Lewis Acidity of Gallium Halides

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The Lewis acidity of GaF_3, GaF_2Cl, $GaFCl_2$, and $GaCl_3$ in acid–base interactions has been studied by taking ammonia as their electron-donating counterpart. We have derived an unoccupied reactive orbital that shows the maximum localization on the Ga atomic center for each species. The orbital is located lower in energy compared to those in the corresponding boron and aluminum halides. In contrast to boron halides, the unoccupied reactive orbital of the acid site tends to be delocalized considerably on the halogens as the fluorines are substituted by chlorines in gallium halides. The trend observed in the effects of fluorine and chlorine on the acidity of the gallium halides is opposite to those found in the boron halides. This cannot be interpreted solely in terms of the electron-accepting strength of the gallium center, but can be understood by including electrostatic interactions and closed-shell repulsion with ammonia in the adducts. The origin of the difference in Lewis acidity of BCl_3, $AlCl_3$, and $GaCl_3$ has been clarified.

Introduction

The acid and base are defined in the Lewis theory as an electron-pair acceptor and an electron-pair donor, respectively.[1] Pearson divided Lewis acids and bases into two classes which he termed *hard* and *soft*.[2,3] According to the principle of hard and soft acids and bases (HSAB), hard acids like hard bases and soft acids like soft bases. The stability of complexes formed between acids and bases is understood on this base. The electrostatic interaction has been assumed to be the dominant source of stabilization in a complex between a hard acid and a hard base, while electron delocalization between the frontier orbitals has been thought to play a key role in the interaction between a soft acid and a soft base.[4]

The complexes of boron halides with bases have been investigated extensively both from experimental[5–10] and from theoretical points of view.[11–26] The Lewis acidity of mixed boron halides, BF_xCl_{3-x} ($x = 0, 1, 2, 3$), is known to increase with decreasing x.[27] That is, BCl_3 is a stronger Lewis acid

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than BF_3, being opposite to the order expected from the relative electronegativities and the steric effects of the halogens.[28,29] It seems to be a common belief in inorganic chemistry that the order of Lewis acidity described above appears, because the boron $p\pi$ orbital is conjugated more strongly with the attached halogens in BF_3 than in BCl_3, bringing a larger distortion energy to BF_3 upon complexation.[28–34] Branchadell et al. analyzed the nature of the B–X bonds in boron trihalides[34c] by applying the topology of the charge density $\rho(r)$[35] and its Laplacian $\Delta^2\rho(r)$[36] and the valence bond (VB) method.[37,38] They could show that the calculated pyramidalization energies for BX_3 increased in the order $BBr_3 < BCl_3 < BF_3$ and, thus, they conjectured that the relative Lewis acidity of boron trihalides was due, to a certain extent, to a variation in the distortion energy that resulted from the difference in B–X double-bond strength.

On the other hand, there have been some studies which suggest that the π-conjugation is not necessarily stronger in BF_3.[39–41] Brinck et al. showed that the calculated atomic charges and electrostatic potentials were consistent with the electronegativities of the halogen atoms, but not with the back-bonding concept.[41] They explained the observed trend in the Lewis acidity in terms of the charge capacity κ that was defined by the inverse of the difference between the ionization potential and the electron affinity determined experimentally.[42,43] We investigated recently the Lewis acidity of BF_3, BF_2Cl, $BFCl_2$, and BCl_3 by deriving the unoccupied reactive orbital that showed the maximum localization on the boron $p\pi$ orbital function in each species.[26] The analysis revealed that the unoccupied reactive orbital of BCl_3 was located lower in energy compared with that of BF_3, owing to a stronger polarizability or a smaller value of acidic hardness of the boron center.[26]

In boron compounds, BF_3 and BCl_3 are classified as hard acids, while BH_3 is classified as a soft acid.[3] In contrast to the boron case, GaF_3 and $GaCl_3$ are grouped with soft acids, while GaH_3 is located on the borderline between hard and soft acids.[3] There seems to be some differences in the effect of halogens on the Lewis acidity of boron and gallium halides. It has been shown theoretically that the Lewis acid strength decreases for aluminum and gallium halides in the order $MF_3 > MCl_3$.[34b,44,45] A similar trend in acidity also has been found in silicon compounds.[28] It is interesting therefore to investigate the effect of halogens on the first row elements and that on the higher row elements.

