Teaching with Technology ————————————

A Lewis Acid–Base Computational Exercise
for Advanced Inorganic Chemistry

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The concept of Lewis acids and bases is commonly discussed in advanced inorganic chemistry courses. Yet there are few laboratory experiments on Lewis acids and bases, other than those involving coordination chemistry or calorimetry, that can be carried out successfully without high-vacuum apparatus. Therefore, a computational chemistry exercise that enables students to explore many of the facets of acid–base chemistry has been developed.

For a gas-phase reaction between a Lewis acid and a Lewis base

$$A(g) + :B(g) \rightarrow A:B(g)$$
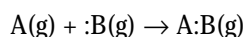
the binding energy is given by the difference between the energy of the adduct and that of the individual acid and base moieties:

$$\Delta E = E_{A:B} - E_A - E_{:B}$$

The goals of the exercise are:

1. To determine the relative strengths of the Lewis acids and Lewis bases by calculating the binding energies of the adducts.

2. To examine possible factors that might influence the binding energies, including:

   a. The relative energies of the highest occupied orbital on the base and the lowest unoccupied orbital on the acid.

   b. The charge capacity of the acid.

   c. The extent of charge transfer between the base and the acid upon adduct formation.

   d. Electrostatic interactions between the acid and the base in the adduct.

   e. The relative hardness and softness of the acid and base.

   f. The reorganizational energy that is required to change the geometry of the acid and base into that present in the adduct.

   g. Steric interactions between the acid and the base.

3. To examine structural changes that occur upon adduct formation.

   a. Bond lengths

   b. Bond angles

These effects have been the subject of several recent ab initio quantum mechanical investigations of adducts of boron or aluminum hydrides and halides with Lewis bases containing N or P donor atoms (*1–19*). However, high level ab initio calculations are not well suited for an advanced inorganic

chemistry course because they are too time-consuming for investigation of several adducts during a 4-hour laboratory period. Although the semiempirical MNDO model (*20*) has been employed by students in our advanced inorganic chemistry course (*21*), binding energy trends are not well reproduced at the semiempirical level. With the advent of faster computers, it is now possible to do ab initio calculations in a reasonable amount of time. Therefore, small basis set 3-21G (*22, 23*) ab initio quantum mechanical calculations are recommended for this exercise. Quantitative agreement with sophisticated ab initio methods cannot be expected from such low-level methods; however, trends in binding energies and geometrical parameters are well reproduced at the 3-21G level. Reasonable conclusions concerning factors that influence binding energies also can be drawn from the 3-21G results (*1, 3*).

Description of the Exercise

Most students have only limited exposure to molecular modeling prior to this exercise. Therefore, it is necessary to demonstrate to them how to build molecules, select the computational model, carry out geometry optimizations, and view the calculated properties once convergence has been attained. No attempt is made to provide a detailed background description of the quantum mechanical model employed. Such a description would certainly be appropriate if the exercise were used as part of a junior or senior level course in physical chemistry or molecular modeling.

The 3-21G ab initio basis set or semiempirical MNDO model, as implemented in the Windows 95 version of HyperChem 4.5 or 5.1 (*24*), is employed for the calculations. BH_3, BF_3, BCl_3, AlH_3, and $AlCl_3$ are used as the Lewis acids, and NH_3, PH_3, pyridine, 3,5-dimethylpyridine, and 2,6-dimethylpyridine as the Lewis bases. Additional considerations, such as the existence of B_2H_6 and Al_2Cl_6 as dimers in the gas phase, can be incorporated easily into the exercise. The procedure for the exercise is as follows.

STEP 1. The geometry of each free base is optimized and its total energy obtained. Values of the energy of the highest occupied and lowest unoccupied molecular orbitals of the base at its optimized geometry are recorded. The absolute hardness of the base can be approximated by $\frac{1}{2}$ the energy of the HOMO–LUMO gap (*25*). Preliminary information about the relative strength of the bases is obtained by calculating their proton affinities. Finally, the partial charge on the donor atom of the base is noted.

