Ni(t-BuCOMe)$_2^+$, 80719-33-1; Ni(Et$_2$CO)$_2^+$, 80719-34-2; Ni(NH$_3$)$_2^+$, 80719-35-3; Ni(MeNCS)$_2^+$, 80719-36-4; Ni(Me$_2$S)$_2^+$, 80719-37-5; Ni(MeCOEt)$_2^+$, 80737-27-5; Ni(EtCO$_2$Et)$_2^+$, 80737-28-6; Ni(EtCO$_2$Me)$_2^+$, 80719-38-6; Ni7Me$_2$CO)$_2^+$, 80719-39-7; Ni(THF)$_2^+$, 80719-40-0; Ni(1,3-butadiene)$_2^+$, 80719-41-1; Ni(benzene)$_2^+$, 80719-42-2; Ni(t-BuCHO)$_2^+$, 80719-43-3; Ni(Et$_2$O)$_2^+$, 80719-44-4; Ni(MeCO$_2$Me)$_2^+$, 80719-45-5; Ni(EtSH)$_2^+$, 80719-46-6; Ni(C$_6$H$_5$Cl)$_2^+$, 80719-47-7; Ni(i-PrCHO)$_2^+$, 80719-48-8; Ni(HCN)$_2^+$, 80719-49-9; Ni(n-PrCHO)$_2^+$, 80719-50-2; Ni(i-PrOH)$_2^+$, 80719-51-3; Ni(EtCHO)$_2^+$, 80719-52-4; Ni(n-BuOH)$_2^+$, 80719-53-5; Ni(MeSH)$_2^+$, 80719-54-6; Ni(n-PrOH)$_2^+$, 80737-29-7; Ni(Me$_2$C=CH$_2$)$_2^+$, 80719-55-7; Ni(1,4-dioxane)$_2^+$, 80719-56-8; Ni(EtOH)$_2^+$, 80719-57-9; Ni(EtCH=CH$_2$)$_2^+$, 80719-58-0; Ni(Me$_2$O)$_2^+$, 80719-59-1; Ni(MeCHO)$_2^+$, 80719-60-4; Ni(HCO$_2$Me)$_2^+$, 80719-61-5; Ni(furan)$_2^+$, 80719-62-6; Ni(oxirane)$_2^+$, 80719-63-7; Ni(MeOH)$_2^+$, 80737-14-0; Ni(allene)$_2^+$, 80719-64-8; Ni(C$_2$H$_2$)$_2^+$, 80719-65-9; Ni(MeCH=CH$_2$)$_2^+$, 80719-66-0.

Relative Bond Dissociation Energies for Two-Ligand Complexes of FeBr$^+$ with Organic Molecules in the Gas Phase

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Abstract: Relative two-ligand dissociation enthalpies, $\delta D(\mathrm{FeBr^+{-}2L})$, for FeBr$^+$ with 24 organic molecules are determined. A pulsed laser volatilization–ionization source is used to generate Fe$^+$ which reacts with MeBr to give FeBr$^+$. With various organic molecules present, FeBr$^+$ reacts to give FeBr(ligand)$_2^+$ complexes. Equilibrium constants are measured for the ligand-exchange reactions which occur when pairs of ligand molecules are present. Free energies for two-ligand exchange are obtained from the equilibrium constants for the reaction $\mathrm{FeBr(A)_2^+ + 2B \rightleftarrows FeBr(B)_2^+ + 2A}$. The free-energy differences are added to give a scale of relative free energies for ligand exchange. These are converted to enthalpies to give $\delta D(\mathrm{FeBr^+{-}2L})$. The results are compared to available results for other reference acids: H$^+$, Al$^+$, Mn$^+$, Co$^+$, Cu$^+$, Ni$^+$, and CpNi$^+$. These comparisons show that FeBr$^+$ is a moderately soft acid. It is harder than Co$^+$, Ni$^+$, Cu$^+$, and CpNi$^+$, slightly softer than Mn$^+$, and much softer than Al$^+$ or H$^+$. Comparison of the FeBr$^+$ and Mn$^+$ scales shows that the bonding interactions in FeBr(L)$_2^+$ and Mn(L)$^+$ complexes are similar. This is expected because the iron in FeBr$^+$ is formally isoelectronic with Mn$^+$. FeBr$^+$–ligand bonding interactions are influenced by steric effects which result from the presence of the bulky Br atom on the iron.

Relative gas-phase ligand-binding energies for various metal cations have recently been obtained by using a combination of ion cyclotron resonance (ICR) spectroscopy and a pulsed laser volatilization–ionization source of atomic metal cations. One-ligand binding energies, $D(\mathrm{M^+{-}L})$, were measured for Al$^+$ and Mn$^+$,[2,3] while two-ligand binding energies have been determined for Cu$^+$, Co$^+$, and Ni$^+$.[4-6] Comparisons between different scales can be quite informative and have revealed some interesting aspects of metal–ligand interactions. Recent work in our laboratory has shown that complexes of FeBr$^+$ with two ligands can be readily produced and do not react further except by ligand-exchange reactions. Determinations of relative binding energies in two-ligand complexes of FeBr$^+$ are therefore possible. These two-ligand binding energies should reveal effects due to the presence of the large bromine atom on the metal atom when compared to two-ligand binding energies for bare metal cations. Formally, the iron atom in FeBr$^+$ is a dipositive Fe(II) species. Different bonding effects might be observed for such an ion when compared to unipositive metal ions. Comparison of Mn$^+$ and FeBr$^+$ results is also of interest since they are formally isoelectronic systems. In the present paper we report relative dissociation energies of 24 organic molecules in two-ligand complexes of FeBr$^+$. The results are compared to available gas-phase basicity scales for other reference acids: H$^+$, Al$^+$, Mn$^+$, Co$^+$, Ni$^+$, CpNi$^+$, and Cu$^+$.

