Analyzing Fluoride Binding by Group 15 Lewis Acids: Pnictogen Bonding in the Pentavalent State

Logan T. Maltz and François P. Gabbaï*

ABSTRACT: We report the results of a computational investigation into fluoride binding by a series of pentavalent pnictogen Lewis acids: pnictogen pentahalides (PnX₅), tetraphenyl pnictogeniums (PnPh⁺), and triphenyl pnictogen tetrachlorocatecholates (PnPh₃Cat). Activation strain and energy decomposition analyses of the Lewis adducts clearly delineate the electrostatic and orbital contributions to these acid-base interactions, but they also highlight the importance of Pauli repulsion and molecular flexibility in determining relative Lewis acidity among the pnictogens.

INTRODUCTION

Among Lewis acids, antimony holds a special place. SbF₅, in particular, is a Lewis superacid that has had profound impacts on chemistry as exemplified by the works of Olah involving magic acid. Recently, our group and others have effectively employed the unique Lewis acidity of Sb to develop transmembrane anion transporters and anion-recognition platforms. But what is it that distinguishes Sb from the other elements in the pnictogen (Pn) group? As chemists, we turn to chemical bonding and the competition between covalency and ionicity to answer this question.

Being saturated or hypervalent, pentavalent pnictogen uses an empty σ*-orbital to accept electron density. At the same time, the coincident σ-hole provides Coulombic stabilization to the newly formed linkage. Steiner detailed the importance of these effects in his original definition of the pnictogen bond using trivalent elements. Obviously, the distinction between the pnictogens must rely on amplification of whichever form of bonding predominates. Is the interaction more covalent? Then we might look to relative LUMO energies to provide insight into the increasing Lewis acidity down the group. Does ionicity dominate the bonding interaction? Then we might look to measures of the electrostatic potential to understand the increased Lewis acidity of Sb derivatives.

Wanting simple, intuitive descriptions of chemical bonding, we sometimes forget its complexity. Fortunately, chemists have developed models to better conceptualize complex interactions. Computational energy decomposition analysis (EDA) provides a convenient way to break down an interaction into various energetic contributions: London dispersion interactions (ΔE_{disp}), electrostatic interactions (ΔE_{el}), orbital interactions (ΔE_{oa}), and Pauli repulsion (ΔE_{Pauli}). In our constant debates about the covalency or ionicity of an interaction, we often neglect London dispersion and Pauli repulsion.

Hypervalent SbF₅ reminds us that with any interaction—but especially closed-shell interactions—we need to consider Pauli repulsion: the destabilizing interaction occurring when two filled orbitals interact with each other. This repulsion is the underlying electronic basis for what we term “steric interactions” and is also at play in our discussions of ionic and covalent bonding. In this paper, we contend that Pauli repulsion rivals electrostatic and orbital interaction contributions in its importance to the Lewis acidity of the pnictogens.

In the past decade, the utility of the activation strain model (ASM) has been repeatedly demonstrated. This model bifurcates the overall interaction energy ΔE into the energy necessary to strain the interacting species into their interacting geometries (ΔE_{strain}) and the energy associated with allowing these strained species to interact (ΔE_{int}). To fully understand the interactions in these systems, ΔE_{int} is then parsed into its constituent components using EDA in the Amsterdam Density Functional (ADF) program (Figure 1). ΔE_{strain} and ΔE_{Pauli} serve as convenient metrics to quantify interaction components not as comfortably approachable as ΔE_{el} and ΔE_{oa}.

Inspired by Bickelhaupt and co-workers’ analysis of trivalent pnictogen trihalides,8 we have undertaken a similar analysis on a series of pentavalent pnictogen Lewis acids: pnictogen pentahalides (PnX₅), tetraphenyl pnictogeniums (PnPh⁺), and triphenyl pnictogen tetrachlorocatecholates (PnPh₃Cat) (Figure 1). The last two families of compounds were selected because of their extensive use by our group as anion-binding platforms, anion sensors, and anion transporters. Unlike the previous work on trivalent pnictogens,8 we expanded the scope of Lewis acids beyond the homoleptic halides but narrowed the scope of Lewis bases, focusing on these acids’ interactions with fluoride (F). As such, we are effectively decomposing fluoride