STEP 2. The geometry of each free acid is optimized and its total energy obtained. The geometry of the MX_4^- anion formed from the acid is then optimized to give idealized bond angles of 109.5°. An X^- ion is removed to give the neutral acid with an idealized, pyramidal structure. Although this

simple procedure gives M–X bond lengths that are somewhat too long, trends within the series of acids are correctly reproduced. From the difference in energy between the idealized pyramidal structure of the acid and its optimized planar structure, the reorganizational energy necessary to form the pyramidal structure can be calculated. The value of the partial charge on the acceptor atom of the pyramidal acid is noted, and the hardness of the pyramidal acid is determined from $\frac{1}{2}$ the energy of the HOMO–LUMO gap. Finally, the vertical electron attachment energy of the acid at its idealized pyramidal geometry is determined. This energy depends on the energy of the lowest unoccupied molecular orbital of the acid and its charge capacity.

STEP 3. The binding energies and geometrical parameters of acid–base adducts are calculated.

1. The geometries of the adducts are optimized, and the total energies, bond lengths, bond angles, and partial charges on the atoms in the adducts are recorded.

2. The base is deleted from the adduct, and the energy, E^A_{AB}, of the acid at its geometry in the adduct is calculated. The reorganizational energy of the acid is $E^A_{AB} - E^A_0$, where E^A_0 is the energy of the free acid at its optimized geometry.

3. The acid is deleted from the adduct, and the energy, E^B_{AB}, of the base at its geometry in the adduct is calculated. The reorganizational energy of the base is $E^B_{AB} - E^B_0$, where E^B_0 is the energy of the free base at its optimized geometry.

4. The extent of charge transfer from the base to the acid upon adduct formation is determined from the partial charges on all of the atoms of the acid.

Theoretical Model

Basis Set

Before discussing the results of the 3-21G calculations, a brief word about the quality of the calculations at different levels of theory is appropriate. Calculated values of several properties of the free bases, the free acids at idealized pyramidal geometries, and the adducts using MNDO and AM1 (26) semiempirical Hamiltonians or STO-3G (27, 28), 3-21G and 6-31G* (29) ab initio basis sets are shown in Tables 1–4. Trends in proton affinities of the bases are well reproduced by all except the STO-3G calculations. Trends in geometrical properties of the adducts are reasonably well reproduced by all of the methods, but the 3-21G model is the lowest level of theory that gives a good correlation with 6-31G* binding energies. Therefore, the 3-21G model represents the best compromise between speed and accuracy.

Geometry Optimization

Geometries were optimized to a gradient of 0.01 kcal/mol Å. The time required to optimize the geometries of the adducts can be decreased by optimizing the geometries using the MM+ molecular mechanics force field before optimizing the geometries at the ab initio level. Eigenvector following was the most efficient optimization method for the quantum mechanical calculations. If desired, vibrational frequencies can be calculated to assure that the stationary points correspond to energy minima. However, the time required for these calculations at the 3-21G level precludes routine vibrational calculations.

Discussion of Illustrative Results

Free Acids and Bases

Calculated proton affinities of several Lewis bases, the energies of their highest occupied molecular orbitals (HOMOs), their lowest unoccupied molecular orbitals (LUMOs), their calculated hardness ($\frac{1}{2}$ the HOMO–LUMO gap), and the partial charges on their donor atoms are given in Table 5. Nitrogen is a better donor atom than P, and the electron-releasing effects of the methyl groups and the electron-withdrawing effects of fluorine are reflected. The positive charges on the donor atoms of NF_3 and PH_3 should substantially decrease their base strengths electrostatically. The hardness of the bases decreases in the order $NF_3 > NH_3 > N(CH_3)_3 > PH_3 >$ pyridine $> 3,5$- dimethylpyridine $\sim 2,6$-