Experimental Section

Experiments were carried out by using ICR instrumentation and techniques which have been previously described.[7,8] The output of a pulsed YAG laser is focused onto a stainless steel target mounted on the end plate of the ICR cell. The mass spectrum for this source with no added gases shows ions of mass 52 (18), 53 (2), 54 (4), 56 (74), and 57 (2), with ion abundances (in percent) given in parentheses. This corresponds to the isotope distribution expected for a target consisting of 80% Fe and 20% Cr. The small amounts of Cr$^+$ produced were not found to be a problem because Cr$^+$ does not react with MeBr. Cr$^+$ reaction products with various ligand species were only formed in small quantities and in all cases could be easily distinguished from FeBr$^+$ complexes. Chemicals used were from commercial sources and were degassed by repeated freeze–pump–thaw cycles before use. All experiments were carried out at an ambient temperature of 25 °C. Gas mixtures were prepared in the cell and partial pressures measured by difference as has been previously described. Accuracy of pressure ratios is limited to about ±30% because the ion gauge used for pressure measurements is not individually calibrated for each gas.

Results

Formation of FeBr$^+$. Reaction of Fe$^+$ with MeBr results in rapid formation of FeBr$^+$,[9] reaction 1 ($k = 4.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). In the presence of only MeBr, FeBr$^+$ does not react further except to undergo bromine isotope exchange (reaction

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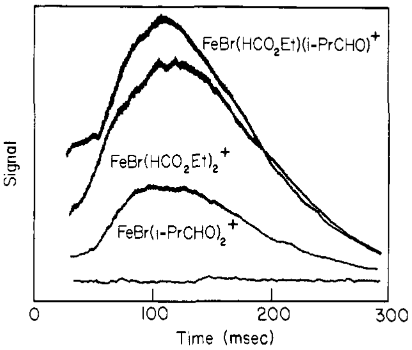

Figure 1. Variation of ion abundances with time typical of the equilibrium determinations of this study. When $FeBr^+$ is generated in the presence of HCO_2Et and i-PrCHO at a total pressure of 4.5×10^{-6} torr, initial reactions lead to the formation of three two-ligand complexes: $FeBr(i\text{-}PrCHO)_2^+$, $FeBr(i\text{-}PrCHO)(HCO_2Et)^+$, and $FeBr(HCO_2Et)_2^+$. These ionic species undergo ligand-exchange reactions with the HCO_2Et and i-PrCHO neutrals. Equilibrium is eventually reached—in this example after 180 ms. The overall equilibrium constant for exchange of two i-PrCHO ligands for two HCO_2Et molecules is calculated from the ratio of ion abundances and the pressures of the reactants. The decrease in the signals at long times in this figure is due to ion loss from the ICR cell by diffusion to the walls.

Table I. Measured Free Energies for Exchange of Both Ligands, ΔG_{exch}, Measured Enthalpies of Stabilization of the Mixed-Ligand Species, Q, and Relative Two-Ligand Dissociation Enthalpies, $\delta D(FeBr^+\text{–}2L)$, for Two-Ligand Complexes of $FeBr^+$ in the Gas Phase[a]

Ligand (L)	Measured ΔG_{exch} and Q	$\delta D(FeBr^+\text{-}2L)$[b]
Me_3N		15.30
	1.04 0.17	
C_6H_5CN		14.31
	0.05 0.34	
Me_2NH		14.26
	1.21 -0.01	
n-PrCN		13.05
$MeNH_2$		12.43
	0.73 -0.02 0.05 0.49	
MeCOEt		12.38
	0.06 0.02	
EtCN		12.32
	0.31 0.16	
$EtCO_2Me$		12.07
	1.91 0.30	
THF[c]		10.16
Me_2CO		10.15
	0.69 0.11	
$MeCO_2Me$		9.56
	0.68 0.08 0.09 0.01	
MeCN		9.47
	1.80 0.44	
Et_2O		7.67
	0.77 0.48	
HCO_2n-Bu		6.90
	0.81 -0.06	
HCO_2n-Pr		6.09
	1.34 0.04	
HCO_2Et		4.75
	0.77 -0.18	
i-PrCHO		3.98
	0.92 0.11	
NH_3		3.88
	0.05 0.56	
n-PrCHO		3.83
	1.12 0.09	
EtCHO		2.71
	1.99 -0.02 1.79 0.52	
1,4-dioxane		1.22[d]
HCO_2Me		1.84
	1.84 0.26	
n-PrOH		1.08
	1.08 0.08	
Me_2O		0.00

[a] All data in kcal/mol. [b] Values are relative to $\delta G(FeBr^+\text{–}2Me_2O) = 0$. Free energy differences, ΔG_{exch}, are added to give relative free energies $\delta G(FeBr^+\text{–}2L)$. These are converted to relative enthalpies, $\delta D(FeBr^+\text{–}2L)$, by assuming that entropy changes can be neglected except for corrections for symmetry number changes. [c] Tetrahydrofuran. [d] In converting the relative free energy to relative enthalpy, a correction of $T\Delta S = -0.82$ kcal/mol is made for 1,4-dioxane to account for a decrease in symmetry number by a factor of 2 for each ligand molecule on formation of the $FeBr(ligand)_2^+$ complex.

