Binding Energies of Some Aluminum Chloride Complexes of Poly(*p*-phenylenebenzobisthiazole) (PBZT) Model Compounds

John W. Connolly*

Department of Chemistry, University of Missouri—Kansas City,
Kansas City, Missouri 64110-2499

Douglas S. Dudis

Polymer Branch, Materials Laboratory, Wright Patterson Air Force Base,
Dayton, Ohio 45433-6533

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ABSTRACT: *Ab initio* molecular orbital calculations on aluminum chloride complexes of benzothiazole show that aluminum chloride binds more tightly to the nitrogen atom (D_e = 36.5 kcal) than to the sulfur atom (D_e = 10.2 kcal) and it is energetically more feasible for Al_2Cl_6 to complex at the nitrogen atom than for $AlCl_3$ to complex simultaneously at the nitrogen and at the sulfur. These results have relevance regarding the structure proposed for PBZT dissolved in Lewis acid containing aprotic solvents. New calculational results are also reported for $AlCl_3$–NH_3 (D_e = 42.1 kcal), $AlCl_3$–H_2S (D_e = 13.7 kcal), and Al_2Cl_6–NH_3 (D_e = 30.6 kcal for dissociation to NH_3, D_e = 7.2 kcal for dissociation to $AlCl_3$–NH_3 and $AlCl_3$).

Introduction

Recently, it has been reported that thermally stable rigid-chain and ladder polymers can be solubilized in *aprotic* solvents containing Lewis acids.[1,2] Rigid-chain polymers are among the best organic polymers known for tensile strength, environmental resistance, and thermooxidative stability.[3–5] Recently, they have also been investigated for electrical conductivity[5,6] and nonlinear optical (NLO) properties.[7] These new solubility findings are of considerable importance because a significant drawback to the utilization of rigid-chain polymers has been the severely acidic conditions required for their processing; e.g., films and fibers have been formed almost exclusively from poly(phosphoric acid) or methanesulfonic acid solutions. By contrast, in a recent application, aprotic solutions of PBZT containing Lewis acids have been used to prepare molecular composites of PBZT and polyamides, and NLO properties of the composites have been measured.[8]

Detailed measurements were reported[2] on aprotic solutions of benzimidazole–benzophenanthroline type ladder (BBL) and semiladder (BBB) polymers as well as poly(*p*-phenylenebenzobisthiazole) (PBZT) and poly(*p*-phenylenebenzobisoxazole) (PBO) rigid-chain polymers. (See Figures 1 and 2 for structures.) All these polymers contain aromatic and heterocyclic units in the backbone. Convincing evidence has been obtained that the solubilization process does not involve formation of a π-electron charge-transfer complex between the polymer and the Lewis acid.[2] Furthermore, the solution process requires a Lewis acid–polymer repeat unit ratio of at least 4:1 in each case, and pure polymer can be recovered from the Lewis acid complexed form by washing with a nonsolvent such as water. It has been suggested[2] that four Lewis base sites on each polymer repeat unit are complexed with Lewis acid; the IR red shift of the carbonyl band in BBL on solubilization supports the idea that it is complexed by a Lewis acid. Recent NMR data obtained in nitromethane solution containing PBZT and aluminum chloride show two ^{27}Al signals, one of which is assigned to nitromethane-complexed aluminum chloride and the other to PBZT-complexed aluminum chloride.[9]

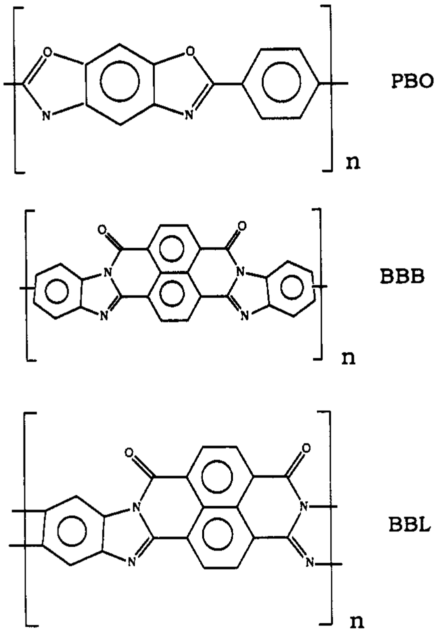

Figure 1. Structures of rigid-chain and ladder polymer repeat units.

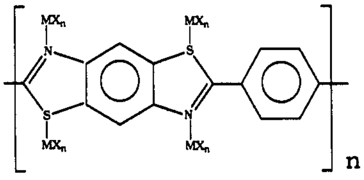

Figure 2. Proposed[2] structure of the soluble Lewis acid complex of PBZT.

Figure 2 shows the proposed[2] structure of the 4:1 Lewis acid–PBZT repeat unit complex. In the case where MX_n is aluminum chloride, which is one of the Lewis acids used to solubilize PBZT, aluminum chloride would simultaneously be complexed to two nitrogen atoms and two sulfur atoms.

