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Nitrogen-14 Nuclear Quadrupole Resonance Spectra of Coordinated Pyridine. An Extended Evaluation of the Coordinated Nitrogen Model[1]

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The ^{14}N NQR spectra at 77 K of several solid pyridine complexes with a wide range of Lewis acids have been measured by a double-resonance method. The data are interpreted in terms of a coordinated nitrogen model, which permits an estimation of σ, the occupancy of the nitrogen donor orbital directed toward the Lewis acid. The values observed for σ in a series of pyridinium salts permit an ordering of the strength of hydrogen bonding to the anions: $HSO_4^- \approx NO_3^- > Cl^- > ClO_3^- > Br^- > ClO_4^-$. The ^{14}N NQR data correlate well with the NQR data for the hydrogen-bonded ^2H in these compounds. From comparisons of σ values it is possible to order the acidities of the Lewis acids as follows: $Li^+ < Ag^+ < Cd^{2+} \approx Mo(0) \approx Cr(0) < Zn^{2+} \approx Hg^{2+} \sim Fe(0) < BR_3 < BCl_3 < BBr_3 < SO_3 < H^+ \approx CH_3^+$. The relative positions in a few cases are uncertain because an insufficient number of complexes have been studied to date.

The advent of the double-resonance, level-crossing techniques for determination of ^{14}N NQR spectra[2] has for the first time permitted systematic study of the electronic environment about coordinated nitrogen. The NQR spectra of complexes containing coordinated glyoximes,[3] pyridine,[4] 1,10-phenanthroline,[5] imidazole,[6] and other ligands[7,8] have recently been reported. The ^{14}N NQR data have been interpreted in terms of a model for coordinated nitrogen based upon adaptation of the classic Townes–Dailey model.[9] In the Townes–Dailey model, the field gradient is accounted for in terms solely of the valence level p orbitals of the atom containing the quadrupolar nucleus. Adaptation of this model to coordinated nitrogen provides a straightforward means by which the NQR data may be interpreted in terms of nitrogen orbital populations. For a base such as pyridine, the model permits an estimation of the donor orbital occupancy; i.e., it provides a means of assessing the degree of electronic charge transfer from nitrogen to the Lewis acid to which it is bound.[4]

If the coordinated nitrogen model can be shown to give a reasonable accounting of the charge distribution about nitrogen in a wide range of Lewis acid–base adducts of pyridine, the NQR experiment can then be used to probe the acidities of acid sites via the effects of those acids upon the electric field gradient (EFG) parameters of the bound nitrogen. Our first report of the application of this model to pyridine adducts was based upon a fairly limited number and variety of Lewis acids.[4] Since that time a much broader range of acid–base adducts has been studied. The results show, first of all, that ^{14}N NQR data can be obtained for a wide range of Lewis acid types. Second, the data obtained permit a reevaluation of the model and a more thorough and extensive testing of its range of applicability. Our purpose in this contribution is to present the extended data set, to test the range of applicability of the model, and to illustrate the application of the results to several problems of chemical interest.

Experimental Section

Sample Preparation. Pyridinium perchlorate, $C_5H_5NHClO_4$, was prepared by adding an excess of pyridine to concentrated perchloric acid. Most of the excess water was then allowed to boil off and the solution cooled to room temperature. The solid was filtered, recrystallized from 95% ethanol, and dried under vacuum over concentrated H_2SO_4 to remove any excess pyridine.

Pyridinium chlorate, $C_5H_5NHClO_3$, was prepared by dissolving 30 g of $Ba(ClO_3)_2$ (0.1 mol) and 16 mL of pyridine (0.2 mol) in 60 mL of water followed by the dropwise addition of 5.5 mL of 9 M H_2SO_4 (0.1 mol). This mixture was cooled with ice and filtered to remove the precipitated $BaSO_4$. The water solution was evaporated to a volume of 30 mL and cooled. The pyridinium chlorate precipitate was purified similarly to pyridinium perchlorate.

The extremely hygroscopic **pyridinium chloride,** C_5H_5NHCl, was prepared by using anhydrous hydrogen chloride via literature methods,[10] but in preparing pyridinium-d_1 chloride it was necessary to begin with DCl in D_2O. Ten milliliters of pyridine was added to 10 mL of concentrated DCl in D_2O. This solution was placed in the left portion of a drying tube and warmed while evacuating to pull off most of the D_2O. Phosphorus pentoxide was added to the right compartment, and the pyridinium chloride was dried 12 h at 70 °C. The temperature was raised to approximately 130 °C in order to slowly sublime the pyridinium chloride onto the walls of the central section. Drying followed by sublimation was repeated.

Pyridinium hydrogen sulfate, $C_5H_5NH(HSO_4)$, was prepared by the dropwise addition of a stoichiometric quantity of concentrated sulfuric acid to dry pyridine in dry CCl_4 at 0 °C. The precipitate was filtered and dried for 2 days under vacuum over concentrated H_2SO_4 followed by 2 days over P_2O_5.

Pyridinium bromide, C_5H_5NHBr, was prepared from the adduct of pyridine with bromine. Repeated washing of the red py–Br_2 adduct with wet chloroform gave a white product characterized as pyridinium bromide.

(Pyridine)lithium chloride, $Li(C_5H_5N)Cl$, was prepared by adding 15 g of anhydrous LiCl to 80 mL of anhdyrous pyridine. The solution was refluxed several minutes and filtered. The solution was cooled to 60 °C; the $Li(C_5H_5N)Cl$ that crystallized was filtered and dried under vacuum 12 h over concentrated H_2SO_4, giving a yield of 6.1 g.

Bis(pyridine)aquochlorolithium, $Li(C_5H_5N)_2(H_2O)Cl$, was prepared from the $Li(C_5H_5)Cl$ filtrate. To the filtrate was added 4 mL of H_2O. This mixture was warmed to give a clear solution and then cooled to precipitate $Li(py)_2(H_2O)Cl$. This product was dried under vacuum 20 min over concentrated H_2SO_4 to give a 7 g yield. Prolonged drying converts the product back to LiCl. For both lithium complexes the stoichiometry was adjusted such that no excess pyridine would be present in the products.