2). $FeCl^+$ can be produced from MeCl in a process analogous to reaction 1 (reaction 3). $FeCl^+$ reacts with MeBr to form $FeBr^+$ (reaction 4). The reverse reaction is not observed.

$$Fe^+ + MeBr \rightarrow FeBr^+ + Me \tag{1}$$

$$Fe^{79}Br^+ + Me^{81}Br \rightleftarrows Fe^{81}Br^+ + Me^{79}Br \tag{2}$$

$$Fe^+ + MeCl \rightarrow FeCl^+ + Me \tag{3}$$

$$FeCl^+ + MeBr \rightarrow FeBr^+ + MeCl \tag{4}$$

Complexes and Equilibria. Most of the neutral ligand molecules examined in this work react rapidly with $FeBr^+$ to give two-ligand complexes, $FeBr(ligand)_2^+$. $FeBr(ligand)_n^+$ complexes with $n = 3$ are formed very slowly or not at all. With many of the more strongly bound ligands, complexes are generated by direct condensation of the neutral molecule with $FeBr^+$ and $FeBr(ligand)^+$. In those cases in which direct condensation of the neutral with $FeBr^+$ and $FeBr(ligand)^+$ does not occur, $FeBr(ligand)^+$ and $FeBr(ligand)_2^+$ complexes are generally formed in two-step reaction sequences involving elimination and displacement steps.

As in studies of other transition-metal cations, amines in general and ammonia in particular were observed to react only very slowly with $FeBr^+$.[6] The reason for this is not immediately apparent but may involve comparatively slow radiative stabilization rates in these complexes.[10]

Benzene was not included in the two-ligand displacement studies because $FeBr(C_6H_6)_2^+$ could not be formed. When $FeBr^+$ was generated in the presence of benzene, only reaction to give $FeBr(C_6H_6)^+$ was observed. There was no evidence for formation of a two-ligand complex. Furthermore, $FeBr(C_6H_6)_2^+$ could not be produced by ligand displacement. $FeBr(C_6H_6)(L)^+$ could be formed with a variety of ligands, L. But even Me_2O, the weakest ligand on the $FeBr^+$ scale, could not be displaced from $FeBr(C_6H_6)(Me_2O)^+$ to give $FeBr(C_6H_6)_2^+$.

With two ligand molecules A and B present, initial reactions forming $FeBr(ligand)_2^+$ complexes are followed by ligand-exchange reactions 5 and 6, M = FeBr. The enthalpy expressions for these reactions follow from the definition of the heterolytic bond dissociation energy for a single ligand in a two-ligand complex (reaction 7). Overall, reactions 5 and 6 together result in the exchange of both ligands (reaction 8) where $D(M^+\text{–}2L)$ is the enthalpy for dissociation of both ligands in a two-ligand complex (reaction 9).

$$AMA^+ + B \overset{K_5}{\rightleftarrows} AMB^+ + A \tag{5}$$

$$\Delta H_5 = D(AM^+\text{–}A) - D(AM^+\text{–}B)$$

$$AMB^+ + B \overset{K_6}{\rightleftarrows} BMB^+ + A \tag{6}$$

$$\Delta H_6 = D(BM^+\text{–}A) - D(BM^+\text{–}B)$$

$$AMB^+ \rightarrow AM^+ + B \qquad \Delta H_7 \equiv D(AM^+\text{–}B) \tag{7}$$

$$AMA^+ + 2B \xrightarrow{K_8} BMB^+ + 2A \tag{8}$$

$$\Delta H_8 = D(M^+\text{–}2A) - D(M^+\text{–}2B)$$

$$LML^+ \rightarrow M^+ + 2L \qquad \Delta H_9 \equiv D(M^+\text{–}2L) \tag{9}$$

Figure 1 shows the variation of ion abundance with time for some of the species formed when $FeBr^+$ is produced in the presence of a mixture of i-PrCHO and HCO_2Et. Initial reactions yield $FeBr(i\text{-}PrCHO)_2^+$, $FeBr(i\text{-}PrCHO)(HCO_2Et)^+$, and $FeBr(HCO_2Et)_2^+$ as the final product ions in this system. Ligand-exchange reactions 5 and 6 for these ions with the i-PrCHO and HCO_2Et neutrals are shown by double resonance to be rapid and approach equilibrium. Under typical conditions ($P_{A+B} = 2 \times 10^{-6}$, $P_{MeBr} = 2 \times 10^{-6}$ torr) equilibrium is reached roughly 150 ms after the formation of Fe^+. The equilibrium constants for reactions 5, 6, and 8 can be calculated from the ratios of ion abundances

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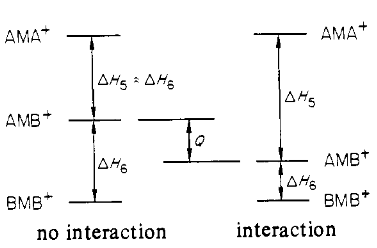
(10) See for example: Woodin, R. L.; Beauchamp, J. L. *Chem. Phys.* **1979**, *41*, 1-9.

Scheme I



at long times and the measured partial pressures of *i*-PrCHO and HCO_2Et. The equilibrium constants are conveniently expressed as free energies using the relation $-\Delta G° = RT \ln k$.