Theoretical studies of gallium halides so far reported are not many. The scalar relativistic effects on the atomization energy of GaF_n have been investigated theoretically.[45] Stability of adducts between substituted gallanes with arsines was studied at various theoretical levels by Bock et al.[46] They found that there were bonding contributions between the halogen atoms attached to the gallium atom and the arsenic center, in the adducts of fluoro- and chlorogallanes. A theoretical study of adducts of the B, Al, Ga, and In hydrides with ammonia and phosphine was reported by Zahradnik et al.[47] It was shown that adducts of these halides with ammonia were stable, but adducts with phosphine were not. Ball et al. performed ab initio calculations on adducts of GaH_3, GaF_3, and $GaCl_3$ with H_2O.[48] They found that structures and binding energies were very similar to those in the corresponding aluminum complexes. Interestingly, the Ga–O bond was found to be shorter in the GaF_3 adduct than in the $GaCl_3$ adduct. Structures and properties of the complexes of aluminum and gallium halides with H_2O were investigated by using calorimetry, cryoscopy, dielectrometry, and IR spectroscopy and by applying the PM3 theoretical method by Malkov et al.[49] Frenking et al. studied the π-donor ability of YH_2X and YX_3 (Y = B, Al, Ga, In, and Tl; X = F, Cl, Br, and I) by looking at the $p\pi$ electron population of Y and the isodesmic reaction of YH_2X with YH_4^- to give YH_3 and YH_3X^- and that of YX_3 with YH_4^- to give YH_3 and YHX_3^-.[50] They found that the effect of halogens on the gallium was the same in trend as that in boron halides. Timoshkin et al. showed that the theoretically estimated dissociation energy of the adducts between GaX_3 and some electron donors decreased in the order F > Cl > Br > I.[51a] It was pointed out that there was no correlation between the dissociation energy and the extent of charge transfer. They examined also the complexes of gallium halides with pyridine, finding that those complexes were not rigid systems located on flat potential surfaces.[51b]

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The effect of halogens on the Lewis acid strength of gallium halides reported so far looks completely different from what we have observed for boron halides. In this paper, we present the results of our analysis on GaF_xCl_{3-x} ($x = 0$, 1, 2, 3) to compare the effects of F and Cl on the Lewis acidity with those in the mixed boron halides, BF_xCl_{3-x}.

Computational Method

The geometries and electronic structures of gallium halides and the complexes of those halides with ammonia, as well as BCl_3-NH_3 and $AlCl_3-NH_3$, have been calculated at the B3LYP/6-311++G** level of theory[52] by applying the Gaussian 98 program.[53] All the species have a C_3 axis or a σ_v plane. Harmonic vibrational frequencies were obtained by vibrational analysis of fully optimized geometries. The dissociation energies were corrected for zero point vibrational energies (ZPVE) obtained at the B3LYP/6-311++G** level of theory from unscaled harmonic vibrational frequencies. Thermal enthalpy and thermal Gibbs free energy corrections were also made to enable comparison with the experimental data at 298.15 K, 1 atm. The basis set superposition error (BSSE) correction was evaluated by the counterpoise method.[54] The RHF/6-311++G**//B3LYP/6-311++G** calculations have shown that the difference in the dissociation energies of $GaF_xCl_{3-x}-NH_3$ adduct is somewhat larger than that obtained in the B3LYP/6-311++G** calculations, but is very similar in trend.[55] Thus, evaluation of the affinity of gallium to lone pairs of electrons of bases and acidic strength of the gallium center was made by using the MOs obtained at the RHF level of theory with the 6-311G** basis set.

Results and Discussion

The results of calculations on the structures and dissociation energies in $(GaF_xCl_{3-x})-NH_3$ adducts are presented in Table 1. The calculations show that these adducts are lowest in energy in an *eclipsed* conformation, making a clear contrast to the boron and aluminum halide complexes with NH_3 which favor a *staggered* conformation. The energy difference between the two conformations is very small in the case of $x = 1$, being 1.04 kJ/mol, but the *staggered* conformation has been confirmed to be the transition state for internal rotation by a vibration analysis. It is interesting to see that the Ga−N bond length increases monotonically with decreasing x in $(GaF_xCl_{3-x})-NH_3$ in the *eclipsed* conformation. Thus, the dissociation energy decreases with decreasing x. Gas-phase structural data are known for some gallium halides with ammonia.[56] The calculated value of the

