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.

Contribution from the School of Chemical Sciences and the Materials Research Laboratory,
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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	$C = 0$		$C \neq 0$	
			σ	δ, MHz	σ	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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Information regarding the charge distributions in the pyridine–halogen complexes has been obtained from NQR studies of the halogens. In this manuscript we report on the preparation and the ^{14}N nuclear quadrupole resonance spectra of a series of pyridine–halogen complexes. These include both complexes with neutral diatomic molecules and with halogen cations.

Experimental Section

Materials. Iodine, bromine, and iodine bromide were used without further purification. Chlorine was purified by bubbling it through concentrated H_2SO_4 and condensing with dry ice. IBr and BrCl were prepared in solution by addition of stoichiometric amounts of the appropriate halogen. Cyanogen iodide[32] and cyanogen bromide[33] were prepared by literature methods.

The pyridine–dihalogen compounds were prepared by two methods, both of which depend upon the the slow addition of a stoichiometric amount of a halogen solution to a pyridine solution. The solid product is then filtered, washed, and dried under vacuum. Only py·ICl and py·IBr could be recrystallized, and this was done by using ethanol. In the literature method CCl_4 is used as the solvent, and the reaction is carried out at 0 °C;[34] this method was used to prepare the pyridine–ICl, –ICN, –BrCl, and –Br_2 adducts. (As noted below, the Br_2 adduct should be written as $[(\text{py})_2\text{Br}]\text{Br}_3$ and is listed as such in Table I.) In a modification of this method diethyl ether was used as the solvent for py·I_2 and py·Cl_2; the reactions were carried out at −78 °C. py·IBr was prepared similarly except that a diethyl ether–chloroform mixture was used as the solvent for IBr due to the lower solubility of IBr in diethyl ether. All preparations were done by using Schlenk techniques to avoid contact with both oxygen and water.

The Cl_2 adduct decomposes with evolution of heat near room temperature. It is also extremely hygroscopic, producing pyridinium ions. Diethyl ether for this preparation was successively extracted with aqueous 5% NaOH, 25% H_2SO_4, and saturated NaCl solutions to remove alcohol, aldehyde, and acetone impurities before drying and storing over Na wire. Due to its instability no elemental analysis could be obtained for py·Cl_2. Nevertheless, it should be emphasized that the NQR data were reproducible in separate sample preparations.

Pyridine was found not to react with BrCN in diethyl ether. A solution IR spectrum shows only bands due to uncomplexed pyridine and BrCN.

Bis(pyridine)bromine(I) perchlorate, $[(\text{C}_5\text{H}_5\text{N})_2\text{Br}]\text{ClO}_4$, was prepared from bis(pyridine)silver(I) perchlorate.[35] A similar procedure was followed for the analogous iodine compound, except that the product precipitated from the chloroform–pyridine solvent along with the AgI. The product was extracted with anhydrous methanol and recrystallized from boiling methanol. Some decomposition was noted at 65 °C in methanol.

Bis(pyridine)silver(I) hexafluorophosphate was prepared by dissolving AgNO_3 and an excess of KPF_6 in water. An excess of pyridine was added to precipitate the desired product which was subsequently dried. With this as a starting material, bis(pyridine)bromine(I) hexafluorophosphate, $[(\text{C}_5\text{H}_5\text{N})_2\text{Br}]\text{PF}_6$, was prepared analogously to bis(pyridine)bromine(I) perchlorate described above.

Satisfactory elemental analyses for C, H, and N and halogen were obtained for all substances other than py·Cl_2.

NQR Spectra. The ^{14}N NQR spectra were measured on the polycrystalline solids at 77 K, by using the double-resonance techniques described elsewhere.[36,37] The halogen NQR spectra were obtained on a Wilks Model NQR-1A superregenerative spectrometer.