Equilibria were measured for various pairwise combinations of 24 organic molecules as ligands. Values for the free energy difference for exchange of both ligands $\Delta G_{\text{exchange}}$ calculated from the measured equilibrium constants for reaction 8 are given in Table I. Each value represents the average of at least three determinations. The results are combined into a ladder to give a scale of relative free energies for ligand binding, $\delta\Delta G_{\text{exchange}}$. The zero of this scale is arbitrarily chosen by setting the value for Me_2O, the weakest ligand measured, equal to zero.

The measured equilibria for reaction 8 take no account of the relative abundance of the mixed-ligand species AMB$^+$. This abundance may be used to establish the values of the separate equilibria for reactions 5 and 6. This is conveniently expressed as an energy difference (Scheme I). If there were no interaction between two ligand sites on the FeBr$^+$ species, then the enthalpies, for reaction 5 and 6 would be equal, $\Delta H_5 = \Delta H_6$, defining a relative value for the enthalpy of the mixed species AMB$^+$ as the average of the enthalpies for the species AMA$^+$ and BMB$^+$. The actual relative enthalpy for AMB$^+$ is conveniently expressed as the deviation Q from this average value, where $Q = (\Delta H_6 - \Delta H_5)/2 = [D(\text{AM}^+\text{–B}) + D(\text{BM}^+\text{–A}) - D(\text{AM}^+\text{–A}) - D(\text{BM}^+\text{–B})]/2$ (Scheme I). In terms of the equilibrium constants, Q is given as $Q = (1/2)RT \ln (K_5/4K_6)$; the factor of a quarter is a statistical correction arising because the mixed species can be formed in two ways as AMB$^+$ or BMA$^+$. Other entropy corrections cancel or are small and can be neglected.[11] Values of Q calculated from the measured equilibria among the 24 ligands studied are given in Table I. Note that $Q \equiv (\Delta H_6 - \Delta H_5)/2$ is sometimes larger than $\Delta H_5 + \Delta H_6$; in these cases ΔH_5 and ΔH_6 are of opposite sign.

Discussion

Relative enthalpies for dissociation of both ligands from FeBr(ligand)$_2^+$ complexes, $\delta D(\text{FeBr}^+\text{–2L})$, are given in Table I for the 24 molecules studied. These are given relative to $\delta D(\text{FeBr}^+\text{–2Me}_2\text{O}) = 0$ which is chosen arbitrarily. The absolute zero of this enthalpy scale cannot be determined from the present work. The enthalpy scale is obtained from the free energy scale by the assumption that entropy changes are small and tend to cancel so that they may be neglected except for corrections for symmetry changes.[12] The symmetry correction is necessary when a ligand which has symmetry number greater than one as a free molecule binds in the FeBr(ligand)$_2^+$ complex so as to reduce its symmetry. This is clearly the case for 1,4-dioxane which loses a twofold symmetry axis when bonding to FeBr$^+$. The relative free energy for 1,4-dioxane is therefore corrected by adding $T\Delta S = -2RT \ln 2 = -0.82$ kcal/mol in calculating the relative enthalpy. No such symmetry correction is made for any of the other molecules studied as ligands in this work.

It has been noted in a previous paper dealing with two-ligand complexes of Cu$^+$,[4] that relative two-ligand dissociation energies, $\delta D(\text{M}^+\text{–2L})$, are not simply related to one-ligand dissociation energies, $\Delta D(\text{M}^+\text{–L})$. There is no reason to expect that the bonding of one ligand to FeBr$^+$ is independent of the other. For such complexes, in fact, the dissociation energy for the second ligand should be significantly less than that for the first: $D(\text{LFeBr}^+\text{–L}) < D(\text{FeBr}^+\text{–L})$. A particular kind of nonideal behavior in the bond enthalpies of two-ligand complexes was demonstrated in a previous study.[13] Cooperative bonding effects, resulting in energetic stabilization, were seen in two-ligand complexes of Co$^+$, Cu$^+$, and Ni$^+$ with certain combinations of the two different ligands. The ligands studied fall into four groups: (1) σ bases (alkyl halides, alcohols, ethers, aldehydes, ketones, esters, isocyanates, and nitro compounds); (2) sulfur bases (alkyl mercaptans and sulfides); (3) nitrogen bases; (4) π bases (olefins and aromatics). Complexes with both ligands from the same group showed no special stability for the mixed AMB$^+$ species. The σ-base/π-base pairs show the largest stabilization; $Q \sim 0.8$, 1.2, and 0.9 kcal/mol for Co$^+$, Ni$^+$ and Cu$^+$ complexes, respectively. Smaller stabilizations are seen for σ-base/S-base, σ-base/N-base, *s*-base/π-base and N-base/π-base complexes.

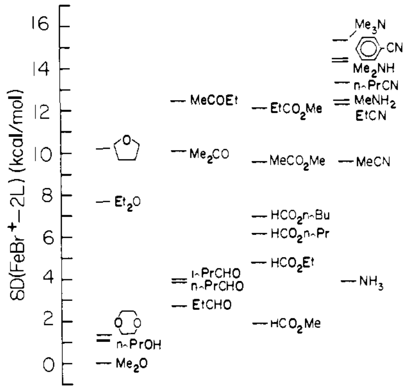


Figure 2. Relative two-ligand dissociation enthalpies for FeBr$^+$, $\delta D(\text{FeBr}^+\text{–2L})$, arranged by functional group. The value for Me_2O is arbitrarily chosen as zero for this scale.