Table 1. Calculated Proton Affinities and Hardness of Lewis Bases

Base	Calculation	$E_{HOMO}/$ eV	$E_{LUMO}/$ eV	Hardness/ eV	$PA^a/$ kcal mol^{-1}
NF$_3$	—	—	—	—	136[b]
	6-31G*	-12.33	6.84	9.59	142
	3-21G	-15.01	6.02	10.52	127
	STO-3G	-10.69	12.21	11.45	185
	AM1	-13.18	0.93	7.06	74
	MNDO	-13.93	0.71	7.32	49
PH$_3$	—	—	—	—	188[b]
	6-31G*	-8.79	3.92	6.36	197
	3-21G	-10.36	4.92	7.64	184
	STO-3G	-8.13	13.40	10.77	244
	AM1	-10.42	1.31	5.87	128
	MNDO	-11.34	1.67	6.51	121
NH$_3$	—	—	—	—	204[b]
	6-31G*	-9.68	5.14	7.41	217
	3-21G	-10.58	7.49	9.04	227
	STO-3G	-9.76	17.01	7.32	227
	AM1	-10.42	4.22	7.32	157
	MNDO	-11.19	4.34	7.77	156
Pyridine	—	—	—	—	222[b]
	6-31G*	-9.36	3.45	6.41	—
	3-21G	-9.69	3.54	6.62	241
	STO-3G	-8.19	6.54	7.37	277
	AM1	-9.93	0.14	5.04	163
	MNDO	-9.69	0.01	4.85	168
N(CH$_3$)$_3$	—	—	—	—	227[b]
	6-31G*	-9.44	6.10	7.77	240
	3-21G	-9.08	6.92	8.00	248
	STO-3G	-7.88	15.77	11.83	248
	AM1	-9.11	3.19	6.15	160
	MNDO	-9.58	2.95	6.27	157
3,5-Dimethyl-pyridine	—	—	—	—	228[b]
	6-31G*	-8.81	3.70	6.26	—
	3-21G	-9.07	3.81	6.44	246
	STO-3G	-7.60	6.78	7.19	282
	AM1	-9.42	0.13	4.78	166
	MNDO	-9.50	-0.15	4.68	168
2,6-Dimethyl-pyridine	—	—	—	—	230[b]
	6-31G*	-8.78	3.77	6.28	—
	3-21G	-9.06	3.73	6.40	250
	STO-3G	-7.59	6.77	7.18	288
	AM1	-9.40	0.19	4.80	171
	MNDO	-9.46	-0.10	4.68	158

[a]ΔE value for the reaction $BH^+ \rightarrow B + H^+$.
[b]Experimental proton affinity (ΔH) (33).

dimethylpyridine. Calculated vertical electron attachment energies, HOMO and LUMO energies, hardness of the acids at their idealized pyramidal geometries, and the partial charges on their acceptor atoms are shown in Table 6. The magnitude of the electron attachment energies decrease in the order $AlCl_3 > BCl_3 >> AlH_3 > BF_3 > BH_3$. $AlCl_3$ and BF_3 should have the strongest electrostatic contribution to their acid strengths based on the charges on their acceptor atoms. The energy required to reorganize the structure of the acid from trigonal planar to the idealized pyramidal geometry is much greater for BF_3 and BCl_3 than for the other acids. Finally, the hardness of the acids decreases in the order $BF_3 > BH_3 > BCl_3 > AlH_3 > AlCl_3$.

Acid–Base Adducts

The calculated binding energies, structural features, reorganizational energies of the acid and base, charges on the donor and acceptor atoms, and the amount of charge trans- ferred from the base to the acid upon adduct formation are shown in Table 7 for adducts of NH_3 and of PH_3.

When a Lewis base binds to a Lewis acid, several changes occur in the calculated geometries of the acids (Table 7). M–X bond lengths within the acid get longer, and the X–M–X bond angles get smaller upon adduct formation. Geometrical changes in the acids upon adduct formation are in good agreement with high-level ab initio results (3, 5, 8, 15).

Toward the hard base NH_3, the acid strength varies in a similar fashion to the electron attachment energies: $AlCl_3 >> BCl_3 > AlH_3 \sim BF_3 > BH_3$. NH_3 is a considerably stronger base than PH_3 toward neutral group 13 Lewis acids irrespective of the hardness of the acid.

Table 2. Calculated Properties of Idealized (Θ = 109.50) Pyramidal Boron and Aluminum Hydrides and Halides