1-(Methyl-d_3)pyridinium Iodide, $C_5H_5NCD_3I$. A quantity of CD_3I was condensed into a flask on a vacuum line; diethyl ether as solvent

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Table I. Nitrogen-14 NQR Transition Frequencies (kHz) for Coordinated Pyridine at 77 K

compd	ν_+	ν_-	ν_0
py·HCl	841	556	286
py·HBr	565	387	(178)
py·$HClO_3$	741	391	350
py·$HClO_4$	503	466	(37)
py·H_2SO_4[a]	1325	1070	255
	890	591	299
py·DCl[a]	818	563	255
	842	547	295
Li(py)Cl	3512	2810	702
Li$(py)_2(H_2O)$Cl	3523	(2758)	765
py·BCl_3	935	636	301
py·BBr_3	842	530	312
py·BR_3[a, b]	1394	(941)	453
py·CD_3I	418	399	(19)
py·Cl_2	1527	979	548
py·O[a]	1100	(690)	410
py·SO_3[a]	767	535	332
$[Zn(py)_4](ClO_4)_2$	2036	1876	(160)
$[(py)_2Br]PF_6$	1122	1001	(121)
$[(py)_2Br]Br_3$	1255	1091	(164)
	1021	925	(96)
$[(py)_2Br]ClO_4$[c]	1396	1222	(172)
	722	680	(42)
py·BrCl	879	820	(59)
$Cd_2(py)_3(NO_3)_4$[a]	2370	2040	330
	2370	1960	410
Fe(py)$(CO)_4$	2047	1664	438
Mo$(py)_2(CO)_4$[d]	2589	2136	453
$[Ag(py)_2]ClO_4$	2275	1901	374
	2227	1711	516
$[Ag(py)_4]ClO_4$	2638	2137	501
	3130	(2460)	670
	2638	(2045)	593
py·ICN	2844	2307	537
py·ICl	1432	1263	(169)
py·IBr	1528	1334	194
py·I_2	2219	2751	368
$[(py)_2I]I_7$	1313	1288	(85)
Hg(py)Cl_2	1652	1439	213
	2182	1776	406

[a] Resonances are measured to ±20 kHz due to weak signals or broad lines. [b] BR_3 = 7-bora-1,2,3,4,5,6,7-heptaphenylbicyclo[2.2.1]heptadiene. The compound was supplied by Professor J. J. Eisch. [c] Reported previously but reexamined and reassigned. [d] Compound prepared by Peter A. Bellus, University of Illinois.

and an excess of pyridine were then added. The mixture was allowed to react for several days in the dark. The precipitate was filtered, recrystallized twice from ethanol, and dried under vacuum.

Pyridine–boron trichloride, $C_5H_5N{\cdot}BCl_3$, and **pyridine–boron tribromide** were prepared similarly from pyridine and respective boron halide. The BBr_3 was initially stirred with a drop of mercury in order to remove excess Br_2, while the BCl_3 was used directly from a gas cylinder. Stoichiometric quantities of pyridine and boron trihalide were condensed together and slowly warmed to room temperature. The flask was evacuated and warmed to remove unreacted acid or base. The pyridine–boron trihalides were recrystallized twice by using benzene and dried under vacuum. All operations were carred out by using Schlenk techniques.

Tetrakis(pyridine)silver(I) perchlorate, $[Ag(C_5H_5N)_4]ClO_4$, was prepared by recrystallizing bis(pyridine)silver(I) perchlorate from a 5:1 chloroform–pyridine mixture. The product was washed with diethyl ether and air-dried to give a pyridine:silver ratio of approximately 4:1. Satisfactory analyses were not obtained due to loss of pyridine in handling the compound.

A preparation of **(pyridine)tetracarbonyliron(0)**, $Fe(C_5H_5N)(CO)_4$, is reported in the literature with $Fe_2(CO)_9$ as a starting material.[11] We employed $Fe(CO)_5$ as starting material in a modification of the preparation of (trimethylamine)tetracarbonyliron(0).[12] A solution of 2.5 g of $(CH_3)_3NO{\cdot}2H_2O$ in 30 mL of tetrahydrofuran (THF) was cooled in a salt–ice bath. A large excess of pyridine (8 mL) was added, followed by 3.6 mL of $Fe(CO)_5$ (a 20% excess) in 30 mL of THF. The resultant solution was warmed to room temperature and allowed to react for 7 h. The THF, trimethylamine, pyridine, and $Fe(CO)_5$ were evaporated off under vacuum. The product was recrystallized three times from low-boiling petroleum ether by dissolving the compound at 0 °C, collecting the precipitate at −78 °C, and drying under vacuum at room temperature. All steps were performed in inert atmosphere. The orange product is air stable and is thermally stable at room temperature for several weeks. Attempts to prepare this compound directly, by using pyridine *N*-oxide in analogy to the preparation of $(CH_3)_3NFe(CO)_4$ from trimethylamine *N*-oxide,[12] gave no reaction.

Pyridine–sulfur trioxide,[13] tris(pyridine)tetranitrodicadmium(II),[14] and pyridinedichloromercury(II)[15] were prepared by literature methods. Preparation and ^{14}N NQR spectra for the remaining compounds are described elsewhere.[4,16] Elemental analyses were obtained for all samples prepared in our laboratory. Except where noted, the analytical results were satisfactory.