Results and Discussion

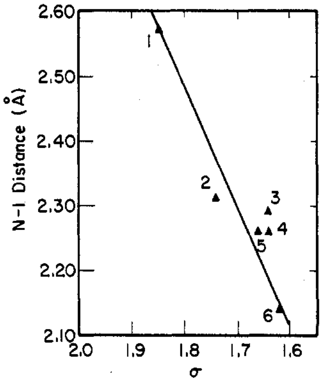

Figure 1. N–I bond distance vs. nitrogen donor orbital occupancy, σ, for pyridine–iodine complexes: 1, py·ICN; 2, γ-pic·I_2; 3, py·ICl; 4, py·ICl; 5, py·IBr; 6, bis(pyridine)–iodine(I) heptaiodide.

The ^{14}N NQR data of the compounds of interest here are listed in Table I of the previous paper.[38] For convenience the values of e^2Qq/h and η are listed in Table I. Also listed under the heading $C = 0$ are values of donor orbital occupancy, σ, and the root-square deviation between calculated and observed field gradient tensor components, δ, from application of the model described in the previous paper, in which $A = 0.446$ and $B = 0.087$. It is noteworthy that for several compounds studied the values of δ are rather large. Accordingly, an attempt was made to fit the data more closely by employing a third empirical parameter, C, which alters the π-electron system inductive parameter, a, as follows:

$$a = a_0 + (A + C_\pi)(2 - \sigma) \qquad (1)$$

In using this expression, the quantity $(A + C_\pi)$ represents the net result of the ordinary inductive effect response, plus the effects of any direct π-bond interaction between pyridine and the Lewis acid which results in a flow of electron density into or out of the p_π orbital of nitrogen.

Among the pyridine–halogen complexes, the optimal value of A in the expression $a = a_0 + A(2 - \sigma)$ is substantially lower than the value of A which provides the best overall fit for all compounds studied (see Table III of the previous paper). This means that the value of C_π in eq 1 must be negative. In terms of a model which ascribes the variations in A to π-bonding effects, this means that pyridine must be acting as a π donor toward the Lewis acids in these systems. Such an interpretation appears to have rather dubious utility. Rather, it seems more appropriate simply to say that the large, polarizable character of the Lewis acids results in a different response of the σ and π systems of pyridine toward the acid–base adduct formation than is the case for a small, hard, relatively nonpolarizable acid such as H^+ or Zn^{2+}. In this sense C must be regarded for the present as an empirical parameter that compensates for departures of the real system from the simple model. The values of C which provide the best fit to the model are listed in Table I. (For py·Cl_2 and py·ICN the optimal value of C is essentially zero.) Perhaps the most significant fact to be noted is that the addition of this third parameter does not result in large changes in σ. None of the interpretations of the data which follow depend in a significant way upon the choice of model employed for the determination of σ. Accordingly, we have elected in the interests of simplicity to employ the values of σ determined for the simplest model, applicable to all of the Lewis acids studied, i.e., that for which $C = 0$.

Since crystal structures have been reported for several complexes in which pyridine is bound to iodine, it is of interest to relate the N–I distance to the donor orbital occupancies in the complexes. Figure 1 shows a graph of the N–I bond distance versus σ for the six compounds for which requisite data are available. Although the uncertainties in the N–I distances in some of the structures are rather large, a rea-

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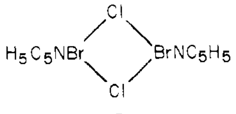
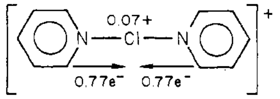
sonable correlation of the expected form results: a shorter N–I distance, indicative of a stronger acid–base adduct interaction, results in a larger degree of a transfer of electron density from nitrogen to the Lewis acid acceptor.

With two exceptions, interaction of pyridine with the diatomic halogen molecules appears to result in formation of a simple 1:1 acid–base adduct. The exceptions are py·Cl_2 and py·BrCl. The solid structure of py·BrCl exhibits selection rules in the IR and Raman spectra which indicate a centrosymmetric structure.[10] Appropriate bands for a BrCl anion are not seen, precluding a $[(py)_2Br]^+$ cation. However, a bridging structure of form I is possible. The ^{14}N NQR data do not provide new information relevant to this question but are consistent with a structure such as I.