Calculation	E_{HOMO}/ eV	E_{LUMO}/ eV	Hardness/ eV	$\Delta E_{EA}{}^a$/ kcal mol^{-1}	$E_{reorg}{}^b$/ kcal mol^{-1}	$Q_{AA}{}^c$
			BH_3			
6-31G*	−12.77	1.42	7.10	+11.9	25.0	+0.18
3-21G	−12.86	1.15	7.00	+8.2	25.9	+0.03
STO-3G	−12.06	5.25	8.66	+96.4	28.3	+0.16
AM1	−11.36	0.05	5.71	−1.8	25.1	+0.29
MNDO	−12.42	−0.72	5.85	−19.5	28.4	+0.22
			BF_3			
6-31G*	−17.12	0.72	8.92	−5.1	52.7	+1.09
3-21G	−16.96	0.47	8.72	−5.7	46.2	+1.19
STO-3G	−12.28	5.38	8.83	+109.6	49.1	+0.59
AM1	−14.57	−1.11	6.73	−28.3	36.0	+0.46
MNDO	−15.84	−2.27	6.79	−55.4	45.9	+0.56
			AlH_3			
6-31G*	−11.11	−0.15	5.48	−13.2	19.7	+0.58
3-21G	−11.04	−0.21	5.42	−13.9	20.3	+0.71
STO-3G	−8.89	6.48	7.69	+136.2	25.9	+0.85
AM1	−11.02	−1.77	4.63	−44.4	14.6	+0.24
MNDO	−11.02	−0.91	5.06	−22.9	17.0	+0.79
			BCl_3			
6-31G*	−12.41	−0.57	5.92	−46.4	45.5	+0.35
3-21G	−12.85	−1.39	5.73	−63.8	40.8	+0.31
STO-3G	−11.25	1.49	6.37	−1.5	43.6	+0.51
AM1	−12.16	−2.79	4.69	−72.2	39.4	+0.33
MNDO	−12.89	−3.51	4.69	−89.1	38.5	+0.33
			$AlCl_3$			
6-31G*	−12.39	−1.44	5.48	−50.5	26.0	+0.96
3-21G	−12.79	−2.28	5.26	−68.5	21.1	+1.39
STO-3G	−10.67	2.10	6.39	+30.7	24.7	+1.25
AM1	−12.06	−3.29	4.39	−79.2	40.9	+0.67
MNDO	−12.68	−3.16	4.76	−75.9	19.6	+1.06

^{a}The vertical electron attachment energy that occurs when an electron is added to the neutral MX_3 molecule at the idealized pyramidal optimized geometry.

^{b}The reorganizational energy necessary to change the geometry of the acid from trigonal planar to the idealized pyramidal structure.

^{c}The partial charge on the acceptor atom.

Table 3. Adducts of Ammonia with Lewis Acids

Calculation	ΔE^a/ kcal mol^{-1}	$r_{MN}{}^b$/ Å	$\Delta r_{MX}{}^c$/ Å	$\angle XMX^d$ (°)	$E_{reorg}{}^e$/ kcal mol^{-1}	$\Delta Q_{BA}{}^f$
			$H_3N:AlCl_3$			
ab initio (16)	−35.6	2.03	0.04	116.6	—	—
6-31G*	−41.8	2.02	0.04	116.3	8.7(0.1)	0.25
3-21G	−67.0	1.98	0.04	116.5	5.4(0.5)	0.25
STO-3G	−63.0	1.93	0.03	116.3	7.6(0.2)	0.25
AM1	−22.3	1.86	0.06	115.5	10.3(0.4)	0.38
MNDO	−31.1	1.96	0.05	115.8	7.3(0.2)	0.35
			$H_3N:AlH_3$			
ab initio (4)	−30.2	—	—	—	—	—
6-31G*	−29.6	2.10	0.02	117.4	4.9(0.1)	0.18
3-21G	−42.9	2.04	0.02	116.9	5.4(0.2)	0.19
STO-3G	−39.1	2.00	0.00	117.4	5.8(0.2)	0.26
AM1	−39.2	1.82	0.02	112.6	10.1(0.3)	0.47
MNDO	−24.4	1.95	0.02	115.6	6.6(0.2)	0.34
			$H_3N:BCl_3$			
ab initio (4)	−22.6	1.63	0.08	113.8	—	0.36
6-31G*	−25.4	1.63	0.09	113.5	26.9(0.1)	0.37
3-21G	−49.2	1.63	0.11	113.5	25.1(0.0)	0.36
STO-3G	−52.0	1.64	0.08	114.0	23.7(0.8)	0.45
AM1	−35.9	1.60	0.10	111.9	29.8(0.5)	0.52
MNDO	−22.9	1.61	0.08	112.3	26.8(0.6)	0.55
			$H_3N:BH_3$			
ab initio (19)	−26.0	1.66	0.02	113.8	—	0.35
6-31G*	−23.5	1.69	0.02	114.1	13.6(0.1)	0.26
3-21G	−35.6	1.71	0.02	114.0	13.6(0.2)	0.26
STO-3G	−46.1	1.62	0.00	114.2	14.9(0.5)	0.37
AM1	−38.3	1.56	0.02	113.1	15.9(0.3)	0.48
MNDO	−28.1	1.59	0.02	112.3	20.2(0.4)	0.52
			$H_3N:BF_3$			
ab initio (19)	−19.2	1.68	0.05	114.6	—	0.28
6-31G*	−20.5	1.69	0.05	114.7	24.5(0.1)	0.22
3-21G	−42.1	1.68	0.05	114.3	23.3(0.3)	0.21
STO-3G	−15.8	1.90	0.03	117.0	11.6(0.3)	0.22
AM1	−12.4	1.78	0.03	113.2	20.8(0.3)	0.33
MNDO	−6.8	1.71	0.04	113.9	23.4(0.3)	0.42