One of the assumptions inherent in the simple molecular orbital model used to explain the occurrence of mixed-ligand complex stabilization was that the species involved are linear. Two-ligand complexes of FeBr$^+$ cannot be linear. One would therefore not expect to see synergistic stabilization in mixed ligand complexes with FeBr$^+$ if linearity is important. Examination of the Q values for various ligand pairs with FeBr$^+$ (Table I) reveals, however, several cases which clearly manifest cooperative bonding. Three of these cases (Me_2NH/MeCOEt, $Q = 0.49$; MeCN/Et_2O, $Q = 0.44$; and NH_3/*n*-PrCHO, $Q = 0.56$) are σ-base/N-base combinations, and the magnitude of the stabilization observed for them is comparable to the stabilization energy seen in σ-base/N-base complexes with Ni$^+$. Other apparent cases of stabilization of the mixed-ligand species (Et_2O/HCO_2-*n*-Bu, $Q = 0.48$; *n*-PrCHO/1,4-dioxane, $Q = 0.52$, and possibly C_6H_5CN/Me_2NH, $Q = 0.34$, although the last is a relatively small effect) do not fit the previously established pattern. They may arise because of steric or other effects due to the presence of the Br atom in the FeBr(A)(B)$^+$ complexes.

$FeBr(C_6H_6)_2^+$ was not observed in this study. Under the conditions used in these experiments $FeBr(C_6H_6)_2^+$ is formed neither by direct reaction of Fe$^+$ with benzene nor by displacement of weaker ligand molecules from an FeBr(L)$_2^+$ species. This fact is particularly interesting because when FeBr$^+$ is produced in the presence of C_6H_5CN, $FeBr(C_6H_5CN)_2^+$ is rapidly formed. Furthermore when Fe$^+$ is produced in the presence of benzene, rapid condensation with two ligand molecules occurs to give $Fe(C_6H_6)_2^+$.[14] Lack of reaction to give $FeBr(C_6H_6)_2^+$ can be explained in terms of steric repulsions between the large bromine atom and the two bulky benzene ligands which probably bond face on to Fe$^+$. Observation of a two-ligand complex with cyanobenzene suggests that the primary interaction of FeBr$^+$ with C_6H_5CN is through the –CN group.

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[11] Corrections for symmetry number changes cancel because Q is a difference.

[12] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley Interscience: New York, 1976; p 76.

[13] Kappes, M. M.; Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 888–889.

[14] Uppal, J. S.; Staley, R. H., unpublished results.

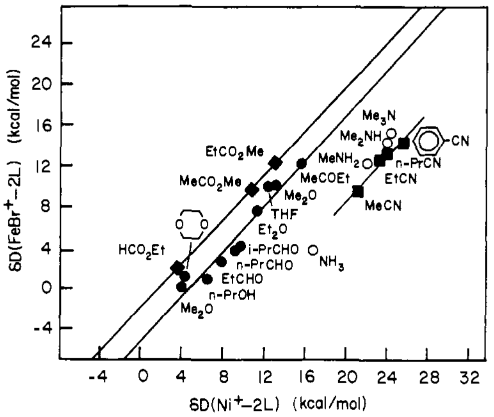

Figure 3. Comparison of the relative ligand dissociation enthalpies for $FeBr^+$ to relative two-ligand dissociation enthalpies for Ni^+. The upper solid line is a least-squares fit to the data for the three esters (♦): $\delta D(FeBr^+–2L) = 1.07\delta D(Ni^+–2L) - 2.0$ kcal/mol (correlation coefficient, $r = 1.000$). A least-squares fit to the data for 10 oxygen bases (●) gives the middle line: $\delta D(FeBr^+–2L) = 1.12\delta D(Ni^+–2L) - 5.23$ kcal/mol ($r = 0.928$). The lower solid line is a least-squares fit to the data for the four nitriles: $\delta D(FeBr^+–2L) = 1.06\delta D(Ni^+–2L) - 12.8$ kcal/mol ($r = 0.965$) (■).

Relative two-ligand dissociation enthalpies for the 24 molecules studied in this work, arranged by functional group, are plotted in Figure 2. Within each functional group series, alkyl substituent effects are apparent. Substitution of a larger alkyl group for a smaller one leads to a systematic increase in $\delta D(FeBr^+–2L)$. Similar effects have been seen for proton affinities,[15,16] for one-ligand binding energies to Li^+,[17] Al^+,[2] NO^+,[18] Mn^+,[3] and $CpNi^+$ [19] and for two-ligand binding energies to Co^+,[5] Cu^+,[4] and Ni^+.[6]

The bonding interaction of $FeBr^+$ with ligand molecules may be expected to reflect both ionic and covalent factors. $FeBr^+$ can be regarded as containing a dispositive iron cation interacting with a bromine anion. Ionic effects in which ligands are attracted by interaction of intrinsic and induced ligand dipoles with the charge on Fe^{2+} are probably more important than covalent factors. Covalent bonding could occur by delocalization of electrons from occupied ligand orbitals into the empty 4s and 4p orbitals on Fe^+. Another possibility for covalent bonding is delocalization of 3d electrons on Fe^+ into unoccupied π^* or d orbitals on the ligands, π-back-bonding. This can occur only for ligand molecules with suitable orbitals available.