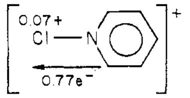


I

The very unstable adduct formed between pyridine and Cl_2 is not well characterized in the solid state. The compound is quite unstable and must be prepared and maintained at low temperatures to avoid rapid decomposition. The ^{14}N NQR data indicate a large degree of charge transfer from nitrogen to the Lewis acid, since σ is only 1.23. Because the compound is thermally unstable and extremely hygroscopic, we were unable to obtain satisfactory elemental analyses. A large degree of charge transfer from nitrogen suggests an ionic formulation for the compound, since Cl_2 would not be expected to be a particularly strong Lewis acid as a neutral diatomic molecule. Two formulations suggest themselves:[39] $[(py)_2Cl]Cl$ or [pyCl]Cl. A ^{35}Cl NQR resonance was observed for the complex at −100 °C, at 60.02 MHz, and confirmed by location of the corresponding ^{37}Cl transition at 47.30 MHz. With the Townes–Dailey model,[40,41] these data may be employed to estimate the net charge on chlorine, by assuming either of the two alternative structures II and III. The numbers below the arrows indicate the estimated charge flow from nitrogen to chlorine based on the ^{14}N NQR data. Although neither model provides a totally consistent picture of the charge distribution in the cation, it would appear that III is the preferable formulation at this point. It should be noted that only one NQR transition ascribable to chlorine was seen in the spectrum. That is, no evidence was obtained for a lower lying transition ascribable to the Cl^- ion.



II



III

The values of σ obtained from analysis of the ^{14}N NQR data enable us to order the relative acidities of the diatomic halogens as follows: ICN < I_2 < IBr < ICl < BrCl. The inclusion of BrCl in this listing is questionable because its structure may be different from those of the other adducts, as indicated above. The Cl_2 is omitted entirely, because its structure is obviously quite different. From the available *E* and *C* values for the substances involved,[42] the predicted enthalpies of interaction with pyridine in solution (kcal/mol) are I_2 (7.8) < ICl (11.3) < IBr (12.8). Although ICl and IBr are reversed in order, both the σ and ΔH values for the two acids are closely similar, and they may be regarded as essentially equivalent in their interaction with pyridine. A simple molecular orbital treatment of amine–halogen complexes[43] suggests that charge transfer from nitrogen should be in the order I_2 < IBr < ICl, in agreement with our analysis of the ^{14}N NQR data.

Table II. Comparison of Donor Orbital Populations Calculated from ^{14}N and Halogen NQR

compd	charge on X (halogen NQR)	charge on X′ (halogen NQR)	(based on halogen NQR)	(based on ^{14}N NQR)[a]	Δ[b]
py·ICl	0.35+[c]	0.61−[c]	1.74	1.64	0.10
py·ICl	0.35+[d]	0.65−[d]	1.70	1.64	0.06
py·IBr	0.30+[d]	0.55−[d]	1.75	1.66	0.09
py·I_2	0.19+[e]	0.36−[f]	1.83	1.74	0.09
$[(py)_2Br]Br_3$	0.10+[d]	0.30−[d]	1.80	1.59	0.21
$[(py)_2I]^+$	0.39+[e]		1.70	1.62	0.08

[a] From Table I. Values are averaged when there is more than one nonequivalent pyridine. [b] $\Delta = \sigma(\text{halogen}) - \sigma(\text{nitrogen-14})$. [c] Reference 48. [d] Using 3,5-dibromopyridine; ref 43. [e] Reference 51. [f] This work; ^{127}I resonance at 227 MHz, 295 K.

From an ESCA study of the py·ICl complex, a net increase of 0.1+ in the charge on nitrogen in this compound as compared to free pyridine is estimated.[44] From the ^{14}N NQR data, with $\sigma = 1.64$ and with the inductive effect parameters which provide for the best overall fit, a net increase of 0.14+ can be calculated for the charge on the nitrogen. The ESCA results are therefore in reasonable agreement with the interpretation of the ^{14}N NQR data.