^{a}Binding energy.

^{b}Donor atom–acceptor atom bond distance in the adduct.

^{c}Change in the M–X bond distance in the acid upon adduct formation.

^{d}Value of the X–M–X bond angle in the acid of the adduct.

^{e}Reorganizational energy of the acid (base) upon adduct formation as a result of a change in structure.

^{f}Net Mulliken charge transfer from the base to the acid upon adduct formation.

Table 4. Adducts of Phosphine with Lewis Acids

Calculation	ΔE/ kcal mol^{-1}	r_{MN}/ Å	Δr_{MX}/ Å	$\angle XMX$ (°)	E_{reorg}/ kcal mol^{-1}	ΔQ_{BA}
H$_3$P:AlCl$_3$						
6-31G*	-18.4	2.52	0.04	116.6	7.5(2.2)	0.25
3-21G	-27.2	2.54	0.04	116.7	6.1(2.6)	0.14
STO-3G	-36.2	2.38	0.03	115.9	8.7(4.1)	0.33
AM1	-2.7	2.68	0.03	117.6	4.5(0.2)	0.09
MNDO	-5.0	2.55	0.02	118.5	2.3(0.7)	0.12
H$_3$P:AlH$_3$						
ab initio (15)	-15.2	2.54	—	—	—	—
6-31G*	-11.5	2.62	0.01	118.4	2.9(1.1)	0.15
3-21G	-12.7	2.72	0.01	118.7	2.2(0.8)	0.06
STO-3G	-20.6	2.45	0.00	118.1	4.2(1.5)	0.20
AM1	-8.5	2.45	0.01	119.1	1.2(0.2)	0.22
MNDO	-1.1	2.66	0.01	119.5	0.7(0.2)	0.08
H$_3$P:BH$_3$						
ab initio (19)	-20.1	1.95	0.02	114.4	—	0.63
6-31G*	-9.8	2.02	0.02	115.0	11.4(1.6)	0.37
3-21G	-8.4	2.21	0.01	116.8	7.0(1.1)	0.27
STO-3G	-30.6	2.01	0.00	114.7	13.5(3.3)	0.41
AM1	-29.1	1.51	0.02	102.5	43.6(10.1)	1.41
MNDO	-9.8	2.00	0.01	117.6	6.0(1.0)	0.28
H$_3$P:BF$_3$						
ab initio (19)	-3.0	3.09	0.00	114.6	—	0.02
6-31G*	-2.2	3.44	0.00	120.0	0.3(0.2)	0.00
3-21G	-5.7	3.03	0.00	119.7	0.9(0.2)	0.01
STO-3G	-3.3	2.92	0.00	119.8	0.6(0.1)	0.04
AM1	-0.9	3.82	0.00	120.0	0.0(0.0)	0.00
MNDO	-0.5	4.20	0.00	120.0	0.0(0.0)	0.00
H$_3$P:BCl$_3$						
ab initio (19)	-5.4	2.01	0.08	113.9	—	0.67
6-31G*	1.1	2.04	0.09	113.7	26.5(4.1)	0.56
3-21G	-7.7	2.06	0.10	113.9	23.8(4.4)	0.66
STO-3G	-25.1	2.04	0.08	113.4	25.9(7.3)	0.56
AM1	-1.2	3.66	0.00	120.0	0.0(0.0)	0.33
MNDO	-2.1	2.06	0.05	116.6	11.4(1.4)	0.28

Note: See footnotes to Table 3 for definitions of column headings.