Comparisons to Basicity Scales for Other Reference Acids. Comparison of the relative two-ligand dissociation enthalpies for $FeBr^+$ with available results for other reference acids reveals some interesting points about the nature of the bonding interactions occurring in $FeBr(L)_2^+$ complexes. Figure 3 shows a plot of ligand binding energies to $FeBr^+$, $\delta D(FeBr^+–2L)$, vs. the results for Ni^+,[6] $\delta D(Ni^+–2L)$. Ten oxygen bases including alcohols, ethers, ketones, and aldehydes fall approximately on a single line. A least-squares fit to this data gives $\delta D(FeBr^+–2L) = 1.12\delta D(Ni^+–2L) - 5.2$ kcal/mol (correlation coefficient, $r = 0.928$). A separate line could probably be drawn through the ethers, but this is not done here, and the ether data points are included with the other oxygen compounds. The three ester data points do clearly define a line which has a similar slope to, but is offset from, the oxygen base correlation line: $\delta D(FeBr^+–2L) = 1.07\delta D(Ni^+–2L) - 2.0$ kcal/mol ($r = 1.000$). The offset of the ester correlation line by -2.4 kcal/mol on the $D(Ni^+–2L)$ axis indicates a stronger interaction between $FeBr^+$ and esters than is observed for Ni^+. Similar deviations from the main oxygen base line have been seen for esters in other correlations and may be explained by the differing abilities of the two reference acids to bond efficiently to *both* oxygens of the ester group. Four nitriles define a third line which is offset from the oxygen base correlation line by 8 kcal/mol on the $D(Ni^+–2L)$ axis: $\delta D(FeBr^+–2L) = 1.06\delta D(Ni^+–2L) - 12.8$ kcal/mol ($r = 0.965$). This result implies that nitriles bond relatively more strongly to Ni^+ than to $FeBr^+$. Considering that nitriles are soft bases it can be concluded that $FeBr^+$ is a comparatively harder acid than Ni^+.

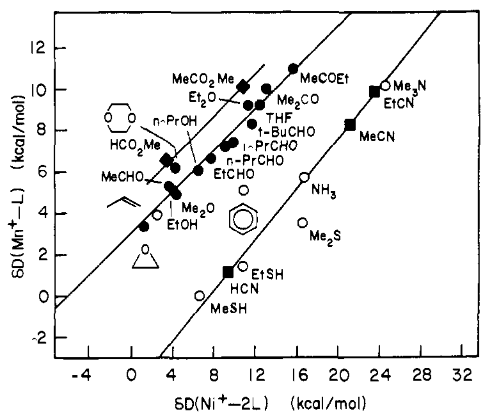

Figure 4. Comparison of ligand dissociation enthalpies for Mn^+ to relative two-ligand dissociation enthalpies for Ni^+. Two esters define the upper solid line (♦): $\delta D(Mn^+–L) = 0.48\delta D(Ni^+–2L) = 4.7$ kcal/mol. A least-squares fit to the data for 14 oxygen bases (●) gives the middle line: $\delta D(Mn^+–L) = 0.49\delta D(Ni^+–2L) + 3.06$ kcal/mol ($r = 0.954$). The lower solid line is a least-squares fit to the data for the three nitriles (■): $\delta D(Mn^+–L) = 0.61\ \delta D(Ni^+–2L) - 4.53$ kcal/mol ($r = 0.998$).

Due to poor data overlap, comparisons of the $FeBr^+$ data to basicity scales obtained for Co^+, Cu^+ and $CpNi^+$ [4,5,19] do not provide any new insights into bonding interactions in FeBr complexes. All 12 data points in the Cu^+–$FeBr^+$ correlation are oxygen bases. A least-squares fit to this data gives $\delta D(Cu^+–2L) = 0.85\delta D(FeBr^+–2L) + 11.48$ kcal/mol ($r = 0.980$). Similarly the 10 data points in the Co^+–$FeBr^+$ comparison are all oxygen bases. Statistical analysis of these numbers yields a straight-line fit of $\delta D(Co^+–2L) = 0.78\ \delta D(FeBr^+–2L) + 3.79$ kcal/mol ($r = 0.992$). Comparison of $FeBr^+$ and $CpNi^+$ basicity scales is somewhat more interesting. Eight oxygen compounds fall on a line given by $D(CpNi^+–L) = 0.407\delta D(FeBr^+–2L) + 50.4$ kcal/mol ($r = 0.896$). Offset from this line by about 8 kcal/mol on the $D(FeBr^+–2L)$ axis are five nitrogen compounds which include nitriles and amines. The offset of these soft acids indicates comparatively stronger bonding to $CpNi^+$ and consequently implies that $CpNi^+$ is a softer acid than $FeBr^+$.

A correlation diagram very similar to Figure 3 is obtained when ligand binding energies to Mn^+,[3] $\delta D(Mn^+–L)$, are plotted against the results from Ni^+,[6] $\delta D(Ni^+–2L)$ (Figure 4). Fourteen oxygen compounds fall on one line. At least-squares fit gives $\delta D(Mn^+–L) = 0.491\delta D(Ni^+–2L) + 3.1$ kcal/mol ($r = 0.954$). Two esters define a line which is offset toward Mn^+: $\delta D(Mn^+–L) = 0.484\delta D(Ni^+–2L) + 4.70$ kcal/mol. Three nitriles fall on a third line which is offset from the oxygen base correlation by 11 kcal/mol on the $D(Ni^+–2L)$ axis: $\delta D(Mn^+–L) = 0.607\delta D(Ni^+–2L) - 4.5$ kcal/mol ($r = 0.998$).