Figure 1. Top: Lewis acids surveyed in this study. Bottom: Energy components comprising the overall interaction energy between the Lewis acids studied and F⁻.
Table 1. Activation strain and energy decomposition analyses (in kcal mol\(^{-1}\)) at optimized geometries.\(^{a}\)

<table>
<thead>
<tr>
<th>Acid</th>
<th>(\Delta E)</th>
<th>(\Delta E_{\text{strain}})</th>
<th>(\Delta E_{\text{int}})</th>
<th>(\Delta E_{\text{dd}})</th>
<th>(\Delta E_{\text{disp}})</th>
<th>(d_{\text{HF-\text{F}}}) ((\text{\AA}))</th>
<th>Charge(^b)</th>
<th>(E_{\text{LUMO}}) (eV)(^c)</th>
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<tr>
<td>PF(_3)</td>
<td>-49.6</td>
<td>18.5</td>
<td>-68.1</td>
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<td>230.7</td>
<td>1.739(^d)</td>
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<td>-80.2</td>
<td>-161.0</td>
<td>-81.5</td>
<td>162.2</td>
<td>1.989(^e)</td>
<td>1.67</td>
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<td>5.8</td>
<td>-78.7</td>
<td>-142.9</td>
<td>-62.9</td>
<td>127.1</td>
<td>2.119(^e)</td>
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<td>-215.1</td>
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<td>-98.7</td>
<td>159.6</td>
<td>2.065</td>
<td>0.75</td>
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\(\Delta E_{\text{disp}}\) omitted for clarity. \(^a\) Mulliken charge in strained acid without F. \(^b\) LUMO energy in strained acid without F. \(^c\) Smaller of two Pn···F distances. \(^d\) Isomer with F\(_{\text{trans}}\) to Ph. For the complete table, see Table 1 in the ESI.

Chart 1. Bar graph depicting the data from the activation strain and energy decomposition analyses of PnF\(_3\) and PnF\(_3\) Lewis acids. \(\Delta E_{\text{disp}}\) has been omitted for clarity.

The computations and analyses presented in this article illustrate that despite having lower magnitudes of stabilizing contributions from \(\Delta E_{\text{d}}\) and \(\Delta E_{\text{dd}}\), Sb displays the highest Lewis acidity (most negative \(\Delta E\)) in almost every case analyzed. This result is due to Sb also having lower magnitudes of destabilizing contributions from \(\Delta E_{\text{strain}}\) and \(\Delta E_{\text{pauli}}\).

**RESULTS AND DISCUSSION**

Our lab has previously demonstrated that oxidizing the pnictogen center from the +3 state to the +5 state increases its Lewis acidity.\(^{21}\) This conclusion is corroborated by the ~40 kcal mol\(^{-1}\) increase in the magnitude of \(\Delta E\) for all pnictogens going from PnF\(_3\) to PnF\(_3\) (Table 1). Gratifyingly, this data vindicates our assertion that oxidation leads to an increase in the electrostatic contribution to the interaction through a deepening of the σ-hole and an increase in the orbital contribution through the lowering of the σ*-based LUMO (Chart 1). As expected with an increased number of substituents attached to the central

**COMPUTATIONAL METHODS**

For computational efficiency, we optimized the initial geometries of the Lewis acids and their fluoride adducts in Orca 5.0.2\(^{22}\) using PBEh-3c/def2-mSVP\(^{10}\) with the default def2grid2 settings. Frequency calculations were performed at the same level of theory to verify that all optimized structures were at a local minimum on the potential energy surface. Where possible, structures were re-optimized from previously optimized coordinates.\(^{8,11}\) All other structures were initially produced using either GaussView 6.1.1\(^{12}\) or Avogadro\(^{13}\) or by substituting one atom for another in the input file before performing the optimization. For the F\(_3\) adducts of the PnPhCat species, two isomers were possible: F\(_{\text{trans}}\) to Ph or F\(_{\text{trans}}\) to O in the tetrachlorocatecholate. In the main text, the isomer with F\(_{\text{trans}}\) to Ph is discussed as it is the lowest-energy isomer for Sb and similar trends are seen among both isomers. For completeness, both isomers were fully analyzed, and that data is presented in Table S1 and Graphs S7-S9.