Table 5. 3-21G Calculated Properties of Lewis Bases

Lewis Base	E_{HOMO}[a]/eV	E_{LUMO}/ eV	Hardness[b]/ eV	PA[c]/ kcal mol^{-1}	Q_{DA}[d]
NF$_3$	-15.01	6.02	10.52	127	+0.65
PH$_3$	-10.36	4.92	7.64(6.0)	184	+0.09
NH$_3$	-10.58	7.49	9.04(8.2)	227	-0.88
Pyridine	-9.69(-10.89)	3.54	6.62(5.0)	241	-0.67
3,5-Dimethylpyridine	-9.07(-10.57)	3.81	6.44	246	-0.68
N(CH$_3$)$_3$	-9.08	6.92	8.00(6.3)	248	-0.68
2,6-Dimethylpyridine	-9.06(-10.67)	3.73	6.40	250	-0.74

[a]The number in parentheses for pyridine and its derivatives corresponds to the energy of the lone pair orbital.
[b]Experimental value in parentheses is from ref 25.
[c]Calculated energy change for the reaction BH$^+$(g) → B(g) + H$^+$(g).
[d]Partial charge on the donor atom.

Table 6. 3-21G Calculated Properties of Idealized (Θ = 109.5°) Pyramidal Boron and Aluminum Hydrides and Halides

Molecule	E_{HOMO}/ eV	E_{LUMO}/ eV	Hardness/ eV	ΔE_{EA}[a]/ kcal mol^{-1}	E_{reorg}[b]/ kcal mol^{-1}	Q_{AA}[c]
BH$_3$	-12.86	1.15	7.00	+8.2	25.9	+0.03
BF$_3$	-16.96	0.47	8.72	-5.7	46.2	+1.19
AlH$_3$	-11.04	-0.21	5.42	-13.9	20.3	+0.71
BCl$_3$	-12.85	-1.39	5.73	-63.8	40.8	+0.31
AlCl$_3$	-12.79	-2.28	5.26	-68.5	21.1	+1.39

[a]Vertical electron attachment energy that occurs when an electron is added to the neutral MX$_3$ molecule at the idealized pyramidal geometry.
[b]The reorganizational energy necessary to change the geometry of the acid from trigonal planar to the idealized pyramidal structure.
[c]The partial charge on the acceptor atom.

Toward the soft base PH$_3$, the acid strength decreases with the hardness of the acid except for the reversal of BH$_3$ and BCl$_3$: AlCl$_3$ > AlH$_3$ > BH$_3$ ~ BCl$_3$ > BF$_3$.

The reorganizational energies are closely related to the angle changes that occur within the acids upon adduct formation. Except for the pyridine and substituted pyridine adducts, these angle changes are less than 7°. Therefore, the reorganizational energies are considerably smaller than estimated using the pyramidal free acids, in which the angle change is 10.5°.

The binding energy of the 2,6-dimethylpyridine–BCl$_3$ adduct is much smaller than those for the pyridine or 3,5-dimethylpyridine adducts. This results from the severe steric hindrance that occurs between the methyl groups on the base and the chlorine atoms on the acid. Most of the difference in binding energy can be accounted for by the large increase in reorganizational energy that results from steric interactions.

Traditionally, the lower acidity of BF$_3$ compared to BCl$_3$ is attributed to the stronger pπ–pπ bonding in planar BF$_3$

leading to a higher reorganizational energy (3, 30, 31). This argument has been refuted by Brinck, Murray, and Politzer (5), who attribute the lower acidity of BF$_3$ to its lower charge-accepting capacity. Robinson et al. (32) suggested that BF$_3$ is a weaker acid than BCl$_3$ because the increased ionic character of the B–F bonds makes it energetically less favorable for these bonds to lengthen upon adduct formation. The 3-21G results indicate that the F–B–F bond angles in H$_3$N:BF$_3$ are larger than the Cl–B–Cl bond angles in H$_3$N:BCl$_3$. Thus, the reorganizational energy is actually larger for the BCl$_3$ adduct. Results in Table 6 suggest that the much more favorable electron accepting ability of BCl$_3$ compared to BF$_3$ (as indicated by their vertical electron attachment energies at idealized pyramidal geometries) is largely responsible for the greater binding energy in the BCl$_3$ adduct (5).