The ^{14}N NQR measurements were carried out as described previously.[3,4]

Results

The observed ^{14}N NQR spectra of coordinated pyridine newly reported in this paper are listed in Table I. In certain cases ν_0 transitions fell in a range inaccessible with our instrumentation (below about 200 kHz); in other cases the ν_- transitions were very weak. The values listed in Table I in parentheses were not observed but were calculated from the other two assigned transition frequencies. In general, ν_+ and ν_0 are measured to within about 1 kHz, and ν_- is observed to within about 2 kHz. In a few cases, because the signals were very weak or exceptionally broad, the uncertainties are larger. The compounds for which this is the case are denoted by the appropriate footnote in Table I. Table II lists the values calculated for the quadrupole coupling constant, e^2qQ/h, and asymmetry parameter, η, for all coordinated pyridine systems, including those reported earlier.

Discussion

In extending the Townes–Dailey type of analysis to nitrogen, the three components of the diagonalized field gradient tensor, q_{xx}, q_{yy}, and q_{zz}, are expressed in terms of the nitrogen atom 2p orbital occupancies, N_{p_x}, N_{p_y}, and N_{p_z}:

$$\begin{aligned} q_{xx} &= [N_{p_x} - \tfrac{1}{2}(N_{p_y} + N_{p_z})]q_0 \\ q_{yy} &= [N_{p_y} - \tfrac{1}{2}(N_{p_x} + N_{p_z})]q_0 \\ q_{zz} &= [N_{p_z} - \tfrac{1}{2}(N_{p_x} + N_{p_y})]q_0 \end{aligned} \tag{1}$$

Here, q_0 is the field gradient parameter for one electron in the nitrogen 2p orbital directed along the *z* axis. For a nitrogen atom in a bonding environment with C_{2v} site symmetry, hybrid

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Table II. ^{14}N Quadrupole Coupling Constant, Asymmetry Parameter (η), and Donor Orbital Occupancy (σ) for Coordinated Pyridine Complexes[a]

compd	e^2Qq/h,[17] MHz	η	σ	δ,[b] MHz
py	4.584	0.396	1.999	0.008
py·HNO_3	1.090	0.509	1.543	0.108
py·H_2SO_4	1.197	0.426	1.556	0.123
	0.987	0.606	1.530	0.094
py·HCl	0.931	0.612	1.524	0.051
py·DCl	0.921	0.624	1.523	0.050
	0.926	0.637	1.523	0.063
py·$HClO_3$	0.755	0.928	1.501	0.065
py·HBr	0.635	0.560	1.469	0.005
py·$HClO_4$	0.646	0.115	1.450	0.053
Li(py)Cl	4.215	0.333	1.947	0.111
$Li(py)_2(H_2O)Cl$	4.187	0.365	1.947	0.017
py·BR_3	1.247	0.144	1.570	0.076
py·BCl_3	1.047	0.575	1.537	0.121
py·BBr_3	0.915	0.682	1.521	0.081
py·SO_3	0.801	0.829	1.507	0.060
	0.712	0.927	1.497	0.020
py·CD_3I	0.545	0.070	1.440	0.055
py·O	1.227	0.619	1.283	0.160
$Zn(py)_3(NO_3)_2$	3.172	0.251	1.813	0.080
	3.180	0.231	1.813	0.234
$Zn(py)_2Cl_2$	2.977	0.207	1.787	0.118
	2.913	0.202	1.779	0.109
$Zn(py)_2I_2$	2.942	0.208	1.783	0.106
	2.900	0.201	1.777	0.108
$Zn(py)_2Br_2$	2.923	0.209	1.780	0.099
	2.855	0.198	1.771	0.101
$Zn(py)_2(NCS)_2$	2.888	1.181	1.774	0.143
$Zn(py)_2(NO_3)_2$	2.672	0.180	1.748	0.080
	2.649	0.166	1.745	0.098
$[Zn(py)_4](ClO_4)_2$	2.608	0.123	1.737	0.160
py·ICN	3.434	0.313	1.850	0.004
py·I_2	2.580	0.285	1.744	0.127
py·IBr	1.908	0.203	1.659	0.177
py·ICl	1.797	0.188	1.645	0.190
$(py)_2I]\,I_7$	1.694	0.100	1.621	0.104
$[(py)_2I]\,ClO_4$	1.693	0.142	1.619	0.151
$[(py)_2Br]\,ClO_4$	1.745	0.199	1.639	0.218
	0.936	0.090	1.536	0.269
$[(py)_2Br]Br_3$	1.564	0.210	1.602	0.155
	1.297	0.149	1.575	0.046
$[(py)_2Br]PF_6$	1.415	0.171	1.587	0.036
py·BrCl	1.133	0.105	1.558	0.164
py·Cl_2	1.671	0.656	1.226	0.007
$[Ag(py)_4]ClO_4$	3.727	0.360	1.890	0.051
	3.183	0.315	1.819	0.053
	3.122	0.380	1.817	0.201
$Cd(py)_2Cl_2$	3.432	0.320	1.850	0.013
$Cd(py)_3(NO_3)_2$	3.327	0.268	1.833	0.081
	3.174	0.252	1.814	0.074
$Mo(py)_2(CO)_4$	3.150	0.288	1.813	0.004
$Cd_2(py)_3(NO_3)_4$	2.940	0.224	1.783	0.074
	2.887	0.284	1.781	0.055
$[Ag(py)_2]\,ClO_4$	2.784	0.269	1.768	0.051
	2.625	0.393	1.756	0.306
$Hg(py)Cl_2$	2.639	0.308	1.753	0.154
	2.061	0.207	1.677	0.139
$Fe(py)(CO)_4$	2.402	0.319	1.724	0.222

[a] $A = 0.446$; $B = 0.087$. [b] The standard deviation of δ is δ_σ(min) = 0.12 MHz.

atomic orbital populations may be written in terms of 2s and 2p atomic orbital occupancies:

$$a = N_{p_y}$$
$$b = \tfrac{1}{2}[\cot^2(\alpha/2)]N_{p_z} + \tfrac{1}{2}[1 - \cot^2(\alpha/2)]N_s + \tfrac{1}{2}N_{p_x} \tag{2}$$

$$\sigma = [1 - \cot^2(\alpha/2)]\,N_{p_z} + [\cot^2(\alpha/2)]N_s \tag{3}$$

The parameter a represents the population of the nitrogen p_π orbital; b represents the population of the nitrogen orbitals in the σ bonds to carbon; σ represents the population of the nitrogen orbital in the acid–base σ bond to the Lewis acid A (we term this the donor orbital occupancy); α represents the CNC internal bond angle (Figure 1).