Single-point energy calculations and EDA\(^{14}\) were conducted in ADF 2022.101\(^{15}\) using the M06 functional\(^{16}\) paired with the D3 model to account for dispersion effects.\(^{17}\) The QZ4P basis set\(^{18}\) as implemented in the ADF program was used without frozen-core approximation and with good numerical quality. The zeroth-order regular approximation (ZORA) Hamiltonian was employed to account for scalar relativistic effects.\(^{19}\) The dependencies were fixed for the PnPhCat species due to their size. \(\Delta E_{\text{strain}}\) was determined by subtracting the single-point energy of the free Lewis acid from the single-point energy of the strained Lewis acid with no F\(_{\text{bound}}\). EDA directly provided \(\Delta E_{\text{disp}}, \Delta E_{\text{dd}}, \Delta E_{\text{dd}},\) and \(\Delta E_{\text{pauli}}\). Mulliken charges and LUMO energies were obtained from ADF as well. As expected for a hard ion such as F\(_{\text{-}}, \Delta E_{\text{disp}}\) is negligible for all Lewis acids considered, reaching a maximum magnitude of ~0.5 kcal mol\(^{-1}\) in the PnPh\(_3\) and PnPhCat species which is expected given their larger surface areas (Table S1).

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pnictogen, we also see an increase in $\Delta E_{\text{strain}}$ and $\Delta E_{\text{Pauli}}$ moving from PF$_3$ to PF$_5$. Thus, for oxidation from Pn$^{\text{III}}$ to Pn$^{\text{V}}$, the substantial increase in stabilization energy leads to greatly enhanced Lewis acidity despite a simultaneous increase in destabilizing interactions. As we will discuss, this scenario is inverted when looking at the periodic trends across the pentavalent pnictogens.

We focus our analysis on the PnF$_5$ series as the trends seen hold for the other series. With a $\Delta E$ of -120.3 kcal mol$^{-1}$—in line with previously computed fluoride ion affinities$^{20}$—SbF$_5$ is the strongest Lewis acid in this series. Down the group, there is a 28.7 kcal mol$^{-1}$ increase in the magnitude of $\Delta E$ from -91.6 kcal mol$^{-1}$ for PF$_5$. This general trend of increasing Lewis acidity down the group has been observed experimentally as well.$^6$ While the destabilization from $\Delta E_{\text{strain}}$ decreases from 51.8 kcal mol$^{-1}$ in PF$_3$ to 23.7 kcal mol$^{-1}$ in SbF$_5$, $\Delta E_{\text{strain}}$ stays nearly constant, seemingly only a 0.7 kcal mol$^{-1}$ increase in magnitude.

The decrease in $\Delta E_{\text{strain}}$ follows from the larger size of the pnictogen center allowing increased flexibility of the coordinated ligands. This flexibility was highlighted in Moc and Morokuma’s 1997 study on hypervalent pnictogenes wherein they concluded that the larger pnictogens enjoy a reduced barrier to Berry pseudorotation due to an increased ease in adjusting their Pn-F bond lengths from the ground state $D_{3h}$ structure to achieve the transitional $C_{3v}$ structure.$^{22}$ Their values for the pseudorotation barrier are comparable to those calculated by Breidung and Thiel in 1992.$^{23}$ During this conversion from $D_{3h}$ to $C_{3v}$, the pnictogen-centered HOMO-1 increases in energy while the predominantly ligand-based HOMO decreases in energy.$^{24}$ Accordingly, decreasing the destabilization of the pnictogen-based HOMO-1 corresponds with a decrease in the pseudorotation barrier. Given this analysis, it seems that the most influential factor in the PnF$_3$ series is the weaker bonds formed down the group resulting from greater atomic radius and increased orbital diffuseness which both lead to less effective orbital overlap. Steric repulsion also plays a role in decreased $\Delta E_{\text{strain}}$ as larger atoms allow more room between the ligands as they become compressed in the $C_{3v}$ geometry.

Turning our attention from $\Delta E_{\text{strain}}$, we see that though the change in $\Delta E_{o}$ is small down the group, the magnitude of $\Delta E_{\text{strain}}$ is three to six times greater than that of $\Delta E_{\text{strain}}$ and thus contributes significantly to $\Delta E$. As expected with increased atomic radius, $\Delta E_{o}$ decreases consistently down the group with SbF$_5$ having an electrostatic contribution that is 10.8 kcal mol$^{-1}$ less stabilizing than that in PF$_5$. $\Delta E_{o}$ sees a dramatic decrease of 52.7 kcal mol$^{-1}$ in stabilization going from PF$_5$ to SbF$_5$ which can be attributed to the increased diffuseness of the pnictogen center’s orbitals leading to decreased overlap with the incoming Lewis base due to the size mismatch. This combination of increasing atomic radius and increasing orbital diffuseness progressively favors the ionic contribution down the group with $\Delta E_{o}$ increasing from 59% of the stabilizing contribution in PF$_5$ to 67% in SbF$_5$.

