHCl_2$, or CH_3CN. Fifty percent solutions of DMF in methanol or ethanol cause more important downfield shifts $\simeq 2$ to 3 ppm. The influence of $Cr(AcAc)_3$ on $\delta^{15}N$ was checked by studying the ^{15}N resonance of enriched materials without using T_1 reagent. The addition of 0.1 M $Cr(AcAc)_3$ to DMF and DMA (**2**) brings about a small upfield shift ($\simeq 1.5$ ppm) for $\delta^{15}N$.

Materials. Commercially produced amides, thioamides, and carbamoyl derivatives were carefully dried and distilled (**1–4, 10–13, 20, 21, 24**). The iminium salts and acceptor–donor complexes (**14–19**) were synthetized as previously described.[37] Vinylamides (**6, 7**) and enamines (**8, 9, 22, 23**) were prepared according to conventional procedures.[31,41,42]

Labeling experiments: 5% ^{15}N enriched DMA was synthetized by the reaction of acetyl chloride with a cold solution of 5% ^{15}N dimethylamine in hexamethylphosphoramide; 5% ^{15}N DMF was prepared from the reaction of CCl_3CHO with enriched dimethylamine dissolved in $CHCl_3$ (40% yield).[44] Five percent ^{15}N dimethylamine hydrochloride was prepared from 5% ^{15}N ammonium chloride (CEA, Paris) and a 30% aqueous solution of formaldehyde.[43] A solution of 5% ^{15}N $(CH_3)_2NH_2Cl$ in hot water is poured into 10 N NaOH and the gaseous enriched dimethylamine is collected in the appropriate solvent.

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Nitrogen-14 Nuclear Quadrupole Resonance Spectra of Coordinated Pyridine[1]

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Abstract: Nitrogen-14 nuclear quadrupole resonance (NQR) data have been obtained for several pyridine complexes with Zn(II) and Cd(II), $I(C_5H_5N)_2ClO_4$, $Br(C_5H_5N)_2ClO_4$, $HNC_5H_5NO_3$, and $4\text{-}CH_3C_5H_4NO$. The field gradient tensor is substantially altered upon coordination to a Lewis acid. Using a modification of the Townes–Dailey model it is possible to relate the field gradient parameters to the extent of charge transfer from nitrogen to the Lewis acid. ^{14}N NQR signals were also detected for the nitrato nitrogens in several cases and for the NCS^- ligand in $Zn(NCS)_2(C_5H_5N)_2$. The NQR data for this complex are consistent with coordination to Zn(II) through N.

During the past several years the number of reported ^{14}N nuclear quadrupole resonance (NQR) spectra has grown rapidly. Nevertheless, the number and variety of data available for compounds in which a nitrogen atom is coordinated directly to a metal ion or other Lewis acid is quite limited. We have indicated in another contribution the reasons why ^{14}N NQR spectra should be of interest in such systems.[4] The adiabatic demagnetization in the lab frame, double resonance level-crossing technique (drlc),[5-9] is of particular value in obtaining the desired data, because it is sensitive and capable of detecting resonances at frequencies too low for direct detection. The advantages and limitations of the technique have been described by Edmonds.[6,7]

In the present contribution we report the ^{14}N NQR spectra for several adducts of pyridine with various Lewis acids. The compounds studied include several zinc(II) complexes and two complexes of Cd(II). In addition, we have observed the ^{14}N NQR spectrum of the N-bonded coordinated thiocyanate and of nitrate in four different substances.

Experimental Section

Sample Preparations. Dichlorobispyridinezinc(II) ($ZnCl_2(py)_2$), $ZnBr_2(py)_2$, and $ZnI_2(py)_2$ were prepared by precipitation from an ethanol solution of zinc halide by the addition of pyridine.[10] $Zn(NCS)_2(py)_2$ was prepared similarly from aqueous solution.[11] The pyridinium salts were obtained by reaction of equimolar amounts of concentrated acid and pyridine. All were recrystallized from ethanol.

Bispyridinesilver(I) perchlorate, $Ag(py)_2ClO_4$, precipitates when an aqueous $AgClO_4$ solution is mixed with an aqueous pyridine solution.[12] It was dried under vacuum in the dark. From this, bispyridinebromine(I) perchlorate, $Br(py)_2ClO_4$, was prepared by a published procedure.[13] Bispyridineiodine(I) perchlorate, $I(py)_2ClO_4$, was prepared similarly, except that I_2 was added as a solid. The product is fairly insoluble in a pyridine–chloroform mixture and was separated from AgI by dissolving it in methanol.