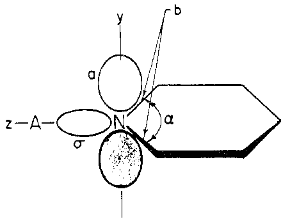

Figure 1. Coordinate system and bond population parameters in coordinated pyridine model. A represents the Lewis acid.

In addition to the assumption of C_{2v} point group symmetry at nitrogen, the model also assumes that no nitrogen atom orbitals above the valence level make a significant contribution. Further, the nitrogen 2p orbitals are assumed to all have equivalent radial character. Contributions to the field gradient from charge distributions outside the valence orbitals are assumed to be negligible. Since the one-electron field gradient operator contains a r^{-3} dependence, neglect of external charges is a reasonable assumption in the molecular systems under consideration here.

The donor orbital occupancy, σ, is of primary interest in the interpretation of the ^{14}N NQR data for coordinated pyridine. We assume that e^2Qq_0/h has a constant value of 9.0 MHz and that α is constant at 117°, as in our previous use of the model.[17] If a and b are written as functions of σ, then q_{xx}, q_{yy}, and q_{zz} are functions of σ only. As before, we assume an inductive response which causes the values of a and b to vary with the degree of charge removal from nitrogen via the acid–base interaction:

$$a = a_0 + A(2 - \sigma) \tag{4}$$

$$b = b_0 + B(2 - \sigma) \tag{5}$$

That is, the populations of the p_π and nitrogen σ orbitals directed toward carbon increase in proportion to the degree of electron withdrawal from nitrogen in the acid–base interaction. The quantities a_0 and b_0 are the occupancies of the nitrogen p_π and σ orbitals in the free base, in which the donor orbital contains the lone pair of electrons and is thus assumed to have a population of 2.

In the simplest application of this model, the constants A and B are assumed to be the same for all acid–base adducts of pyridine. Thus, for a series of j adducts, the number of unknown quantities to be determined from the NQR data is $j + 2$.

The quantity $A + 2B$ represents the fractional charge which moves onto the nitrogen in the π and σ bonds in response to a removal of unit charge from the nitrogen atom via the donor interaction with the Lewis acid. The quantities A and B cannot be varied independently, because there are only two independent parameters in the field gradient tensor. For any one compound, there are three unknown quantities, σ, a, and b. We have previously described the physical limitations which apply to the possible values for A and B. We employ here the same criteria as before that $A + 2B = 0.62$, $a_0 = 1.156$, and $b_0 = 1.290$. The effects on the derived quantity σ of varying the sum $A + 2B$ have been discussed.[4] Only small changes in the values for σ and *no* change in the relative values among compounds result from variation of A and B within physically reasonable limits.

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(17) Because q_0 is negative and Q is positive, e^2Qq_0/h is negative in sign. In any given compound the sign of e^2Qq/h may be positive or negative depending on the nitrogen 2p orbital populations. We have avoided denoting a sign for e^2Qq/h in Table II because the sign is not measured in the NQR experiment. However, the sign of e^2Qq/h can be predicted from the model for any given case by referring to Figure 2.

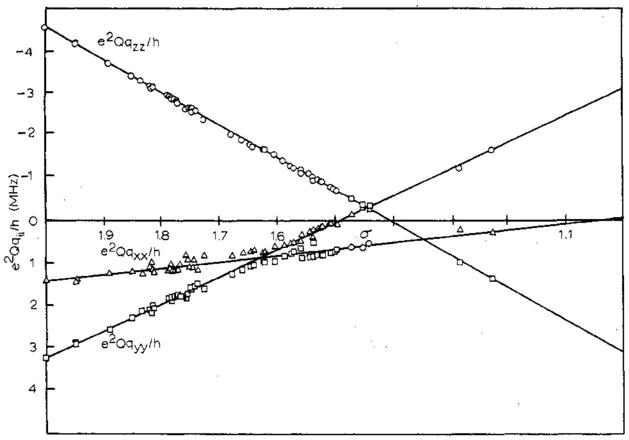

Figure 2. Comparison of calculated and observed ^{14}N field gradient tensor components as a function of donor orbital occupancy, σ, for pyridine complexes. In this figure the circles represent e^2Qq_{zz}/h, that is, the largest component of the field gradient tensor, regardless of sign. Similarly, the triangles and squares represent e^2Qq_{xx}/h and e^2Qq_{yy}/h, respectively. Where the lines cross, there is change in the quadrupolar axis labeling, and there may be a change in the sign of e^2Qq/h.[17]

For each compound, from the experimental quadrupole coupling constant and asymmetry parameter, values for q_{xx}', q_{yy}', and q_{zz}' may be calculated. Prime symbols denote the quadrupole Hamiltonian axis system, as opposed to the molecular axis system depicted in Figure 1. Six possible orientations of the primed axis system with respect to the molecular axis system exist. For each, the major component, q_{zz}, may be positive or negative. In fitting the experimental data to the model, all 12 possibilities are considered, and values of σ are calculated for each compound based upon the most reasonable values for A and B. The extent, δ, to which each set of experimental field gradient parameters results in a deviation from the predictions of the model is calculated as

$$\delta = (\delta_x^2 + \delta_y^2 + \delta_z^2)^{1/2} \qquad (6)$$

In this expression, each δ_i is the difference between one of the diagonal field gradient components calculated from the experimental data and the value of q_{ii} calculated for a particular value of σ for that compound. The values of σ, different for each compound, and A and B, common to all the compounds in the data set, are varied to attain a minimum value of the deviations δ for all of the pyridine EFG data listed in Table II. The minimum standard deviation $\delta_\sigma(\text{min}) = 0.12$ MHz is attained for $A = 0.446$, $B = 0.087$, and the values of σ listed in Table II. The comparison of observed and calculated quantities is shown in Figure 2. The experimentally determined values of e^2Qq_{xx}/h, e^2Qq_{yy}/h, and e^2Qq_{zz}/h are shown as data points. The points for each compound are placed on the figure at the value of σ determined from the minimization routine described above. The calculated variations in e^2Qq_{xx}/h and e^2Qq_{zz}/h as a function of σ, based on the parameters indicated above, are shown as lines.