Table 1. Calculated Results on $GaF_xCl_{3-x}-NH_3$ Adducts

	GaF_3	GaF_2Cl	$GaFCl_2$	$GaCl_3$
Mulliken charge on Ga[a]	+1.531	+1.538	+1.244	+0.686
natural charge on Ga[a]	+2.188	+1.950	+1.684	+1.392
distortion energy (kJ/mol)[b,c]	24.75	24.25	23.94	24.86
dissociation energy (kJ/mol)[b,d]	160.39	148.70	137.96	127.16
correction				
zero-point vibration energy	−12.20	−12.46	−12.41	−12.05
basis-set superposition errors	−7.56	−8.15	−8.68	−9.01
thermal enthalpy	−9.58	−9.76	−9.80	−9.81
(thermal free energy)	(−50.70)	(−53.36)	(−53.23)	(−49.52)
dissociation energy (kJ/mol)[b,d,e]	131.05	118.33	107.07	96.29
	(89.93)	(74.73)	(63.64)	(56.58)
Ga−N bond length (nm)[b]	0.2063	0.2071	0.2084	0.2095
F−Ga−N angle (deg)[b]	100.29	97.46	94.45	
Cl−Ga−N angle (deg)[b]		105.93	103.09	100.59

[a] Calculated at the RHF/6-311++G** level. [b] Calculated at the B3LYP/6-311++G** level of theory. [c] Defined by $E[GaF_xCl_{3-x}(bent)] - E[GaF_xCl_{3-x}(planar)]$, in which the bent structure was taken as the same as in an adduct. [d] Defined by $[E(NH_3) + E(GaF_xCl_{3-x}) - E(GaF_xCl_{3-x}-NH_3)]$. [e] Corrected by ZPVE, BSSE, and thermal enthalpy. Values in parentheses are corrected by ZPVE, BSSE, and thermal free energy.

Ga−N bond length for the $GaCl_3$ adduct is slightly longer than the experimental value, 0.2058 ± 0.011 nm,[56a] and as a result, the calculated dissociation energy is slightly lower than the experimentally observed enthalpic change, 134.2 ± 2.5 kJ/mol.[56a] It has been shown by Ball et al. for the adducts with H_2O that the Ga−O bond is shorter by 0.0012 nm in GaF_3-H_2O than in $GaCl_3-H_2O$.[48] It is suggested, therefore, that the Lewis acidity of gallium halides decreases with decreasing x, making a clear contrast to boron halides.

To examine the effect of reluctance of GaF_xCl_{3-x} toward pyramidalization on the acidic strength, we have computed the distortion energy for these compounds by comparing the energies of the planar and bent structures. The latter has been taken to be the same as the structure of the GaF_xCl_{3-x} fragment in the adducts with NH_3. The change in the calculated distortion energies is much smaller in magnitude relative to the change in the dissociation energy of $GaF_xCl_{3-x}-NH_3$, as given in Table 1. That is, the distortion energy does not interpret the relative acidic strengths of the systems that we are examining. The $n(halogen) \rightarrow 4p\pi$ (Ga) back-donation is not the reason for the difference in the acidity of these halides. We should look for some other reasons why the effect of fluorine and chlorine substituents on gallium halides is opposite that on boron halides.

The method of analysis that we utilize in this study is essentially the same as that we have adopted in our previous works.[26,57] The orbital of the acidic center in an acid molecule utilized to form a bond with the electron-donating center of a base is an atomic orbital (AO) or a linear combination of several AOs. We denote this orbital by δ_r. Then, the orbital that is localized to the maximum extent on δ_r in the unoccupied MO subspace is given by[57]

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$$\phi_{\text{unoc}}(\delta_r) = (\sum_{j=m+1}^{M} d_{j,r}\phi_j)/(\sum_{j=m+1}^{M} d_{j,r}{}^2)^{1/2} \qquad (1)$$

where the summation is taken over all the unoccupied MOs ϕ_j ($j = m + 1$, $m + 2$, ..., M). The coefficients $d_{j,r}$ are determined by expanding δ_r in a linear combination of the canonical MOs. The occupied reactive orbital ϕ_{oc} having the maximum localization on δ_r is given similarly by a combination of the occupied MOs ϕ_i ($i = 1, 2, ..., m$). The level of ϕ_{unoc} is estimated then by[57]

$$\lambda_{\text{unoc}}(\delta_r) = (\sum_{j=m+1}^{M} d_{j,r}{}^2 \, \epsilon_j)/(\sum_{j=m+1}^{M} d_{j,r}{}^2) \qquad (2)$$

where ϵ_j signifies the orbital energy of the canonical MO ϕ_j. The level of the occupied reactive orbital λ_{oc} is estimated similarly by taking a weighted sum of the occupied MO energies. By representing the denominator of eq 2 by $(1 - a^2)$, we obtain[57b]

$$\lambda(\delta_r) = a^2\lambda_{\text{oc}}(\delta_r) + (1 - a^2)\lambda_{\text{unoc}}(\delta_r) \qquad (3)$$

where $\lambda(\delta_r)$ is the energy expectation value for the orbital δ_r in the acid molecule under study. Note that $-\lambda(\delta_r)$ is regarded as representing electronegativity of the reaction center r, having a form similar to the Mulliken electronegativity of a molecule.[58]