The two bisnitratozinc(II) complexes, $Zn(NO_3)_2(py)_2$ and $Zn(NO_3)_2(py)_3$, were prepared by the method of Ouellette,[14] using $AgNO_3$ and Zn as starting materials.

All sample preparations yielded satisfactory elemental analyses for C, H, and N.

Dichlorobispyridinecadmium(II), $CdCl_2(py)_2$, was prepared by precipitation from an aqueous solution of $CdCl_2$ using a large excess of pyridine. Anal. Calcd for $CdCl_2C_{10}N_2H_{10}$: C, 35.2; N, 8.23; H, 2.95. Found: C, 36.2; N, 8.39; H, 3.08. (Since the compound might readily lose pyridine it was prepared and handled in the presence of excess pyridine, to prevent decomposition. Thus, the solid probably contains a slight excess of pyridine, but this will not affect the NQR results.) Dinitratotrispyridinecadmium(II), $Cd(NO_3)_2(py)_3$, was prepared by the method of Ouellette.[14]

NQR Measurements. The ^{14}N NQR measurements were carried out in part as described previously;[4] sample temperature in all cases was 77 K. Values of proton T_1 ranged from 8 s in $Zn(NO_3)_2(py)_3$ to 900 s in $(pyH)(NO_3)$. Approximate values of T_2 were in the range from 6 to 14 μs. During the course of this work the instrument was modified to permit single-coil as opposed to cross-coil operation. Receiver recovery time was shortened by use of active filtering. This modification has resulted in shorter overall recovery time and consequently increased sensitivities.

Table I lists the observed ^{14}N transition frequencies for a variety of compounds in which the pyridine is coordinated to a Lewis acid. For all nitrate-containing substances transitions associated with the nitrate group were also observed. Similarly, the transitions of the nitrogen of the NCS^- ligand were seen in $Zn(NCS)_2(py)_2$. In all instances the transitions were actually observed, rather than calculated from other observed frequencies. The precision with which the frequencies are determined varies, but in general they are measured to within 2 to 5 kHz.

Discussion

Comparisons with Crystal Structure Data. For several of the compounds listed, x-ray crystal structure determinations have been carried out. The number of nonequivalent ^{14}N sites is therefore known for the samples at room temperature. The expected number of lines assigned to pyridine is seen for $ZnCl_2(py)_2$,[15] $CdCl_2(py)_2$,[16] $(pyH)(NO_3)$,[17] $Zn(NO_3)_2(py)_2$,[18] $Zn(NO_3)_2(py)_3$,[19] and $Cd(NO_3)_2(py)_3$.[20]

Interpretation of Data for Coordinated Pyridine. The most obvious message of the pyridine data in Table I is that coordination of the Lewis acid to the lone pair of the pyridine nitrogen causes a substantial decrease in field gradient. This suggests that, aside from whatever detailed interpretations may be placed upon the data, the NQR technique will prove to be a sensitive probe of bond formation at nitrogen. Hopefully the NQR data will be useful in providing information on the nature of the bond from nitrogen to the Lewis acid, for example, as regards covalency. To extract such interpretive detail, however, it is necessary to apply some kind of model to the results.

Table I. Measured ^{14}N Quadrupole Resonance Transitions (kHz) in Pyridine Compounds at 77 K

Compd	ν_+	ν_-	ν_0	e^2qQ/h	η
Pyridine[a] (py)	3892	2984	908	4584	0.396
$ZnCl_2(py)_2$	2387	2078	309	2977	0.207
	2332	2038	294	2913	0.202
$ZnBr_2(py)_2$	2345	2040	305	2923	0.209
	2282	2000	282	2855	0.198
$ZnI_2(py)_2$	2360	2053	307	2942	0.208
	2321	2029	292	2900	0.201
$Zn(NCS)_2(py)_2$	2297	2035	262	2888	0.181
	760	660	100	947	0.211
	715	615	100	887	0.224
$Zn(NO_3)_2(py)_2$	2124	1884	240	2672	0.180
	2097	1877	220	2649	0.166
	572	288	284	573	0.991
$Zn(NO_3)_2(py)_3$	2578	2180	398	3172	0.251
	2569	2201	368	3180	0.231
	547	309	238	571	0.834
$CdCl_2(py)_2$	2850	2298	552	3432	0.320
$Cd(NO_3)_2(py)_3$	2718	2272	446	3327	0.268
	2582	2179	403	3174	0.254
	545	350	195	597	0.654
$(Hpy)^+NO_3^-$	955	678	277	1090	0.509
	584	445		685	0.405
$I(py)_2ClO_4$	1330	1210	120	1693	0.142
$Br(py)_2ClO_4$	1398	725	673	1415	0.951
γ-Picoline[b]	3688	2933	756	4414	0.342
γ-Picoline N–O	1171	586	585	1171	0.999

[a] The pyridine values are an average of four data sets for crystallographically nonequivalent molecules.[b] [b] L. Guibe, *Ann. Phys. (Paris)*, **7**, 177 (1961).