The display of the data indicated in Figure 2 shows that the model described above accounts for the ^{14}N NQR data for coordinated pyridine extraordinarily well, over a wide range of donor orbital occupancies. The variation in the calculated values of e^2Qq_{zz}/h and asymmetry parameter η as a function of donor orbital occupancy is displayed in Figure 3. The asymmetry parameter is given by the expression

$$\eta = (q_{xx}' - q_{yy}')/q_{zz}' \qquad (7)$$

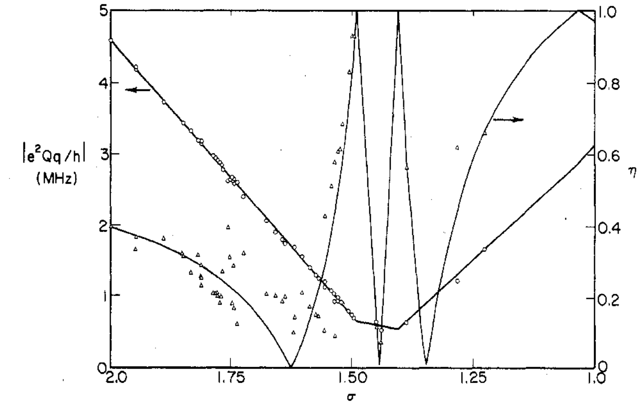

Figure 3. Calculated variation in ^{14}N quadrupole coupling constant and asymmetry parameter as a function of donor orbital occupancy σ. Experimental data are shown by circles (e^2Qq/h) and triangles (η).

The deviations between experimental and calculated field gradient components are magnified in the calculation of the asymmetry parameter. It is thus not surprising that the scatter in η is large, as indicated in Figure 3. Figure 2 represents a more useful indication of the extent of agreement between calculated and observed quantities. To put it another way, in the comparison of calculated and observed quantities, the emphasis should be placed on the fit with e^2Qq_{zz}/h rather than with η.

Some reduction in the deviation between calculated and observed quantities can be achieved by introducing additional empirical parameters. This might be accomplished in several ways. Modification of eq 4 and 5 to give

$$\begin{aligned} a &= a_0 + A(2 - \sigma) + A'(2 - \sigma)^2 \\ b &= b_0 + B(2 - \sigma) + B'(2 - \sigma)^2 \end{aligned} \qquad (8)$$

leads to minimum deviations for values of $A = 0.47$, $B = 0.08$, $A' = -0.03$, and $B' = 0.03$. However, the $\delta_\sigma(\text{min})$ is reduced by this addition of two additional parameters to only 0.11 MHz.

The introduction of an additional parameter related to the bond angle α was made as follows:

$$\alpha = 117° + D(2 - \sigma)$$

A $\delta_\sigma(\text{min})$ of 0.11 MHz is achieved for $A = 0.45$, $B = 0.09$, and $D = 4°$. The very small improvements noted do not justify inclusion of these additional parameters.

The overall quality of fit of the calculated and experimental values of electric field gradient components, as depicted in Figure 3, is very good. The Lewis acids employed span a wide range in terms of acid strength, size, and acid character in terms of hardness/softness[18] or E/C[19] values. Nevertheless, it is true that subsets of compounds within the large set can be fitted with different values of A to produce smaller standard deviations for the set. Table III shows the values of A which give the best fit between calculated and experimental quantities for $B = 0.08$. In several cases, individual compounds which exhibit rather large deviations from the best general fit are also listed.

The value of A would be particularly sensitive to any π bonding between pyridine and the Lewis acid. This π bonding might take the form of a back-bonding, in which case π-electron density is transferred to the nitrogen orbital from the Lewis acid in a synergistic mode. We would expect that the degree of π bonding between the Lewis acid and pyridine should be proportional to the degree of σ-charge donation from pyridine to the Lewis acid. Thus we may write

$$a = a_0 + (A + C_\pi)(2 - \sigma) \qquad (9)$$

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Table III. Optimal Values of A for Individual Compounds and Groups of Compounds for $B = 0.08$

	no. of NQR data sets	A	δ_σ(min), MHz
all compounds	58	0.44	0.12
pyridinium salts	9	0.45	0.04
zinc complexes	12	0.51	0.02
cadmium complexes	5	0.46	0.06
silver and mercury complexes	7	0.36	0.09
pyridine–halogen complexes	13	0.35	0.07
pyridine–IX (X = I, Br, Cl)	3	0.37	0.01
pyridine N-oxide	1	0.60	
Li(py)Cl	1	0.75	
Li(py)$_2$(H$_2$O)Cl	1	0.48	
Fe(CO)$_4$(py)	1	0.34	
Mo(CO)$_4$(py)$_2$	1	0.44	

Here the C term represents that portion of the p_π orbital population on nitrogen which is due to π back-bonding from the Lewis acid to the metal. We may take the pyridinium salts, which can involve only the σ bond of nitrogen, as providing a standard value for A, free of any π-bonding effects. Thus, when the apparent value for A obtained from use of eq 4 is different from 0.46, the changed value might be ascribed to π bonding. Pyridine N-oxide represents an example in which such π-bonding effects are clearly important. A small amount of π back-bonding could be responsible for the larger value of A observed for the 12 zinc-coordinated nitrogens. An extent of π bonding of less than 5% of the σ bonding would not be expected to affect the metal–nitrogen distances materially.[20]

There is also some possibility that π bonding might occur in the opposite direction, i.e., in the form of electron donation from the p_π orbital of nitrogen to the Lewis acid. In this event C_π should be negative in sign. There are few cases in which such an effect is likely. Certainly most of those cases in Table III for which the value of A is markedly less than 0.46 do not represent such examples. We thus conclude that the variation in the optimal value of A is, with just a few exceptions, due to variation in a characteristic of the Lewis acid other than its π-acid or π-base character.