The close resemblance of Figures 3 and 4 indicates that the bonding interactions occurring between the ligands studied and $FeBr^+$ or Mn^+ are very similar. This is not unexpected because Mn^+ is isoelectronic with the formally dispositive iron cation in $FeBr^+$. However, the electronic ground states of the two ions are not the same. Mn^+ has a ^7S ground state corresponding to an $[Ar](3d)^5(4s)^1$ configuration. Fe^{2+} has a ^5D ground state with an $[Ar](3d)^6$ configuration.[20] Excitation of Fe^{2+} from the

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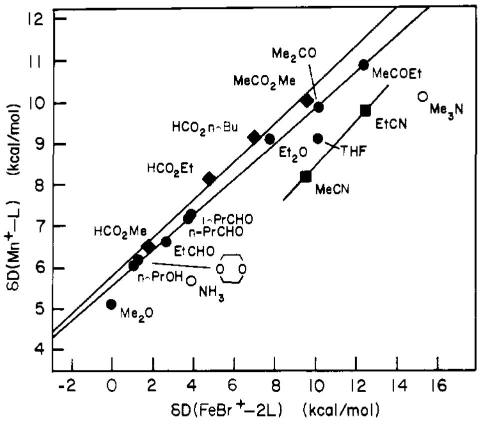

Figure 5. Comparison of ligand dissociation enthalpies for Mn$^+$ to relative two-ligand dissociation enthalpies for FeBr$^+$. Least-squares-fit lines are drawn for 4 esters (♦): $\delta D(\mathrm{Mn^+–L}) = 0.46\delta D(\mathrm{Ni^+–2L}) + 5.79$ kcal/mol ($r = 0.982$) and 10 oxygen bases (●): $\delta D(\mathrm{Mn^+–L}) = 0.43\delta D(\mathrm{Ni^+–2L}) + 5.49$ kcal/mol ($r = 0.975$). Two nitriles define the lower solid line (■): $\delta D(\mathrm{Mn^+–L}) = 0.46\delta D(\mathrm{FeBr^+–2L}) + 5.63$ kcal/mol.

[Ar](3d)^6 ^{5}D ground state to the [Ar](3d)^5(4s)^1 ^{7}S state requires 3.7 eV. It seems unlikely that the presence of the Br$^-$ would stabilize the ^{7}S state sufficiently with respect to the ^{5}D state to make the ^{7}S state the lowest state, but the electronic structure of the FeBr$^+$ molecular ion is not experimentally known. It thus appears that the difference in electronic state between Mn$^+$ and Fe^{2+} does not have a significant effect on bonding interactions.

It is of interest to note that the Mn$^+$ basicity scale is a one-ligand dissociation enthalpy scale, whereas both Ni$^+$ and FeBr$^+$ scales are for two-ligand complexes. As discussed above there is reason to question whether one-ligand binding energies D(M$^+$–L) are simply related to two-ligand binding energies, D(M$^+$–2L). The close similarity of Figures 3 and 4, however, suggests that one- and two-ligand dissociation enthalpies are simply related although likely differing by at least a scale factor.

Results for FeBr$^+$ and Mn$^+$ can be directly compared. Figure 5 shows a plot of ligand binding energies to Mn$^+$,[4] δD(Mn$^+$–L), vs. the results for FeBr$^+$, δD(FeBr$^+$–2L). Close scrutiny of the diagram reveals only very minor differences in bonding between Mn$^+$ and FeBr$^+$. Ten oxygen bases fall on a line given by $\delta D(\mathrm{Mn^+–L}) = 0.425\delta D(\mathrm{FeBr^+–2L}) + 5.5$ kcal/mol ($r = 0.975$). Five esters fall on a separate line which has a similar slope but is slightly offset by −0.8 kcal on the D(FeBr$^+$–2L) axis. Two nitriles define another line which is offset from the oxygen base correlation by 2.2 kcal/mol on the D(FeBr$^+$–2L) axis: $\delta D(\mathrm{Mn^+–L}) = 0.457\delta D(\mathrm{FeBr^+–2L}) + 5.63$ kcal/mol. This result indicates that FeBr$^+$ is a slightly softer acid than Mn$^+$.

A comparison of ligand binding energies to Al$^+$,[2] δD(Al$^+$–L), vs. the results for FeBr$^+$, δD(FeBr$^+$–2L), is shown in Figure 6. Eight oxygen compounds fall on a line given by $\delta D(\mathrm{Al^+–L}) = 0.495\delta D(\mathrm{FeBr^+–2L}) + 0.76$ kcal/mol ($r = 0.967$). A line with a significantly different slope is obtained for the six esters: $\delta D(\mathrm{Al^+–L}) = 0.638\delta D(\mathrm{FeBr^+–2L}) + 0.53$ kcal/mol ($r = 0.997$). Four nitriles define a line which is offset from the oxygen base line by 11 kcal/mol on the D(FeBr$^+$–2L) axis and which again has a slope that is significantly different from that of the oxygen line $\delta D(\mathrm{Al^+–L}) = 0.834\delta D(\mathrm{FeBr^+–2L}) - 8.26$ kcal/mol ($r = 0.964$). The observed offset indicates that FeBr$^+$ is a softer acid than Al$^+$.

Significant variations in slope among correlation lines *within* a specific correlation diagram were not previously observed. This has, to data, been true for all comparisons between two metal cations in which multiple correlation lines can be drawn.[3–6] The variations in slope observed in the Al$^+$–FeBr$^+$ correlation diagram reflect a bonding effect specific to FeBr$^+$ complexes rather than an overlooked effect in Al$^+$ ligand-bonding energies. The observed variations in slope show that the alkyl-substituent effect is most effective in FeBr$^+$ complexes with oxygen bases and least effective for nitriles. This appears to indicate that the nitrile–FeBr$^+$ bonding distance is significantly longer than the corresponding oxygen base–FeBr$^+$ interaction distance. These apparent variations in bonding distance may result from steric repulsions in the nitrile complexes of some other interaction involving the Br$^-$.