For pyridine several ab initio[21-24] as well as more empirical[25,26] molecular orbital calculations have been carried out. Comparison of calculated and observed values for e^2Qq is made more tenuous by the fact that a value of e^2Qq_0 for atomic nitrogen is not accurately known. Typically, the values of e^2Qq obtained from experimental data are in reasonable agreement with calculated values using the current best estimate for Q. On the other hand, the calculated asymmetry parameter, η, is generally not in good agreement. For example, the recent ab initio calculation for pyridine by Ha and O'Konski[24] yielded an η of 0.14, as compared with an observed value of 0.39. More empirical molecular orbital approaches suffer from the necessity to fix values for quite a large number of factors that might affect the field gradient tensor. In addition the field gardient operator itself may be only incompletely evaluated from the basis set of occupied MO's.[25,26]

To understand the changes at nitrogen which accompany Lewis acid–base adduct formation on the basis of a theoretical model, it would appear best to parameterize the model in terms of pyridine as a reference compound. For the present we have elected to employ a modified version of the Townes–Dailey model[27] as a guide. In this model the field gradient at ^{14}N is expressed entirely in terms of the populations of the 2p orbitals at nitrogen. The populations are deduced from the experimental NQR results or assigned empirically. In applying the Townes–Dailey model to pyridine, the axis system shown in Figure 1 is adopted. Assume that the CNC angle is 2θ and that the nitrogen orbitals within the plane of the molecule are hybridized so that they are directed along the N–C bond axes. The occupancy of the nitrogen σ orbital directed toward carbon is assigned a value b_0 and that of the p_π orbital a value a_0. The lone-pair orbital is assumed to have an occupancy of 2. The diagonal components of the field gradient tensor then have values

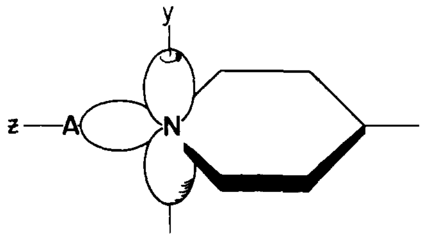


Figure 1. Coordinate system and orbitals involved in pyridine coordination.

$$\begin{aligned} q_{zz} &= [2(1 - \cot^2\theta) - a_0/2 + b_0(\cot^2\theta - \tfrac{1}{2})]q_0 \\ q_{yy} &= [-(1 - \cot^2\theta) + a_0 - b_0(1 + \cot^2\theta)/2]q_0 \quad (1) \\ q_{xx} &= [-(1 - \cot^2\theta) - a_0/2 + b_0(2 - \cot^2\theta)]q_0 \end{aligned}$$

The quadrupole coupling constant e^2Qq_{zz} is then given by $\alpha(e^2Qq_0)$ where $\alpha = [2(1 - \cot^2\theta) - a_0/2 + b_0(\cot^2\theta - \frac{1}{2})]$. The asymmetry parameter η is given by $\eta = (q_{xx} - q_{yy})/q_{zz}$. Manipulation of eq 1 yields an expression for η. Since both e^2Qq_{zz} and η are measured for pyridine, both a_0 and b_0 can be calculated from the data after choosing values for 2θ and e^2Qq_0.