Let us look at the difference in electron-accepting strength of gallium halides in their planar monomeric forms[59] by taking the p-type AO extending perpendicular to the molecular plane as the reference orbital, δ_r. To make this orbital applicable to all of GaF_3, GaF_2Cl, $GaFCl_2$, and $GaCl_3$, the ratio of the inner and outer p-type components in δ_r has been taken to be the same as that of Ga atom in the LUMO of GaH_3. The unoccupied reactive orbitals obtained in this manner are presented in Figure 1 with respect to GaF_3 and $GaCl_3$. They are localized well on the gallium center and bear a close resemblance to each other, though the orbital of $GaCl_3$ is delocalized over the adjacent halogens to a greater extent. The unoccupied reactive orbital derived for the planar structure of a gallium halide is now regarded as giving the major component of the interaction orbital that is utilized for the Ga−N bond upon complexation with NH_3.

Localizability of the unoccupied reactive orbital on the gallium center estimated by $\langle\delta_r|\phi_{\text{unoc}}\rangle^2 = (1 - a^2)$ is 0.859 in GaF_3 and 0.714 in $GaCl_3$, as shown in Table 2. This indicates also that the Ga $4p\pi$-type AO function is found mainly in the unoccupied MO space in these halides, and it is more delocalized over the halogen atoms in $GaCl_3$. The gallium atom is much larger than a boron atom and the empty p orbital on Ga overlaps to a greater extent with the more diffuse occupied p orbitals on chlorines than with the more compact p orbitals of fluorines.[47] This brings a big difference from the case of boron halides, in which the unoccupied
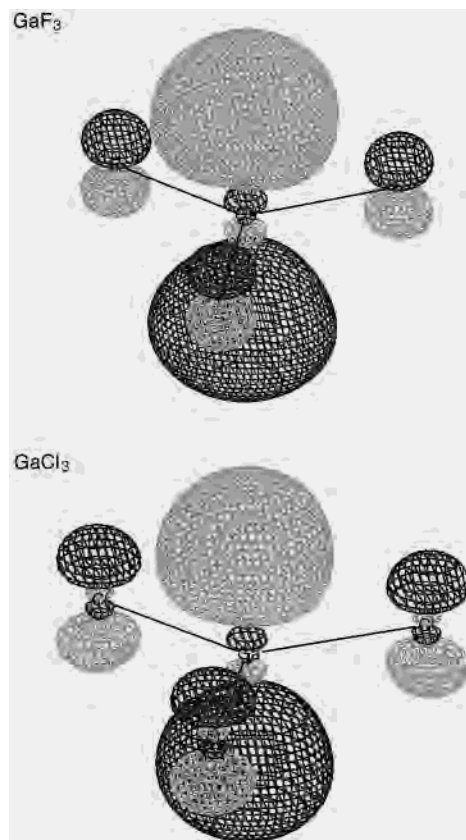
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Figure 1. Unoccupied reactive orbitals of GaF_3 (upper) and $GaCl_3$ (lower) in the planar form obtained by projecting the $p\pi$ AO functions of the central gallium onto the RHF/6-311G** unoccupied MO subspace of these molecules. The D_{3h} structures were optimized at the B3LYP/6-311++G** level of theory.

Table 2. Comparison of the Factors Determining the Electrophilicity of GaF_3, GaF_2Cl, $GaFCl_2$, and $GaCl_3$ in Planar Forms

	GaF_3	GaF_2Cl	$GaFCl_2$	$GaCl_3$
Mulliken charge on Ga [a]	+1.514	+1.265	+0.963	+0.492
natural charge on Ga[a]	+2.291	+2.052	+1.780	+1.473
$(1 - a^2)$	0.859	0.809	0.760	0.714
η (au)	0.356	0.322	0.303	0.291
λ (au)	−0.047	−0.066	−0.085	−0.104
λ_{unoc} (au)	0.053	0.057	0.060	0.062

[a] Calculated at the RHF/6-311++G** level.

reactive orbital is delocalized to a smaller extent on the halogen $p\pi$ AOs in BCl_3 than in BF_3 in the planar form.[26]