For some of the pyridine–halogen compounds, halogen quadrupole coupling constant data are available from ^{129}I Mössbauer spectra[45–47] and from I, Br, and Cl NQR spectra.[42,47–50] The asymmetry parameters for Br and I in all cases do not deviate significantly from zero. An estimate of the halogen p-orbital populations based on the Townes–Dailey model, assuming no sp hybridization, gives the partial charges residing on the halogen atom. With these halogen-based charges, the nitrogen atom donor orbital populations can be estimated and compared with those obtained from the ^{14}N NQR data, as indicated in Table II. The difference between the values of σ estimated from the halogen NQR and ^{14}N NQR data is represented in the table as Δ. In general the agreement is quite good, considering that several assumptions are involved in application of the Townes–Dailey model to either the halogen or ^{14}N data. In particular, in modeling the nitrogen data a value for q_{00} must be chosen since no experimental values of this quantity are available. In addition, neglect of overlap populations in the bonds should be expected to lead to discrepancies on the order of those observed. In general, the same trends in the extent of charge transfer are observed in either the halogen or ^{14}N NQR data.

The only substantial discrepancy in Table II occurs in the case of the Br^+ complex in which the halogen NQR data were obtained by using 3,5-dibromopyridine.[43] The anomalously

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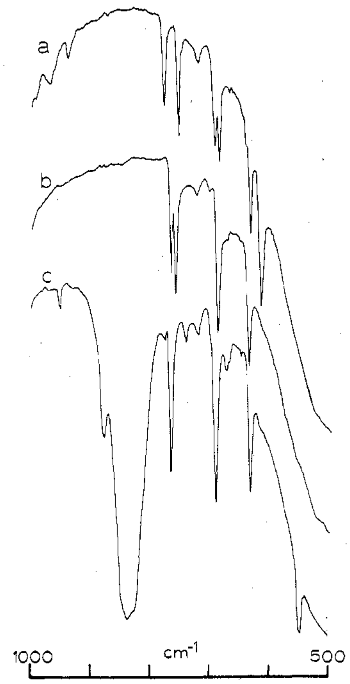

Figure 2. Nujol mull infrared spectra of $[(py)_2Br]ClO_4$ (a), $[(py)_2Br]Br_3$ (b), and $[(py)_2Br]PF_6$ (c). Note the splittings in the bands at 690 and 766 cm^{-1} in b and c, indicative of nonequivalent pyridines.

large difference in σ values for the 3,5-dibromopyridine–bromine complex from the halogen data and the value of σ determined from the ^{14}N NQR data for the pyridine adduct suggests that there may be a difference in the structures. The relatively small degree of charge transfer from the base to Br_2 in the 3,5-dibromopyridine compound suggests that the compound may be molecular rather than ionic in character. On the other hand, 3,5-dibromopyridine should be a substantially weaker Lewis base than pyridine itself. In any case both the IR[10] and ^{14}N NQR data suggest that the pyridine adduct is best formulated as the $[(py)_2Br]Br_3$ salt.

In the bis(pyridine)bromine(I) hexafluorophosphate salt, the bonding of the pyridines is equivalent, while for the Br_3^- salt there is a nonequivalence of the pyridines as determined by the ^{14}N NQR data. The nonequivalence is even larger in the case of the ClO_4^- salt. This trend is confirmed in the IR spectra shown in Figure 2, in which a splitting of the 766 and 690 cm^{-1} pyridine C–C out-of-plane bending vibrations is seen in the spectrum of the Br_3^- salt; an even larger splitting is evident in the spectrum of the ClO_4^- salt. The loss of centrosymmetry in the cation in these salts may be caused by packing effects in which the anion resides above the more positive pyridine ring of the cation. A similar effect is not noted in the $(py)_2I^+$ salts.