When pyridine is bound to a Lewis acid the formerly lone pair orbital becomes the donor orbital. The donor orbital occupancy is reduced in the adduct from 2 in free pyridine to some value σ. It is, of course, this occupancy of the donor orbital that is of major interest. To estimate σ from the value of e^2Qq_{zz} and η for the coordinated pyridine, it is necessary to make assumptions about the effect of coordination on the occupancies of the other orbitals. One possibility, for example, would be to assume that no changes occur in either a_0 or b_0. However, donation of the lone pair electrons on nitrogen to a Lewis acid will cause some increase in the occupancies of the other three orbitals via an inductive effect. We assume that the occupancies of the nitrogen orbitals in the pyridine adducts are given by

$$a = a_0 + A(2 - \sigma) \quad (2)$$

$$b = b_0 + B(2 - \sigma) \quad (3)$$

That is, the populations of the π and N-C σ orbitals increase in proportion to the degree of electron withdrawal from nitrogen, with proportionality constants A and B, respectively. We assume in addition that there is no change in the geometry at nitrogen upon coordination and that the only mode of interaction between pyridine and the acid is via the σ bond from nitrogen. Then, in general

$$\begin{aligned} \alpha = (1 - \cot^2\theta)\sigma + \tfrac{1}{2}[a_0 + A(2 - \sigma)] \\ + (\cot^2\theta - \tfrac{1}{2})[b_0 + B(2 - \sigma)] \quad (4) \end{aligned}$$

$$\alpha\eta = \tfrac{3}{2}\{[b_0 + B(2 - \sigma)] - [a_0 + A(2 - \sigma)]\} \quad (5)$$

By eliminating σ in these two expressions one obtains a linear relationship between $1/\alpha$ and η:

$$1/\alpha = 1/K + (L/K)\eta \quad (6)$$

$$K = \frac{[2(B - A) + (b_0 - a_0) + (Ab_0 - Ba_0)](1 - \cot^2\theta)}{(B - A)} \quad (7)$$

$$L = \frac{2[(1 - \cot^2\theta) + A/2 - B(\cot^2\theta - \frac{1}{2})]}{3(B - A)} \quad (8)$$

These expressions are valid in the range of σ values such that the major axis of the field gradient tensor remains oriented along the donor orbital direction. The linear relationship described by eq 6 is constrained to pass through the pyridine data, for which both α and η are known, and for which σ is 2. As a result, eq 7 and 8 are linearly dependent; A and B are thus linearly related unknowns.

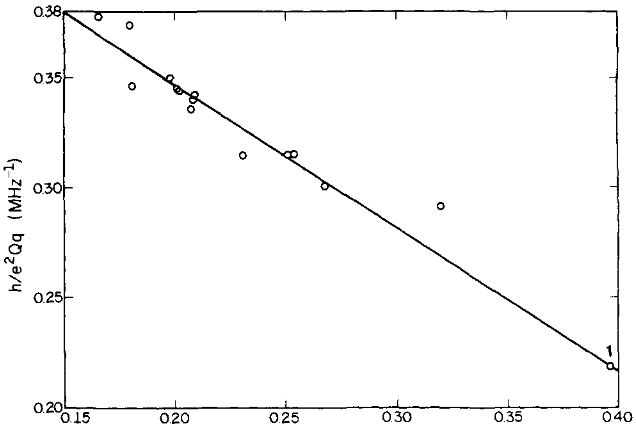


Figure 2. Graph of h/e^2Qq_{zz} vs. η for Zn(II) and Cd(II) complexes of pyridine. The point labeled 1 represents pyridine.

From the experimental data for an appropriate series of pyridine adducts the linear relationship between $1/\alpha$ and η predicted by eq 6 can be tested. In the series of zinc(II) and cadmium(II) complexes the extent of electron transfer from nitrogen to the metal is expected to be in the range of a few tenths of an electronic charge and to vary over a relatively narrow range throughout the series. Accordingly, we have employed these data to test eq 6. It is convenient to graph h/e^2Qq_{zz} vs. η, because $1/\alpha = e^2Qq_0/e^2Qq_{zz}$; values for K and L can then be determined from the graph by simply multiplying slope and intercept by the assumed value for e^2Qq_0/h.

The graphs of h/e^2Qq_{zz} vs. η for all the data for the zinc and cadmium complexes and for pyridine itself are shown in Figure 2. The line is constrained to pass through the pyridine datum. The data do indeed appear to define a reasonably good linear relationship. As an illustration of the application of the relationship we assume that e^2Qq_0/h is 9.0 MHz; and $2\theta = 120°$; this yields values of $a_0 = 1.203$ and $b_0 = 1.337$ for free pyridine. Using these values and the parameters of the line depicted in Figure 2 we obtain the relationship $B = -0.299 + 0.710A$.