The Ga $p\pi$ orbital is partially occupied through conjugation with the F and/or Cl atoms, as indicated by $(1 - a^2) < 1$ in the species under consideration. The referenced $p\pi$ AO is delocalized more strongly over the adjacent halogen atoms and is found to a greater extent in the occupied MO subspace in $GaCl_3$, as mentioned above. As a result, the λ value is located lower in $GaCl_3$ than in GaF_3 and the electron population of the referenced Ga $p\pi$ AO increases in the order $GaF_3 < GaF_2Cl < GaFCl_2 < GaCl_3$. This is the same in trend as the order in boron halides, as has been pointed out by Frenking et al. on the basis of a comparison of the Ga $p\pi$ electron population in GaX_3.[50] An important factor to be considered here is the gap between the levels of the occupied and unoccupied reactive orbitals. Perturbation theory tells us that polarizability of the reaction site r is inversely

proportional to this gap, $(\lambda_{unoc} - \lambda_{oc})$.[60] These unoccupied and occupied reactive orbitals are delocalized to some extent over the attached halogen atoms, out-of-phase and in-phase, respectively. They mix with each other induced by electron delocalization from an approaching base.[60c] This orbital mixing removes electronic charge from the gallium center and places it on the halogen atoms, to make the gallium $p\pi$ orbital engage in the formation of a new σ bond with the base.

We have determined above the reactive orbital ϕ_{unoc} that shows the maximum localization on the gallium $p\pi$ orbital in the unoccupied MO subspace. Delocalization of the reactive orbital over the adjacent halogen atoms elevates the electron-accepting orbital level λ_{unoc} above λ by $2a^2\eta$

$$\lambda_{unoc}(\delta_r) = \lambda(\delta_r) + 2a^2\eta(\delta_r) \qquad (4)$$

in which η is a measure of chemical hardness of the gallium $p\pi$-orbital, defined by[57b]

$$\eta(\delta_r) = (\lambda_{unoc}(\delta_r) - \lambda_{oc}(\delta_r))/2 \qquad (5)$$

This quantity has a formal analogy to the absolute hardness defined by Parr et al. for a whole molecule.[61] Note, however, that $1/\eta$ provides a scale of polarizability of the reaction site r in a molecule in our case.

The reactive orbital ϕ_{unoc} has been determined so as to localize to the maximum extent on the orbital δ_r, but the fraction a^2 (<1) of ϕ_{unoc} is delocalized over the neighboring halogen atoms, and therefore cannot be utilized for the formation of the Ga–N σ bond. Efficient localization of the unoccupied reactive orbital on the reaction site leads to a smaller a^2 value and, consequently, to a lower electron-accepting level. Therefore, $2a^2\eta$ is regarded as giving a measure of hardness against electron acceptance or, in other words, acidic hardness of the reaction site. Table 2 shows that the gallium center of $GaCl_3$ has a smaller η value than that of GaF_3. The acidic center is more polarizable in $GaCl_3$. However, a^2 becomes larger as the fluorines are substituted more by chlorines. Thus, the acidic hardness $2a^2\eta$ of the gallium center increases in the order GaF_3 < GaF_2Cl < $GaFCl_2$ < $GaCl_3$. As a result, the electron-accepting level λ_{unoc} is located higher in $GaCl_3$ compared with that of GaF_3, as illustrated in Scheme 1. This makes a clear contrast to mixed boron halides, BF_xCl_{3-x}, in which BCl_3 has the unoccupied reactive orbital lying 0.049 au lower in energy at the 6-311G** level and being localized on the boron center to a slightly greater extent than that of BF_3.

We have assumed above that gallium compounds should provide an unoccupied orbital that has the maximum amplitude on the gallium atom to form a tight σ bond with a base. The construction of the reactive orbital has dual
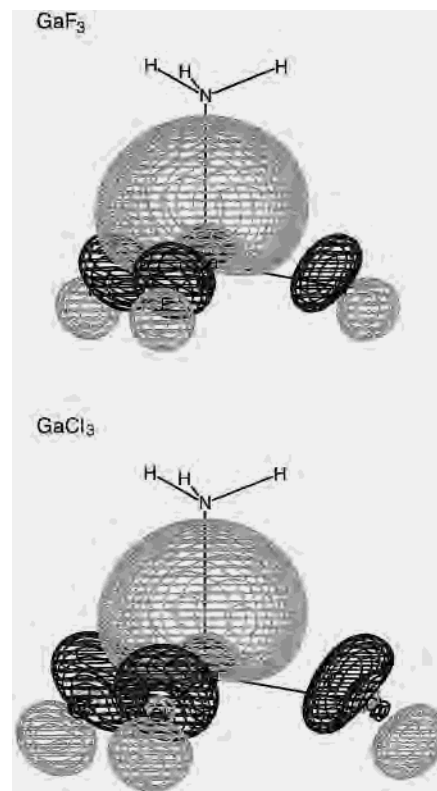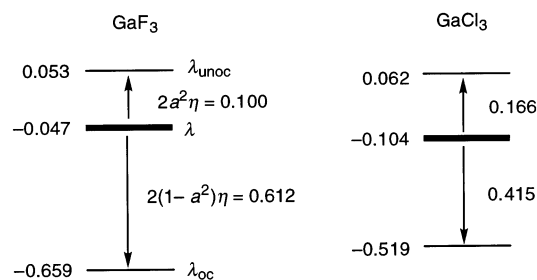
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Scheme 1