If we assume an ionic structure for $py{\cdot}Cl_2$, the acidities of the halogen cations, as reflected in the σ values for the coordinated pyridine, are in the order $I^+ < Br^+ < Cl^+$. The fact that the σ for the chlorine compound, 1.22, is substantially less than the values for the bromine(I) and iodine(I) compounds (around 1.59, and 1.62, respectively) is further argument that structure III is the correct structure for the chlorine compound.

Registry No. $py{\cdot}Cl_2$, 40007-00-9; $py{\cdot}BrCl$, 21300-57-2; $py{\cdot}ICN$, 15802-02-5; $py{\cdot}ICl$, 6443-90-9; $py{\cdot}IBr$, 6443-62-5; $py{\cdot}I_2$, 2078-94-6; $[(py)_2Br]PF_6$, 21584-58-7; $[(py)_2Br]Br_3$, 21682-18-8; $[(py)_2Br]ClO_4$, 53514-32-2; $[(py)_2I]I_7$, 72174-99-3; $[(py)_2I]ClO_4$, 15699-62-4.

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Electron Transfer. 44. Decreases in the Effectiveness of Redox Catalysts with Use[1]

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Pyridine derivatives, which, when uncoordinated, catalyze outer-sphere electron-transfer reactions between metal centers, often undergo loss of catalytic activity with use. The active intermediates in such catalyzed reactions are radicals (cat·) formed by initial reaction of the catalysts with the primary reducing centers. This study examines the deterioration of a number of such catalysts in reactions of Eu^{2+} and V^{2+} with $(NH_3)_5Co(py)^{3+}$. This deterioration, when it occurs, arises from interaction of the catalyst and the reducing center; it does not require Co(III). Degrees of deterioration vary widely. The very powerful catalysts derived from 2,4-pyridinedicarboxylic acid (III) lose much or all of their catalytic activity during the course of a single 1-min run with Eu^{2+} in excess, whereas catalytic erosion of isonicotinic acid (I), its esters, and its nitrile is negligible after treatment with excess reductant for 10–20 min. Erosion is much more marked with Eu^{2+} than with the less strongly reducing V^{2+} and is much less severe when the oxidant, rather than the reductant, is taken in excess. Deterioration in Eu^{2+} systems may be decreased strikingly by addition of excess Eu^{3+} and that in V^{2+} systems by addition of V^{3+}. The spectra of the products formed when the more fragile catalysts react rapidly with Eu^{2+} (in the absence of Co(III)) correspond to those formed by reduction of the catalysts with zinc amalgam, which is presumed to be a two-electron reductant. The more robust isonicotinate catalysts are not affected by Eu^{2+} under similar conditions. Evidence is presented in support of two attrition mechanisms. The catalytic deterioration of 2,4-pyridinedicarboxylic acid in Eu^{2+} systems appears to involve disproportionation of catalyst–radical pairs ($2cat{\cdot} + 2H^+ \rightarrow cat + catH_2$), converting one member of each pair to an inactive dihydro species and returning the other to the catalyst pool. Measurements of the rate of deterioration of this catalyst allow us to estimate the specific rate for the disproportionation as 5.8×10^8 M^{-1} s^{-1}. In systems featuring less fragile catalysts (e.g., isonicotinamide) the steady-state concentration of the radical, cat·, is so low that attrition, if it takes place at all, occurs mainly by reductive deterioration ($cat{\cdot} + Eu^{2+} \xrightarrow{2H^+} Eu^{3+} + catH_2$). In two such instances, comparison of kinetic runs using catalyst preparations that have undergone partial attrition permits an estimate of the specific rates of such deteriorative processes. Although both modes of attrition are presumed to occur in each catalytic system, bimolecular disproportionation appears to compete most favorably with reductive deterioration when the extent of reduction of the catalyst to its radical is greatest.

Previous communications dealing with the catalysis of electron-transfer reactions between metal centers by uncoordinated aromatic species contributed evidence that such catalysis proceeds by preliminary reduction of the aromatic to