If the model chosen is to be physically reasonable, A and B are subject to certain constraints. Both A and B should be positive; withdrawal of the lone pair electrons from nitrogen by a Lewis acid should result in an increase in the orbital occupancies of both the π and the other two σ orbitals. On the other hand, upper bounds for A and B are determined by the assumption that $A + 2B$ should be less than 1. That is, the total increase in populations of the other orbitals on nitrogen should be smaller than the loss in population in the donor orbital. Applied to the linear relationship between A and B indicated above, these considerations suggest that $0 < B < 0.17$ and $0.42 < A < 0.66$; thus, the allowable range for these parameters is not large. It seems reasonable to choose values in the middle of these ranges: $B = 0.08$, $A = 0.50$. Thus $2B + A = 0.66$; that is, about 66% of the charge withdrawn from nitrogen via the acid-base interaction is replaced by inductive electron shifts in the σ and π bonds. It is noteworthy that most of this shift occurs in the more polarizable π electron system, a result consistent with molecular orbital calculations (vide infra).

The evaluation of parameters can be carried through for other choices of e^2Qq_0. This causes changes in the values of a_0 and b_0 but not in the linear relationship between A and B. Similarly, a hybridization other than pure sp^2 could be assumed. The observed CNC angle in pyridine is 117°.[28] When hybridization consistent with this angle is assumed, the re-

Table II. ^{14}N Orbital Populations in Pyridine

e^2Qq_0, MHz	CNC angle, deg	a_0	b_0
8.4	120	1.145	1.290
8.4	117	1.097	1.241
9.0	120	1.203	1.337
9.0	117	1.156	1.290
10.0	120	1.282	1.403
10.0	117	1.240	1.361

Table III. Pyridine Donor Orbital Occupancies

Compd	σ	Compd	σ
py	2.00	$ZnBr_2(py)_2$	1.792 ± 0.001
$CdCl_2(py)_2$	1.87 ± 0.02		1.781 ± 0.002
$Cd(NO_3)_2(py)_3$	1.842 ± 0.001	$ZnCl_2(py)_2$	1.795 ± 0.003
	1.826 ± 0.003		1.789 ± 0.001
$Zn(NO_3)_2(py)_3$	1.826 ± 0.002	$Zn(NCS)_2(py)_2$	1.781 ± 0.006
	1.817 ± 0.006	$I(py)_2ClO_4$	1.640 ± 0.004
$Zn(NO_3)_2(py)_2$	1.767 ± 0.007	$Br(py)_2ClO_4$	1.57 ± 0.03
	1.761 ± 0.004	$HpyNO_3$	1.38 ± 0.01
$ZnI_2(py)_2$	1.793 ± 0.001		
	1.788 ± 0.001		

sultant equation between A and B is $B = -0.293 + 0.707A$. Table II summarizes the values of a_0 and b_0 calculated for various choices of CNC angle and e^2Qq_0.

To provide a basis for testing and applying the model it seems best to adopt a reasonable set of structural and model parameters and then to assume these fixed for all compounds studied. We adopt a CNC angle of 117°, the angle observed in pyridine. There is no evidence from the relatively imprecise crystallographic data for a marked change in this angle upon coordination of pyridine. We assume it remains at 117° in the pyridine adducts. For e^2Qq_0 we chose 9.0 MHz, a value in the midrange of those employed by various workers.[29,30] The effects of a variation in this quantity on the results extracted from the model are discussed below. We further assume that $A = 0.50$, which yields $B = 0.06$, so that $A + 2B = 0.62$. With these choices, it is possible to calculate e^2Qq and η as a function of σ, that is, as a function of the population of the nitrogen donor orbital. Graphs of e^2Qq and η vs. σ are shown in Figure 3. These graphs provide the connection between the NQR data and chemically interesting insights into the interaction between nitrogen and the Lewis acid. For any given compound, given the values of e^2Qq and η, one should be able to locate a place along these curves at which both data fit on their respective curves for the same value of σ. However, there are many factors that might cause either e^2Qq or η to deviate from the expected relationship. Most notably, interactions of the pyridine ring with atoms and ions of the solid lattice other than the one to which the pyridine ring is coordinated could cause distortions of the field gradient tensor. It is not obvious that such interactions would affect one of the two field gradient parameters more than the other. It is evident from the graph that for values of σ in the range 1.6 to 1.4 the dependence of η on σ is very sharp. One might expect relatively poor fits of both e^2Qq and η to the graphs in this region. However, the question of importance is how much uncertainty in σ is involved in fitting the data for a given nitrogen onto the graph.