The Lewis acids considered in this study vary enormously in their Lewis acid strength, size, and polarizabilities. Since the model we are employing is quite simplistic in taking account only of the electron distribution which is presumed to occupy the nitrogen valence orbitals, large variations in bond overlaps and polarization effects could lead to distortions in the electron distribution which would differentially affect the orbitals on nitrogen. It is noteworthy that the systems for which A in Table III is decidedly less than 0.46 are low-valent, polarizable systems.

There seems to be no ready and reliable means at present of making a correction for such ill-defined effects upon the EFG parameters of the coordinated nitrogen. Fortunately, it develops that the values of donor orbital occupancy σ calculated when using the optimal values of A listed in Table III differ very little from those calculated using the values of A and B that give the best overall fit. Thus, our conclusion remains firm: It is possible to assign the relative extent of electron transfer from coordinated nitrogen with good precision on the basis of the quadrupole coupling constant data, employing a simple model which is equally applicable to a wide range of Lewis acids.

In the following sections we discuss the significance of the NQR results for a few groups of related substances. The pyridine–halogen compounds are treated separately in the paper that follows.[16]

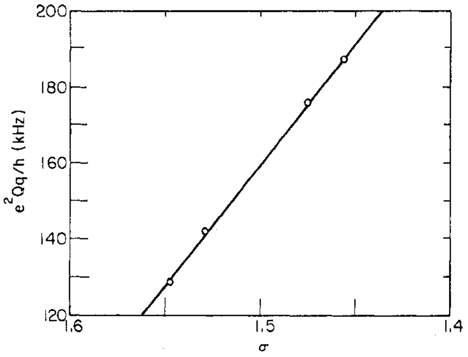

Figure 4. Nitrogen donor orbital occupancy, σ, vs. the ^{2}H quadrupole coupling constant in $C_5H_5N^2HX$ compounds. In order of decreasing σ the compounds represented are $C_5H_5NHNO_3$, C_5H_5NHCl, C_5H_5NHBr, and $C_5H_5NHClO_4$.

Pyridinium Salts. The ^{14}N NQR data provide a quantitative estimate of the hydrogen-bonding interaction between $C_5H_5NH^+$ and the anion. Although there are good reasons to expect that hydrogen bonding of varying strength should exist, there has not been available a means for quantitatively assessing the extent of interaction. In pyridinium chloride the N–Cl distance is 2.95 Å,[21] as compared with 3.3 Å for the sum of the N van der Waals radius and Cl$^-$ ionic radius.[22] The chlorine lies nearly along the twofold axis of the pyridinium ion. In pyridinium nitrate one of the nitrate oxygens is 2.76 Å from the pyridine nitrogen, along the twofold axis.[23] In the nitrate ion the N–O distance to the hydrogen-bonded oxygen is about 0.025 Å longer than the other two N–O distances.

By contrast, in pyridinium iodide[24] and pyridinium tetrachloroantimonate,[25] there seems to be no hydrogen bonding. The $C_5H_5NH^+$ ion is disordered about its pseudo-sixfold axis. We were unable to observe the ^{14}N NQR spectra for these compounds because of short proton relaxation times, presumably related to motions. Ripmeester has investigated rotational motion in the pyridinium halides, which all exhibit a phase transition to a form in which the ring is freely rotating.[26] The iodide salt exhibits the phase transition at lowest temperature, consistent with weakest hydrogen bonding.

Hydrogen bonding should have the effect of increasing σ on the pyridine nitrogen, through an inductive flow of charge as the electron pair donor interacts with the proton. Thus we can rank the extent of hydrogen bonding with the anions in the order $HSO_4^- \approx NO_3^- > Cl^- > ClO_3^- > Br^- > ClO_4^-$.

It is well established that e^2Qq/h for deuterium in a hydrogen bond X–H···Y decreases with increasing extent of hydrogen-bond interaction.[27,28] Goldstein and Ragle have recently reported the ^{2}H NQR spectra for several pyridinium salts, including a value for pyridinium iodide.[29] Figure 4 shows a graph of the nitrogen donor orbital population σ vs. e^2Qq/h for deuterium in the deuterated pyridinium salts. A quite satisfactory correlation is observed. Placement of the ^{2}H datum for C_5H_5NHI on this graph leads to an estimate of $\sigma = 1.43$ for this salt. This may be taken as the value for a hydrogen-bond-free N–H if we assume that there is no hy-

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drogen bonding in the iodide. The correlation shown in Figure 4 proved useful in assigning the correct σ value for C_5H_5NHBr. The data for this compound fit the correlation equally well at $\sigma = 1.469$ or 1.388. However, only the former value fits the correlation with the ^2H data.

No NQR signals that could be attributed to ^{35}Cl were observed in the spectrum of $C_5H_5NHClO_4$. However, in C_5H_5NHCl the ^{35}Cl transition at 5.524 MHz and corresponding ^{37}Cl transition at 4.366 MHz were seen. These values reflect a substantial distortion in the electronic environment about chloride due to hydrogen bonding.