Figure 2. Unoccupied interaction frontier orbitals of GaF_3 (upper) and $GaCl_3$ (lower) taking part in electron delocalization from the lone-pair orbital of NH_3 in GaX_3–NH_3 adducts. These orbitals were obtained by carrying out simultaneous transformations of the unoccupied MOs of the GaX_3 fragment and the occupied MOs of the NH_3 fragment to represent the orbital interactions involved in the wave function of the adducts in terms of paired fragment orbitals. The occupied counterpart of NH_3 in each pair is not shown.

meanings, i.e., the maximum localization in the unoccupied MO space and the maximum localization on the reaction center. To see next what orbitals really participate in electron delocalization in the adducts, we have calculated the interaction frontier orbitals of GaF_3–NH_3 and $GaCl_3$–NH_3 complexes.[62] Figure 2 shows the orbitals of GaF_3 and $GaCl_3$ that play the dominant role in accepting electronic charge, by making an orbital pair with the occupied interaction orbital of NH_3. The orbital of GaF_3, for example, has been derived by representing first the wave function of the GaF_3–NH_3 adduct in terms of various electron configurations of the two

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Table 3. Comparison of the Factors Determining the Stability of Adducts of GaF_xCl_{3-x} and GaH_3 with NH_3

	GaF_3	GaF_2Cl	$GaFCl_2$	$GaCl_3$	GaH_3
electron delocalization (kJ/mol)					
$NH_3 \rightarrow GaF_xCl_{3-x}$	−91.47	−94.17	−97.24	−101.06	−62.77
$GaF_xCl_{3-x} \rightarrow NH_3$[a]	−10.47	−12.55	−14.45	−15.19	−7.04
electrostatic attraction (kJ/mol)	−349.90	−345.01	−339.51	−336.82	−222.24
exchange repulsion (kJ/mol)	251.82	263.64	273.67	286.60	186.40

[a] Sum of the three strongest pairs of orbital interactions.

fragments, GaF_3 and NH_3,[25] and then by applying a pair of unitary transformations to the canonical MOs of two fragments within the unoccupied MO space of the GaF_3 part and within the occupied MO space of the NH_3 part to represent electron delocalization concisely in terms of a few pairs of fragment orbitals. The resulting orbital of the GaF_3 fragment shown in Figure 2 is given by a linear combination of the unoccupied canonical MOs, including contributions of all the unoccupied MOs relevant for the interaction with the attached NH_3. The orbital of $GaCl_3$ has been obtained in a similar manner by utilizing the wave function of $GaCl_3$–NH_3.

The orbitals of GaF_3 and $GaCl_3$ look similar to each other, having large amplitude on the gallium center. The s- and d-type AOs of Ga are seen to hybridize significantly with the p-type AOs to form a tight Ga–N σ bond with NH_3. The occupied paired orbital of the NH_3 fragment has the familiar form of a lone-pair orbital delocalized to some extent over the three hydrogens and is not illustrated in Figure 2. Several pairs of fragment orbitals also have been obtained for back-donation of electrons from the GaX_3 part to the NH_3 part, by carrying out transformations of the canonical MOs within the occupied MO space of the former and the unoccupied MO space of the latter.

To see quantitatively how large the stabilization brought about by the orbital interaction is relative to other types of interactions, we have evaluated the strength of electron delocalization between the unoccupied orbital shown in Figure 2 and the paired occupied orbital of the NH_3 fragment. The results of calculations are given in Table 3.[63] Very interestingly, stabilization due to electron delocalization described by the pair of orbitals has been shown to be unexpectedly larger in the $GaCl_3$–NH_3 adduct, −101.06 kJ/mol, than in the GaF_3–NH_3 adduct, −91.47 kJ/mol. It is obvious that the large delocalization stabilization in the former arises from the subsidiary overlap interactions

between chlorines in the $GaCl_3$ part and hydrogens in the NH_3 part, in addition to the acid−base interaction at the reaction sites. The X--H interactions interpret why the gallium complexes with NH_3 are lower in energy in an *eclipsed* conformation than in a *staggered* conformation.