Because the data for the zinc complexes and for $Cd(NO_3)_2(py)_3$ all fell very close to both curves, the data for these compounds are not shown. The pairs of points that are shown, in the order of decreasing values of σ, represent $CdCl_2(py)_2$, $I(py)_2ClO_4$, $Br(py)_2ClO_4$, and $HpyNO_3$, respectively. Table III lists the values of σ estimated from fittings in Figure 3 for all the compounds studied. The uncertainties assigned to these values are estimates of the uncertainties in fitting the data to the graph.

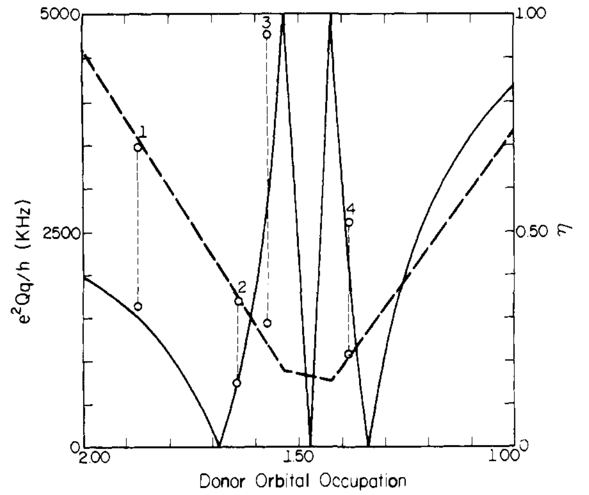


Figure 3. Quadrupole coupling constant, e^2Qq/h (KHz) (dashed line), and asymmetry parameter η vs. nitrogen donor orbital population in coordinated pyridine ($A = 0.50$, $B = 0.06$, $e^2Qq_0 = 9.0$ MHz, ∠CNC = 117°). The values of e^2Qq_0 and η calculated from the data for the Zn and Cd complexes other than $CdCl_2(py)_2$ lie on the lines and are not shown. The compounds for which the data are shown are: (1) $CdCl_2(py)_2$; (2) $I(py)_2ClO_4$; (3) $Br(py)_2ClO_4$; (4) $HpyNO_3$. For each compound the corresponding values of e^2Qq/h and η, connected by a dotted line, are placed along the horizontal scale to obtain the best match of each quantity to the calculated curves.

The nature of the curves for e^2Qq and η as a function of σ is such that in certain ranges of σ there is the possibility of some ambiguity in the placement of the data. For example, the data points for $I(py)_2ClO_4$ might have been placed on the graph at a much lower value for σ, around 1.3, albeit with poorer fit. The value for $Br(py)_2ClO_4$ could similarly have been fitted (though not as well) at lower σ. The points for $HpyNO_3$, on the other hand, could be fit as well at about 1.53 as at 1.38. However, the fits we have chosen can be defended as decidedly the best ones in terms of mimimizing differences between calculated and observed values of e^2Qq and η and on grounds of chemical reasonableness. For a given charge on the Lewis acid and a given coordination number, the value of σ should increase with increasing radius of the Lewis acid. Thus, the values of σ for the cadmium complexes are higher than for analogous zinc species. Similarly, the value of σ for $I(py)_2ClO_4$ should be larger than for $Br(py)_2ClO_4$, as it is in our placement. Finally, the value of σ for $HypNO_3$ should be substantially lower than for the other two monopositive ions examined.

It is perhaps worth pointing out that the points corresponding to values of η of 0 or 1 correspond to points at which the relative values of field gradient components along the molecular axes are changed. Thus, for example, at $\sigma = 1.68$ the x and y components are equal in magnitude. At $\sigma = 1.53$ the major axis direction is shifted to the direction normal to the plane of the molecule.

Significance of Derived Values of Donor Orbital Population. The model which leads to the results shown in Figure 3 and Table III may fail to give a precise description of the orbital populations at coordinated nitrogen for several reasons:

(a) The geometry about nitrogen might change upon adduct formation, contrary to the assumption of the model. So long as the bonding around nitrogen remains planar, small bond angle changes proportional to the energy of acid-base interactions are absorbed in the model in the form of assumptions about the σ orbital occupancies. In any event, the extant crystal structure data do not provide sufficiently accurate data on the geometry about the nitrogen in coordinated pyridine to reveal

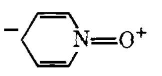
Table IV. Orbital Populations from Molecular Orbital Calculations of NC_5H_5 and $HNC_5H_5^+$ [35]

	Mulliken population	
Nitrogen orbital	NC_5H_5	$HNC_5H_5^+$
Lone pair (donor)	1.95	1.15
p_π	1.08	1.30
N-C σ bond	1.11	1.156

whether bond angle changes do indeed occur. It seems reasonable to suppose that they are small.