Table 2. Comparison of $\Delta E$ and FIA (in kcal mol$^{-1}$)

<table>
<thead>
<tr>
<th>Acid</th>
<th>$\Delta E$</th>
<th>FIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF$_3$</td>
<td>-49.6</td>
<td>47.8$^a$</td>
</tr>
<tr>
<td>AsF$_3$</td>
<td>-60.1</td>
<td>58.3$^a$</td>
</tr>
<tr>
<td>SbF$_3$</td>
<td>-71.2</td>
<td>69.3$^a$</td>
</tr>
<tr>
<td>BiF$_3$</td>
<td>-72.9</td>
<td>—</td>
</tr>
<tr>
<td>PF$_5$</td>
<td>-91.6</td>
<td>91.0$^a$</td>
</tr>
<tr>
<td>AsF$_5$</td>
<td>-104.5</td>
<td>104.1$^a$</td>
</tr>
<tr>
<td>SbF$_5$</td>
<td>-120.3</td>
<td>117.6$^a$</td>
</tr>
<tr>
<td>BiF$_5$</td>
<td>-116.9</td>
<td>115.2$^a$</td>
</tr>
</tbody>
</table>

$^a$FIA values converted from kJ mol$^{-1}$ from Ref.$^{20}$ FIA values obtained as negatives of the reaction energy for PnF$_5$ + F$^-$$\rightarrow$ PnF$_6$ in Ref.$^{22}$

With a smaller-than-expected increase in size, the Bi-F bonds are closer to the incoming F$^-$ than might otherwise be anticipated leading to the smaller-than-expected decrease in Pauli repulsion. As such, the larger-than-expected Pauli repulsion is not as effectively counterbalanced by the stabilizing contributions in Bi as it is in Sb, leading to a reduction in overall Lewis acidity. Owing to the scandide contraction, a similarly small decrease of 10% in $\Delta E_{\text{Pauli}}$ is seen for the transition from P to As; however, this 10% decrease corresponds to a considerable 23.4 kcal mol$^{-1}$ reduction in $\Delta E_{\text{Pauli}}$ while the 8% drop from Sb to Bi only produces a 14.1 kcal mol$^{-1}$ decrease indicating that an increase in covalent radius has a more profound effect on $\Delta E_{\text{Pauli}}$ for smaller atoms.

With these trends in mind, we turn to more complex pnictogen-based Lewis acids, starting with the PnPh$_5^+$ series. These cationic species serve as representative examples of pnictogen-based Lewis acids employed extensively in anion transport.$^{38}$ For these cationic species—and the rest of the species studied—$\Delta E$ seems to oscillate: Sb and Bi have larger $\Delta E$’s than P and As with Bi and As having the lower $\Delta E$’s in these pairs (Chart 2). While this “secondary periodicity” is also seen in the $\Delta E_{\text{strain}}$ of the PnF$_5$ series, it likely manifests in the $\Delta E$ of the PnPh$_5^+$ series due to a slight increase in the importance of $\Delta E_{o}$ as a
result of the cationic charge.\textsuperscript{27} The percentage of $\Delta E_{\text{el}}$’s contribution to the stabilization energy increases from 59-68\% in the PnF\textsubscript{5} series to 62-71\% in the PnPh\textsuperscript{+} series. Furthermore, $\Delta E_{\text{el}}$ increases in magnitude by \textasciitilde 20-30 kcal mol\textsuperscript{-1} for P and Sb but only \textasciitilde 12-16 kcal mol\textsuperscript{-1} for As and Bi. This observed secondary periodicity results from the scandide contraction at As and the lanthanide contraction at Bi which lead to not only smaller radii than would be expected but also higher electronegativities than expected.