Metal Complexes. The σ values characteristic of the metal ion–pyridine complexes, Table II, reveal a dependence not only on charge and radius of the metal ion, as expected, but also on the coordination number and nature of the other ligands. The NQR data thus provide a sensitive probe of the Lewis acidity of the metal center, as discussed earlier.[4-6]

In Li(py)Cl the lithium ion is surrounded by three chloride ions and one pyridine in an approximately tetrahedral array.[30] In $Li(py)_2(H_2O)Cl$ the lithium ion coordination environment consists of two pyridines, a water, and a chloride ion.[31] The σ value for the pyridines is essentially the same as in the previous compound.

A ^{35}Cl NQR transition in Li(py)Cl occurs at 1.609 MHz, whereas in $Li(py)_2(H_2O)Cl$ it occurs at 1.898 MHz. With the assumption of a nearly zero value for the asymmetry parameter, the quadrupole coupling constant is twice these values. It is noteworthy that in gaseous LiCl, with a Li–Cl distance of only 2.02 Å, the ^{35}Cl quadrupole coupling constant is 3.072 MHz.[32] In Li(py)Cl the Li–Cl distances are about 2.38 Å; in $Li(py)_2(H_2O)Cl$ the distance is 2.33 Å. It would thus seem that, in the latter case at least, O–H···Cl hydrogen bonding is responsible for the field gradient at chlorine. A hydrogen-bonding interaction of the 3 and 5 C–H positions of the pyridine ring with chloride has been suggested in Li(py)Cl.[30] The fact that the ^{14}N NQR data for this compound do not fit the correlation well may be the result of such an interaction, but nothing conclusive can be said.

The comparative values for the Zn(II) and Cd(II) complexes have been discussed.[4] The one new cadmium complex $Cd_2(py)_3(NO_3)_4$ exhibits σ values of 1.783 and 1.781, which are notably smaller than for the other two related cadmium complexes. The structure of this complex is not known, but we may speculate that it involves bridging nitrato, with all pyridines coordinated to single metal centers. Unfortunately, the structures of this compound and of $Hg(py)Cl_2$ are not known. This does not, of course, prevent assignment of a value for σ, but it precludes a detailed interpretation of σ in terms of the coordination environment about the metal ion. The σ values for the mercury complex are remarkably low. Even if the mercury ion is only four-coordinate, as supposed, the σ values suggest that mercury(II) is considerably more electron withdrawing than cadmium(II) and comparable with Zn(II). The same conclusion was reached earlier on the basis of ^{14}N NQR data on 1,2-dipiperidinoethane complexes of these metals.[8]

Comparative Lewis Acidities. Several of the data in Table II afford interesting confirmations of relative Lewis acidities. For example, the value of σ for $C_5H_5NCD_3^+$, 1.44, is lower than for any of the $C_5H_5NBX_3$ compounds, as expected from the higher nuclear charge in the former case. Lewis acidity increases in the series $BR_3 < BCl_3 < BBr_3$ which is the expected order.[33] The NQR experiment is a more direct measure of charge transfer in such interactions than any of the previously employed criteria, because it relates to just the electronic environment in the region of the acid–base bond.

The value of σ for the SO_3 adduct is of special interest. While it is clear that SO_3 is strongly acidic, there are no quantitative measures available of its Lewis acidity. We were unable to obtain satisfactory analyses for the pyridine adduct, possibly because it acquired water in the course of handling during analysis. However, samples on which the NQR data were taken were manipulated without significant exposure to air and are deemed satisfactory. The values of σ, 1.507 and 1.497, are the lowest obtained for any neutral acid in Table II. These results establish clearly that SO_3 is a stronger Lewis acid than the boron halides.

Pyridine *N*-oxide fails to fit the model very well, as evidenced by the comparatively large δ of 0.160 MHz. Since oxygen is a small, relatively nonpolarizable atom, a much smaller deviation is to be expected. The results of an ab initio calculation for this compound indicate that there should be substantial π bonding between oxygen and the ring.[34] Application of eq 9 leads to an excellent fit for a C value of -0.14, at $\sigma = 1.43$. This indicates that there is about 0.14 electron returned from oxygen to the nitrogen $2p_\pi$ orbital per electron transferred from nitrogen to oxygen in the σ bond. In agreement with this, the ^{17}O NQR data for γ-picoline *N*-oxide are interpretable in terms of a 0.16 π-bond order.[35]

The ^{14}N NQR spectrum for $Cr(CO)_4$(2,2′-bipyridyl) yields transitions at 2528, 2158, and 370 kHz ($e^2Qq = 3124$ kHz, $\eta = 0.237$).[36] The value for σ for this complex is thus essentially identical with that for *cis*-$Mo(CO)_4(py)_2$. By contrast, σ for $Fe(CO)_4(py)$ is substantially lower; thus Fe(0) in this environment is appreciably more acidic than either Mo(0) or Cr(0) in closely related compounds. The higher acidity of the metal is reflected in the spectra in the region of the CO stretching modes [$Fe(CO)_4(py)$(hexane)[11] 2042, 1970, 1943 cm^{-1}; $Cr(CO)_4(bpy)(CHCl_3)$[37] 2010, 1908, 1888 cm^{-1}; $Mo(CO)_4(bpy)(CHCl_3)$[36] 2014, 1908, 1892 cm^{-1}].

In summary, the model presented for interpretation of the ^{14}N NQR data for coordinated pyridine permits interpretation of these data in terms of the donor orbital occupancy, σ. This quantity in turn provides a quantitative measure of the extent of charge transfer from nitrogen to the Lewis acid. Because the NQR experiment probes the electronic environment in the immediate vicinity of the nitrogen nucleus, it relates more directly to electronic redistribution upon acid–base adduct formation than many other observables, e.g., enthalpies, which measure the net of all steric and electronic contributions to the interaction. Furthermore, the NQR experiment permits comparisons of neutral and charged Lewis acids. The NQR data permit an ordering of Lewis acidities toward pyridine, as follows: $Li^+ < Ag^+ < Cd^{2+} \approx Mo(0) \approx Cr(0) < Zn^{2+} \approx Hg^{2+} \approx Fe(0) < BR_3 < BCl_3 < BBr_3 < SO_3 < H^+ \approx CH_3^+$. In some cases the relative positions in the ordering are uncertain because strictly comparable data are not yet available.