(b) The assumption regarding the values for A and B may be in error. However, within the limitations of the model, changes in A and B do not change the derived values for σ by very much. As an example, if it assumed that $A = 0.60$ rather than 0.50 as in Figure 3, the resulting curves yield a value of σ for $HpyNO_3$ of 1.43 rather than 1.38. The values for the other compounds are increased also by lesser amounts; the effect is to slightly compress the horizontal scale in Figure 3. Conversely, a slight decrease in A extends the horizontal scale slightly, but the changes are not large. Similarly, assumption of the CNC angle of 120° rather than 117° does not produce significant changes in the values for σ. None of these altered assumptions has the effect of changing the ordering of the compounds with respect to relative σ values.

(c) The possibility exists that bonding to the acid may involve the π system of the ring. For example, there might be a back-donation from the acid into the pyridine π^* orbitals. The effects of such bonding would be to increase the value of a over that predicted by eq 2 and possibly reduce the value for b. It is not likely that π bonding effects are important in any of the compounds studied here, except for picoline N-oxide. Bond distance and dipole moment data[31-33] suggest that there is some contribution of resonance structure **1** to the ground state



1

of pyridine N-oxides. It is noteworthy that the NQR data for picoline N- oxide do not fit well on the graph of Figure 3. One would expect σ for the N-oxide to be smaller than for Hpy^+. The presence of the 4-methyl group on the ring is a sufficiently small perturbation so that the picoline data should fit on the pyridine graph quite well. However, there is no reasonable value of σ in the range below 1.4 in which the picoline N-oxide data can be fitted. Modifications to the model presented here will need to be developed to take account of π bonding effects. It seems premature, however, to attempt such an extension at this time; the model requires further testing and development with systems in which π bonding effects can be neglected.

(d) The value chosen for e^2Qq_0 may be in error. Alteration in the assumed value of e^2Qq_0 results in an extension or contraction of the horizontal scale. For example, if it is assumed that e^2Qq_0 is 10.0 MHz, with all other assumptions as in Figure 3, the best value of σ for Hpy^+ is 1.45, as compared with 1.38 for the assumption that e^2Qq_0 is 9.0 MHz. If a consistent choice is made for e^2Qq_0, the relative values of σ are not altered.

There is also the possibility that the value for e^2Qq_0 is not invariant to the charge on nitrogen. Although it is difficult to assess the possible importance of this factor, it seems unlikely that the changes in charge at nitrogen in the systems studied here are sufficiently large to significantly alter the appropriate value for e^2Qq_0.

It thus appears reasonable to assume that the values of σ derived for pyridine in coordination environments in which π bonding effects can be neglected form an internally consistent set of parameters related to the degree of electron transfer from nitrogen to the Lewis acid. There remains the question of whether the values can be taken in any absolute sense as a measure of actual orbital populations. There is an inherent difficulty in attempting to answer this question, because orbital populations do not possess independent operational significance in terms of other experiments. In relating σ values to the results of calculations there is a problem in deciding on an appropriate population analysis. As an example, calculation of the wave functions for NC_5H_5 and $HNC_5H_5^+$ using a parameter-free semiempirical MO method[34] yielded the results shown in Table IV. The orbital populations correspond to a Mulliken Population analysis and include half the overlap populations with AO's on other centers.[29] These results show, as expected, that the lone pair orbital population is considerably decreased on binding to H^+. The calculated orbital population in the pyridinium ion is, in fact, considerably lower than the estimate from the NQR data. The calculations also show that both the σ and π nitrogen orbital populations increase on formation of the ion, in accord with the assumptions of the model. Furthermore, the results show that the π orbital population increases considerably more than the σ orbital population, corresponding to our finding that A is considerably larger than B. The extent of agreement between calculated and derived quantities based on experimental data cannot be pursued beyond these rough comparisons because of the limited basis for comparison, as discussed above.

The ^{127}I NQR data yield an estimate of net charge of +0.39 on the central iodine in the cation in $I(py)_2^+I_3^-$.[36] Assuming that this is the same in the perchlorate salt, this suggests that the value of σ for the coordinated pyridines should be 1.70. Our value of 1.64 is not far from this. It thus appears that in this case an analysis of orbital populations based on the Townes-Dailey model accounts to within about 10% for all of the bonding electrons in the donor-acceptor interactions. It is interesting to apply this consideration to estimate the net charge on zinc in $Zn(py)_2Cl_2$. The ^{35}Cl quadrupole transition in this complex occurs at about 10.2 MHz. This corresponds to an estimated charge on each chlorine of −0.81.[37] Combining this with the σ value of 1.79 for the nitrogens of the two pyridines leads to an estimated charge of +1.2 on the central metal.