On the other hand, the overlap between the occupied orbitals having large amplitude on the Ga−X bonds and those on the N−H bonds produces the exchange repulsion. It is stronger in the $GaCl_3$ adduct than in the GaF_3 adduct, and the larger stabilization due to electron delocalization in $GaCl_3$–NH_3 has been set off by this repulsive interaction. As has been presented in Table 2, the Mulliken population analysis[64] indicates that the positive charge on the gallium center decreases in the order GaF_3 > GaF_2Cl > $GaFCl_2$ > $GaCl_3$, as expected simply from the relative electronegativity of fluorine and chlorine.[65] The natural population analysis gives the same trend, locating greater positive charges on Ga.[66] The electrostatic attraction calculated for the electron configuration in which the GaX_3 and NH_3 fragments retain their lowest energy closed-shell structures but have the same locations of the constituent atoms as those in the adduct is given in Table 3.[67] The attraction is stronger in GaF_3–NH_3 than in $GaCl_3$–NH_3. By taking the effects of electrostatic attraction, exchange repulsion, and electron delocalization on GaX_3–NH_3 adducts into account, the reactivity toward NH_3 is concluded here to be weaker in $GaCl_3$. Electron delocalization is not the primary source of determining the strengths of interaction of these gallium halides, though they have been grouped with soft acids. The other two terms bring a stronger bonding to GaF_3–NH_3.

Finally, let us discuss the difference in Lewis acidity between gallium halides and boron and aluminum halides by comparing $GaCl_3$ with BCl_3 and $AlCl_3$. As shown above, $GaCl_3$–NH_3 is lower in energy in an *eclipsed* conformation than in a *staggered* conformation. Delocalization stabilization is largest in that conformation, owing to X--H overlap interactions. The binding energy is not large, however, relative to the aluminum complex, as presented in Table 4. The *eclipsed* conformation is accompanied by a strong exchange repulsion between the Ga−Cl bonds and the N−H bonds. In the complex of BCl_3, the M−N bond is much

(63) Delocalization stabilization has been determined for the all-electron wave function of an adduct by $2C_0C_I(H_{0,0} - S_{0,0}H_{0,I})$, in which $H_{0,0} = \langle\Psi_0|H|\Psi_0\rangle$, $H_{0,I} = \langle\Psi_0|H|\Psi_I\rangle$, and $S_{0,0} = \langle\Psi_0|\Psi_0\rangle$. Here, Ψ_0 signifies the original electron configuration in which the acid and base fragments retain their initial closed-shell electron configurations and Ψ_I indicates the configuration in which an electron has been shifted from the base to the acid among the pair of interaction frontier orbitals, the GaX_3 orbital being illustrated in Figure 2. The coefficients C_0 and C_I measure the contributions of the electron configurations Ψ_0 and Ψ_I to the electronic structure of the adduct, respectively, being calculated by applying configuration analysis to the wave function of an adduct. The one-electron and two-electron integrals have been supplied from the GAMESS program (Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347). See, for the details of analysis: Imade, M.; Hirao, H.; Omoto, K.; Fujimoto, H. *J. Org. Chem.* **1999**, *64*, 6697.

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Table 4. Comparison of Ga, Al, and B Chlorides

	$GaCl_3$	$AlCl_3$	BCl_3
in adduct with NH_3			
distortion energy (kJ/mol)[a,b]	24.86	28.50	97.84
dissociation energy (kJ/mol)[a,c]	127.16	152.86	94.10
dissociation energy (kJ/mol)[a,c,d]	96.29	119.84	52.37
	(56.58)	(76.32)	(5.23)
M−N bond length (nm)[a]	0.2095	0.2025	0.1627
Cl−M−N angle (degree)[a]	100.59	101.16	105.12
electron delocalization (kJ/mol)			
$NH_3 \rightarrow MCl_3$[e]	−101.06	−92.48	−213.37
$MCl_3 \rightarrow NH_3$[e]	−15.19	−9.63	−9.26
electrostatic attraction (kJ/mol)	−336.82	−341.88	−534.94
exchange repulsion (kJ/mol)	286.60	260.83	698.64
in planar monomeric form			
$(1 - a^2)$	0.714	0.697	0.501
η (au)	0.291	0.297	0.361
λ (au)	−0.104	−0.109	−0.211
λ_{unoc} (au)	0.062	0.071	0.150