Several applications of the NQR data are described here; of particular interest is the potential for quantitatively assessing the strengths of hydrogen-bonding interactions in the solid state. In the paper that follows the interpretation of the ^{14}N NQR data for a large group of pyridine–halogen complexes is described. Applications that await development include use

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of the ^{14}N NQR data to assess pyridine binding on oxide surfaces and development of a more quantitative and broadly based scale of Lewis acidities based on the ^{14}N NQR data.

Registry No. py·HCl, 628-13-7; py·HBr, 18820-82-1; py·$HClO_3$, 15062-22-3; py·$HClO_4$, 15598-34-2; py·H_2SO_4, 543-54-4; py·DCl, 1192-11-6; Li(py)Cl, 36407-75-7; $Li(py)_2(H_2O)Cl$, 14854-81-0; py·BCl_3, 2903-67-5; py·BBr_3, 3022-54-6; py·BR_3, 72138-53-5; py·CD_3I, 22822-04-4; py·Cl_2, 40007-00-9; py·O, 694-59-7; py·SO_3, 26412-87-3; $[Zn(py)_4](ClO_4)_2$, 14239-96-4; $[(py)_2Br]PF_6$, 21584-58-7; $[(py)_2Br]Br_3$, 21682-18-8; $[(py)_2Br]ClO_4$, 53514-32-2; py·BrCl, 21300-57-2; $Cd_2(py)_3(NO_3)_4$, 72275-31-1; $Fe(py)(CO)_4$, 53317-88-7; $Mo(py)_2(CO)_4$, 33570-29-5; $[Ag(py)_2]ClO_4$, 72152-13-7; $[Ag(py)_4]ClO_4$, 27628-95-1; py·ICN, 15802-02-5; py·ICl, 6443-90-9; py·IBr, 6443-62-5; py·I_2, 2078-94-6; $[(py)_2I]I_7$, 72152-14-8; $Hg(py)Cl_2$, 14640-89-2; py, 110-86-1; py·HNO_3, 543-53-3; $Zn(py)_3(NO_3)_2$, 39051-35-9; $Zn(py)_2Cl_2$, 6843-20-5; $Zn(py)_2I_2$, 14025-05-9; $Zn(py)_2Br_2$, 14024-88-5; $Zn(py)_2(NCS)_2$, 13878-20-1; $Zn(py)_2(NO_3)_2$, 25754-93-2; $[(py)_2I]ClO_4$, 15699-62-4; $Cd(py)_2Cl_2$, 14024-90-9; $Cd(py)_3(NO_3)_2$, 39051-34-8; $Fe(CO)_5$, 13463-40-6.

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Nitrogen-14 Nuclear Quadrupole Resonance Spectra of Pyridine–Halogen Complexes[1]

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The ^{14}N NQR spectra at 77 K are reported for adducts of pyridine with Cl_2, Br_2, I_2, ICN, ICl, IBr, BrCl, Br^+, and I^+. The data are interpreted in terms of a model for coordinated nitrogen based on the Townes–Dailey approximations. The model yields estimates of the donor orbital occupancy, σ, for the nitrogen orbital directed toward the Lewis acid. The order of Lewis acid strengths based on relative σ values is ICN < I_2 < IBr < ICl < BrCl. The py·Cl_2 complex appears to be ionic. The most reasonable formulation is [(py)Cl]Cl. Among the halogen cations the order of Lewis acidities is as expected: $I^+ < Br^+ < Cl^+$.

Complexes of the diatomic halogen and interhalogen molecules and halogen cations with pyridine and other nitrogen bases have been widely studied. The interaction between nitrogen bases and the halogens have figured prominently in the development of charge-transfer complex theory.[2-4] Techniques employed in the study of such complexes have included X-ray crystallographic structure determinations for py·ICl,[5,6] py·IBr,[7] py·ICN,[7] γ-picoline–iodine[8] and bis(pyridine)–iodine(I) heptaiodide.[9] In all these cases the halogen atoms lie along the twofold axis which passes through the nitrogen atom. These structural studies have been supplemented by extensive spectroscopic investigations[10-29] and NMR studies of the py·I_2 and py·Br_2 complexes in a nematic phase.[30,31]

Table I. ^{14}N NQR Data at 77 K and Donor Orbital Occupancies for Pyridine-Halogen Complexes

compd	e^2Qq/h, MHz	η	$C = 0$: σ	$C = 0$: δ, MHz	$C \neq 0$: σ	$C \neq 0$: C
py·Cl_2	1.671	0.656	1.22	0.007		
py·BrCl	1.133	0.105	1.56	0.164	1.52	−0.12
py·ICN	3.434	0.313	1.85	0.004		
py·ICl	1.797	0.188	1.64	0.190	1.62	−0.09
py·IBr	1.908	0.203	1.66	0.177	1.64	−0.09
py·I_2	2.580	0.285	1.74	0.127	1.73	−0.09
$[(py)_2Br]PF_6$	1.415	0.171	1.59	0.036	1.56	−0.12
$[(py)_2Br]Br_3$	1.564	0.210	1.60	0.155	1.58	−0.12
	1.297	0.149	1.58	0.046	1.55	−0.12
$[(py)_2Br]ClO_4$	1.745	0.199	1.64	0.218	1.61	−0.12
	0.936	0.080	1.54	0.269	1.49	−0.13
$[(py)_2I]I_7$	1.694	0.100	1.62	0.104	1.61	−0.07
$[(py)_2I]ClO_4$	1.693	0.142	1.62	0.151	1.61	−0.08

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