While electronegativity seemingly decreases down the group according to the Pauling scale, Haïssinsky reminds us that electronegativity increases with oxidation state, leading to electronegativities of 2.2 for As\textsuperscript{3+}, 2.1 for Sb\textsuperscript{5+}, and \textasciitilde 2.3 for Bi\textsuperscript{5+}.\textsuperscript{28} This fluxional electronegativity is seen in the Mulliken charges in the strained geometries: +0.61 for P, +0.44 for As, +0.93 for Sb, and +0.66 for Bi. This reduced positive charge at the pnictogen center in conjunction with the increased radius leads to a significant decrease in $\Delta E_{\text{el}}$ from P to As and from Sb to Bi, ultimately reflected in $\Delta E$ due to the increased prominence of electrostatic contributions in these cationic species.

Despite the apparent increased importance of $\Delta E_{\text{el}}$ in determining $\Delta E$, SbPh\textsuperscript{+} — even with its lower $\Delta E_{\text{el}}$ — is still 16.6 kcal mol\textsuperscript{-1} more acidic than PPh\textsuperscript{+}. While the stabilizing interactions ($\Delta E_{\text{el}} + \Delta E_{\text{eo}}$) decrease by 75.3 kcal mol\textsuperscript{-1}, they are matched by a 77.3 kcal mol\textsuperscript{-1} decrease in $\Delta E_{\text{pauli}}$. The 14.7 kcal mol\textsuperscript{-1} decrease in $\Delta E_{\text{strain}}$ then drives the increased Lewis acidity of SbPh\textsuperscript{+}.

Finally, we analyzed the neutral PnPh\textsubscript{5}Cat series. Oxidation of pnictogens using ortho-chloranil has been repeatedly applied to produce active anion receptors and Lewis acid catalysts.\textsuperscript{30,11} Due to the differing substituents, two isomers are possible upon binding F: one where F is trans to Ph and the other with F trans to Cat. Because the same trends hold in both series (ESI) and the isomer with F trans to Ph is the lowest in energy for Sb, we have focused our analysis on this series. Overall, these $\Delta E$ values are lower than their PnF\textsubscript{5} and PnPh\textsuperscript{+} counterparts yet still higher than those seen for the pnictogen trifluorides. This decreased Lewis acidity is expected due to a reduced σ-hole and a higher-lying σ*-orbital resulting from decreased bond polarity. This reduced polarity produces a less ionic interaction as seen in the relative contributions of $\Delta E_{\text{el}}$ and $\Delta E_{\text{eo}}$. $\Delta E_{\text{eo}}$ contributes 39-46\% to the total stabilizing energy for all pnictogens whereas it contributes 29-41\% in the PnF\textsubscript{5} and PnPh\textsuperscript{+} series (Chart 2). As also seen in the PnF\textsubscript{5} and PnPh\textsuperscript{+} series, Sb has the greatest Lewis acidity despite having the lowest magnitude of stabilizing contributions due to such a significant reduction in destabilizing contributions.

CONCLUSION

Though FIAs provide a way to compare the strengths of Lewis acids, activation strain analysis paired with EDA allows deeper insight into the underlying contributions to Lewis acid strength. We have confirmed that oxidation from Pn\textsuperscript{III} to Pn\textsuperscript{V} produces an increase in $\Delta E_{\text{el}}$ and $\Delta E_{\text{eo}}$ due to a deeper σ-hole and a lower-energy σ*-orbital. While it was already known that Sb-based acids are strong Lewis acids, our analysis highlights the significance of increased molecular flexibility and decreased Pauli repulsion in Sb’s pre-eminence among the pentavalent pnictogens. Despite lower stabilizing contributions from $\Delta E_{\text{el}}$ and $\Delta E_{\text{eo}}$ moving down the group, Sb exhibits greater Lewis acidity due to lower destabilizing contributions from $\Delta E_{\text{strain}}$ and $\Delta E_{\text{pauli}}$. We not only confirmed the importance of electrostatic contributions for cationic Lewis acids but also demonstrated that the pnictogen bond has substantial orbital contribution. Our hope is that this work informs future applications of pnictogen-based Lewis acids.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Complete data table, bar graphs, and optimized structures in XYZ format (PDF)

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Author Contributions

L.T.M. conducted the computational work and data analysis. F.P.G. oversaw the study. L.T.M. and F.P.G. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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Martell Chair of Chemistry). This research was conducted with the advanced computing resources provided by Texas A&M High-Performance Research Computing.

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