[a] Calculated at the B3LYP/6-311++G** level of theory. [b] Defined by $E[MCl_3(\text{bent})] - E[MCl_3(\text{planar})]$, in which the bent structure was taken as the same as in an adduct. [c] Defined by $[E(NH_3) + E(MCl_3) - E(MCl_3-NH_3)]$. [d] Corrected by ZPVE, BSSE, and thermal enthalpy. Values in parentheses are corrected by ZPVE, BSSE, and thermal free energy. [e] Sum of the three strongest pairs of orbital interactions.

shorter compared to that in the complexes of $GaCl_3$ and $AlCl_3$. Though the electron-accepting level is located higher in BCl_3, delocalization stabilization and also electrostatic attraction are very large in magnitude, reflecting the short M−N bond in BCl_3-NH_3. The short M−N bond leads, on the other hand, to a strong exchange repulsion and to a large destabilization due to distortion of the BCl_3 fragment. The sum of these interaction terms does not indicate that the interaction between BCl_3 and NH_3 is stabilized very strongly. The aluminum center in $AlCl_3$ has a strong electron-accepting ability comparable to $GaCl_3$, as represented by the low λ_{unoc} value. The occupied p orbital on nitrogen overlaps to a greater extent with the p orbital on aluminum than with the p orbital on gallium. Then, the smaller $NH_3 \rightarrow MCl_3$ electron delocalization in $AlCl_3-NH_3$ indicates clearly the importance of X--H interactions in stabilizing the adduct of gallium halides. The Al−Cl bonds are polarized, bringing a large electrostatic attraction to $AlCl_3-NH_3$. The exchange repulsion is not so large as that in the gallium case, because $AlCl_3-NH_3$ has a staggered conformation. Thus, $AlCl_3$ exhibits a stronger affinity toward NH_3 than do $GaCl_3$ and BCl_3.

Conclusion

By deriving the unoccupied reactive orbitals which show the maximum localization on the gallium $p\pi$ orbital function, the Lewis acidity of GaF_3, GaF_2Cl, $GaFCl_2$, and $GaCl_3$ has been examined first from two points of view, localizability of the unoccupied reactive orbitals on the gallium center and polarizability of that center. It has been revealed that

localizability of the reactive orbital becomes smaller as the fluorines are substituted by chlorines. On the other hand, polarizability of the gallium center becomes larger in going from GaF_3 to $GaCl_3$. Because of these two competing factors, it has been demonstrated that the Lewis acidic strength of the gallium center is higher in fluorinated species, but the difference in acidic strength should not be large in these gallium halides.

An interaction-frontier-orbital analysis has demonstrated that the overlap between the unoccupied MOs delocalized over the Ga−X bonds in a gallium fragment and the occupied MOs delocalized over the N−H bonds in the NH_3 fragment contributes to electron delocalization from NH_3 to GaF_xCl_{3-x}, in addition to the direct interaction between the acid and base centers. Electron delocalization has been calculated to be stronger in $GaCl_3-NH_3$. The advantage of the $GaCl_3-NH_3$ adduct in electron delocalization is overcome, however, by a strong closed-shell repulsion that arises from the overlap between the Ga−Cl bond orbitals and the N−H bond orbitals in the occupied MO space. The electrostatic attraction is weaker in the $GaCl_3$ adduct than in the GaF_3 adduct. Thus, $GaCl_3$ is made less reactive toward NH_3, relative to GaF_3.

On the other hand, the differences in acid strength between boron, aluminum, and gallium chlorides arise from several factors. Despite the lower electron-accepting level in $GaCl_3$, the σ-type overlap between the Ga 4p AO and the N 2p AO is not efficient, compared with the overlap between the Al 3p AO and the N 2p AO. The adduct of gallium halides with NH_3 tends to gain the assistance of X−H interactions, but the attraction is counterbalanced for the most part by the exchange repulsion. Accordingly, $GaCl_3$ shows a weaker affinity to NH_3. In BCl_3-NH_3, the short B−N bond is accompanied by a strong deformation of the boron fragment. Then, $AlCl_3$ is most reactive toward NH_3, several factors being well-balanced. One notes that acid−base interactions cannot be interpreted simply by means of a single interaction term, e.g., electrostatic attractions or electron delocalization.[4]

Supporting Information Available: Information on the geometries and energies of the species examined in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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