^{14}N NQR Data for NO_3^- and NCS^- Groups. The ^{14}N transitions due to the nitrate ligands were observed in $HpyNO_3$, $Zn(NO_3)_2(py)_2$, $Zn(NO_3)_2(py)_3$, and $Cd(NO_3)_2(py)_3$. The only other field gradient data for ^{14}N in nitrate are derived from the high-field NMR studies of $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$,[38] $UO_2(NO_3)_3\cdot 6H_2O$,[39] and $RbUO_2(NO_3)_3$.[39] In all these cases e^2Qq/h and η are in the vicinity of 0.650 MHz and 0.5, respectively. In at least the case of $UO_2(NO_3)_3\cdot 6H_2O$ the nitrato groups are coordinated in bidentate fashion to the metal. The present data for the zinc complexes differ significantly from the earlier results in that e^2Qq/h is lower and η larger. Since $\eta \approx 0$ in the isolated NO_3^- ion of D_{3h} symmetry, the departure of η from zero might be taken as a measure of the distortion resulting from coordination. Assuming that the major component of the field gradient tensor remains along the idealized threefold axis, the data suggest that the distortions resulting from coordination are more severe in the zinc(II) compounds than in the previously studied cases. In both zinc complexes the nitrato groups are more nearly monodentate than bidentate in relation to the metal, as evidenced by asymmetry in the metal-oxygen distances. In $Cd(NO_3)_2(py)_3$ the nitrato groups are apparently bidentate; the Cd-O distances are considerably longer than the shorter Zn-O distance in each zinc complex. Correspondingly, η is smaller for the cadmium complex. The data thus far available indicate that the NQR experiment could prove to be a sensitive measure of distortions in nitrate groups.

Table V. NQR Data for Thiocyanate and Isothiocyanate

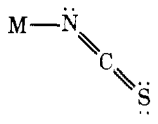
Compd	e^2Qq/h, kHz	η	Ref
CH_3SCN	3515	0.473	*a*
p-$C_6H_4(SCN)_2$	3545	0.467	*a*
LiSCN	2607	0.016	*b*
KSCN	2431	0.028	*c*
HNCS	1200		*d*
$Zn(py)_2(NCS)_2$	947	0.211	This work
	887	0.224	
HNCO	1981	0.205	*e*

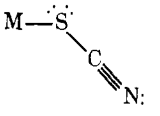
[a] R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **70**, 3626 (1966). [b] T. Oja and E. Schempp, unpublished results, 1968. [c] R. Ikeda, D. Nakamura, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **40**, 701 (1967). [d] J. N. Schoolery, R. G. Shulman, and D. M. Yost, *J. Chem. Phys.*, **19**, 251 (1951) (based on gas phase microwave spectral data). [e] G. L. Peterson and P. J. Bray, *Bull. Am. Phys. Soc.*, **14**, 435 (1969).

However, it will be necessary to acquire a wider range of data for substances with established structures before much progress can be made.

Several spectroscopic studies of $Zn(NCS)_2(py)_2$ with the aim of determining the mode of NCS^- coordination have yielded divergent views,[40-44] with the weight of evidence seeming to favor N-coordination of terminal NCS ligands. It seems clear that more than one pyridine complex of $Zn(NCS)_2$ can be formed.

The ^{14}N NQR spectrum of $Zn(NCS)_2(py)_2$ shows transitions ascribable to coordinated NCS^-. Coordination through S would result in an electronic environment for ^{14}N similar to that in organic thiocyanate species; two examples are listed in Table V. This table also lists ^{14}N EFG parameters for ionic thiocyanate environments, and a single datum from a microwave study for an N-coordinated species, HNCS. It is evident from inspection of the predominant Lewis structures, **2** and **3**,





that the NQR parameters at ^{14}N should differ greatly in the two cases. It is also evident that the ^{14}N data for $Zn(NCS)_2(py)_2$ require N coordination. The present results provide a demonstration that the ^{14}N NQR data can easily distinguish the alternative modes of NCS^- coordination.

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References and Notes

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(3) To whom correspondence and reprint requests should be addressed.
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