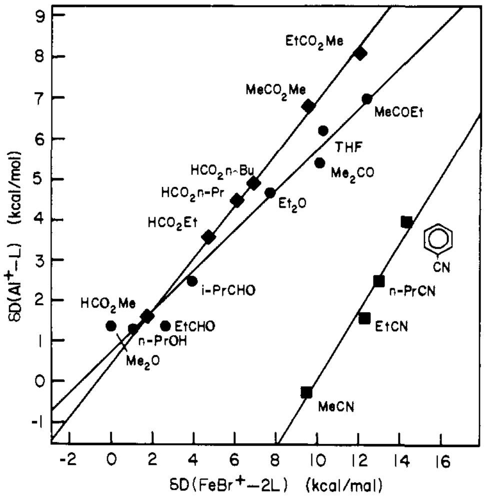

Figure 6. Comparison of ligand dissociation enthalpies for Al$^+$ to relative two-ligand dissociation enthalpies for FeBr$^+$. The upper solid line is a least-squares fit to the data for 6 esters (♦): $\delta D(\mathrm{Al^+–L}) = 0.64\delta D(\mathrm{FeBr^+–2L}) + 0.53$ kcal/mol ($r = 0.997$). A least-squares fit to the data for 8 oxygen bases (●) gives the middle line: $\delta D(\mathrm{Al^+–L}) = 0.50\delta D(\mathrm{FeBr^+–2L}) + 0.76$ kcal/mol ($r = 0.967$). The lower solid line is a least-squares fit to the data for the four nitriles (■): $\delta D(\mathrm{Al^+–L}) = 0.83\delta D(\mathrm{FeBr^+–2L}) - 8.3$ kcal/mol ($r = 0.964$).

A plot of proton affinities, PA(B) ≡ D(B–H$^+$)[15,16] vs. the results for FeBr$^+$ indicates that, as expected, the proton is a harder acid than FeBr$^+$. Eleven oxygen compounds fall on a line given by $\mathrm{PA} = 0.763\delta D(\mathrm{FeBr^+–2L}) + 191.3$ kcal/mol ($r = 0.760$). The four nitriles define a separate line with a different slope which is offset from the oxygen base correlation by about 10 kcal/mol on the D(FeBr$^+$–2L) axis. Interestingly, amines do not fall on, or close to, the nitriles line as was seen in FeBr$^+$–Ni$^+$ and Mn$^+$–FeBr$^+$ correlations. Instead they are significantly offset from the oxygen base line toward stronger bonding to H$^+$. This type of behavior has been seen in a previous correlation of proton affinities and nickel binding energies and probably reflects a specific effect in the interaction of the *proton* with amines.[6]

In conclusion, the relative gas-phase two-ligand dissociation enthalpies for FeBr$^+$, δD(FeBr$^+$–2L), measured in this work show that FeBr$^+$ is a moderately soft acid. It is harder than Co$^+$, Ni$^+$, Cu$^+$, and CpNi$^+$, only slightly softer than Mn$^+$, and softer than Al$^+$ or H$^+$. FeBr$^+$–ligand bonding interactions can be influenced by steric effects which result from the presence of a bulky Br atom on the iron. The comparison of FeBr$^+$ and Mn$^+$ scales shows that the bonding interactions in FeBr(L)$_2^+$ and Mn(L)$^+$ complexes are very similar. This is not unexpected because the iron in FeBr$^+$ is formally isoelectronic with Mn$^+$.

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Registry No. FeBr(Me$_3$N)$_2^+$, 80679-53-4; FeBr(C$_6$H$_5$CN)$_2^+$, 80679-54-5; FeBr(Me$_2$NH)$_2^+$, 80679-55-6; FeBr(n-PrCN)$_2^+$, 80679-56-7; FeBr(MeNH$_2$)$_2^+$, 80679-57-8; FeBr(MeCOEt)$_2^+$, 80679-58-9; FeBr(EtCN)$_2^+$, 80679-59-0; FeBr(EtCO$_2$Me)$_2^+$, 80679-60-3; FeBr(THF)$_2^+$, 80679-61-4; FeBr(Me$_2$CO)$_2^+$, 80679-62-5; FeBr(MeCO$_2$Me)$_2^+$, 80679-63-6; FeBr(MeCN)$_2^+$, 80679-64-7; FeBr(Et$_2$O)$_2^+$, 80679-65-8; FeBr(HCO$_2$$n$-Bu)$_2^+$, 80679-66-9; FeBr(HCO$_2$$n$-Pr)$_2^+$, 80679-67-0; FeBr(HCO$_2$Et)$_2^+$, 80679-68-1; FeBr($i$-PrCHO)$_2^+$, 80679-69-2; FeBr(NH$_3$)$_2^+$, 80679-70-5; FeBr($n$-PrCHO)$_2^+$, 80679-67-0; FeBr(EtCHO)$_2^+$, 80696-73-7; FeBr(1,4-dioxane)$_2^+$, 80679-71-6; FeBr(HCO$_2$Me)$_2^+$, 80679-72-7; FeBr(n-PrOH)$_2^+$, 80679-73-8; FeBr(Me$_2$O)$_2^+$, 80679-74-9.