Not all expected trends are reproduced by the 3-21G calculations. Based on the concept of hard and soft acids and bases, one would expect the energy change for the reaction

$$F_3B:PH_3 + Cl_3Al:NH_3 \rightarrow F_3B:NH_3 + Cl_3Al:PH_3$$
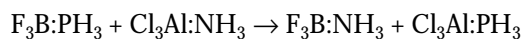
to be negative, since BF$_3$ is harder than AlCl$_3$ and NH$_3$ is harder than PH$_3$. However, the calculated ΔE value is +3.4 kcal/mol. The value is positive even with the 6-31G* basis set. Higher level calculations, using correlated wave functions, would be required to determine whether this result is an artifact of the theoretical model.

Table 7. 3-21G Calculated Properties of Ammonia and Phosphine Adducts of Lewis Acids

Adduct	ΔE^a/ kcal mol^{-1}	$r_{MN}{}^b$/ Å	$\Delta r_{MX}{}^c$/ Å	$\angle XMX^d$ (°)	$E_{reorg}{}^e$/ kcal mol^{-1}	$\Delta Q_{BA}{}^f$	$Q_{DA}{}^g$	$Q_{AA}{}^h$
$H_3N:AlCl_3$	−67.0	1.98	0.04	116.5	5.4(0.5)	0.25	−1.01	1.40
$H_3N:BCl_3$	−49.2	1.63	0.11	113.5	25.1(0.0)	0.36	−0.90	0.27
$H_3N:AlH_3$	−42.9	2.04	0.02	116.9	5.4(0.2)	0.19	−0.96	0.74
$H_3N:BF_3$	−42.1	1.68	0.05	114.3	23.3(0.3)	0.21	−0.96	1.19
$H_3N:BH_3$	−35.6	1.71	0.02	114.0	13.6(0.2)	0.26	−0.86	0.00
$H_3P:AlCl_3$	−27.2	2.54	0.04	116.7	6.1(2.6)	0.14	−0.04	1.43
$H_3P:AlH_3$	−12.7	2.72	0.01	118.7	2.2(0.8)	0.06	0.00	0.80
$H_3P:BH_3$	−8.4	2.21	0.01	116.8	7.0(1.1)	0.27	0.24	−0.18
$H_3P:BCl_3$	−7.7	2.06	0.10	113.9	23.8(4.4)	0.66	0.49	−0.16
$H_3P:BF_3$	−5.7	3.03	0.00	119.7	0.9(0.2)	0.01	0.02	1.20
3,5-Dimethyl-pyridine:BCl$_3$	−48.5	1.61	0.12	111.3(2) 110.6	33.7(0.6)	0.36	−0.95	0.35
py:BCl$_3$	−47.3	1.61	0.12	111.5(2) 110.8	33.0(0.8)	0.35	−0.94	0.35
2,6-Dimethyl-pyridine:BCl$_3$	−26.8	1.63	0.13	105.9(2) 113.7	44.2(9.4)	0.37	−1.01	0.31

^{a}Binding energy.
^{b}Donor atom–acceptor atom bond distance in the adduct.
^{c}Change in the M–X bond distance in the acid upon adduct formation.
^{d}Value of the X–M–X bond angle in the acid of the adduct.
^{e}Reorganizational energy of the acid (base) upon adduct formation as a result of a change in structure.
^{f}Net Mulliken charge transfer from the base to the acid upon adduct formation.
^{g}Charge on the donor atom of the base in the adduct.
^{h}Charge on the acceptor atom of the acid in the adduct.

Conclusions

Ab initio or semiempirical quantum mechanical calculations can be used to investigate Lewis acid–base adducts as a computational chemistry exercise in advanced inorganic chemistry. Trends in binding energies and several of the factors that accompany adduct formation can be demonstrated by the calculations. Calculated trends using 3-21G ab initio basis sets are in good agreement with those obtained from high-level ab initio calculations.

This computational exercise has several advantages. Foremost is that it involves a discovery approach. Possible factors that influence binding energies can be postulated from the results of the calculations. These postulates can then be used as the starting point for a lecture discussion on acids and bases. Second, students are faced with a large amount of raw data that must be interpreted and presented in a logical fashion in a report. This provides them with a good introduction to an important facet of chemical research and enhances their critical thinking skills. Third, it introduces students to an aspect of molecular modeling that is not normally presented in other courses.

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