The well-known hard and soft acid–base (HSAB) theory states that hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases.[10] This theory is based on experimental heats of reaction and has enjoyed considerable success in predicting acid/base reactions. Figure 2 (with MX_n = $AlCl_3$) depicts a hard acid, aluminum chloride, simultaneously binding to a hard base, the nitrogen atom, and a soft base, the sulfur atom. While such a structure is not ruled out entirely, HSAB

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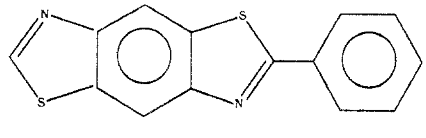


Figure 3. Model PBZT in ref 12.

theory suggests that the Al–N bond will be stronger than the Al–S bond. The chemical literature contains a large number of examples of thiazole–Lewis acid complexes, but hard Lewis acids complex only the thiazole nitrogen atoms.[11] In this context a recently reported AM1 semiempirical calculation on the protonation of a model PBZT structure containing a benzobisthiazole unit[12] (Figure 3) is of interest. Sequential protonation of this structure yielded heats of formation of 147, 217, **345**, and **420** kcal/mol as four protons were added. The two boldfaced numbers are for the protonation of the sulfur atoms. The results suggest that protonation of both nitrogen atoms would occur before either of the sulfur atoms is protonated, which, of course, is consistent with HSAB theory.

We here report the results of an *ab inito* computational study designed to investigate the feasibility of a 4:1 $AlCl_3$–PBZT repeat unit complex as shown in Figure 2. In addition to the type of structure shown in Figure 2, we have also examined an isomeric structure in which Al_2Cl_6 is complexed only to the nitrogen base site of the heterocyclic group.

Calculational Details

All calculations were done using the Gaussian90 suite of programs,[13] implemented at UMKC, the National Center for Supercomputing Applications, University of Illinois at Urbana–Champaign, and the Wright Patterson AFB computational facilities. With one exception, all structures shown in Table 2 were fully optimized using the 6-31G*[14] basis set. The restricted Hartree–Fock self-consistent field approach was used throughout. Since complex IV differs from complex I only by the addition of an aluminum chloride group to one of the chlorines on the ligand aluminum chloride group of complex I, the structure of complex IV was optimized using the frozen benzothiazole structure from optimized complex I and optimizing only the Al_2Cl_6 part of the structure. Split-valence basis (cep-31G*)[15] effective core potentials were used for optimization of this structure; energy and charge calculations were done using the 6-31G* basis set.

Dissociation energies (D_e) are calculated as the difference between the energies of the uncomplexed Lewis acid and base and the energy of the complex. Zero-point energies were obtained for the smaller complexes examined here, and the D_e values corrected for zero-point energy differences are represented as D_0. Atomic charge transfers were calculated as simply the total charge on the complexed $AlCl_3$ (or Al_2Cl_6) using natural bond order values obtained using the version of Gaussian90 at UMKC.

Results and Discussion

Our calculations here are intended to model polymeric species containing coordinated Lewis acids such as aluminum chloride for which no detailed structural information is available and therefore our calculations cannot be experimentally verified. Consequently, it is useful to review the success of *ab initio* calculations on Lewis acid–base complexes involving aluminum chloride. Dissociation energies of $AlCl_3$ complexes of HCl,[16] alkyl halides, alkenes, alkynes, and aldehydes,[17] and ammonia[18] have been calculated at the 6-31G* and higher level of theory. Structural parameters, where available, are reproduced successfully in these calculations. Experimental energies of dissociation are rare and have been less successfully reproduced. However, as is shown below, the dissociation energy of $AlCl_3$–NH_3 is adequately reproduced in our calculations at the 6-31G* level.

Table 1. Vibrational Analysis of $AlCl_3$–NH_3

		vibration	obs[20] (cm^{-1})	calc[a] (cm^{-1})	calc (cm^{-1}) (unscaled)
A_1	ν_1	N–H sym stretch	3302	3299	3666
	ν_2	NH_3 sym def	1263	1337	1486
	ν_3	Al–N stretch	474	450	500
	ν_4	Al–Cl sym stretch	378	348	387
	ν_5	$AlCl_3$ sym def	200	182	202
A_2	ν_6	Al–N torsion	276	67	74
E	ν_7	N–H antisym stretch	3395	3407	3786
	ν_8	NH_3 antisym def	1614	1635	1817
	ν_9	NH_3 rock	702	708	787
	ν_{10}	Al–Cl antisym stretch	536	508	564
	ν_{11}	$AlCl_3$ rock	186	152	169
	ν_{12}	$AlCl_3$ antisym def	123	115	128

[a] 90% of the calculated value.

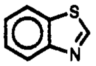
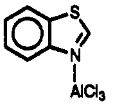
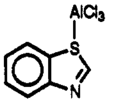
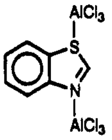
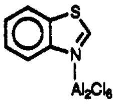
A detailed study has been reported on the effect of the level of basis set and the use of electron correlation in the ammonia–allane complex. The smallest basis set was the double-ζ (DZ) contracted Gaussian basis set consisting of the Huzinaga–Dunning (9s5p/4s2p) on nitrogen, (4s/2s) on hydrogen, and the (11s7p/6s4p) on aluminum. In separate calculations, (1) polarization was added to the heavy atoms (DZd), (2) polarization was added to the hydrogen atoms, (3) much larger triple-ζ basis sets were used, and (4) configurational interaction calculations were done. The conclusion reached was that acceptable results were obtained when polarization was added to the nitrogen atom, which suggests that reliable theoretical results are possible in larger systems in which DZd basis sets are used.[19] The 6-31G* basis set used here is a double-ζ basis set with polarization, similar to the Huzinaga–Dunning DZd.

We find here that the vibrational spectrum of $AlCl_3$–NH_3 is successfully reproduced computationally, with the exception of the Al–N torsional frequency (Table 1) at the 6-31G* level of theory. [Computed values were multiplied by 0.9 to obtain acceptable correlation with experimental values.[21]] Correcting the D_0 value for $AlCl_3$–NH_3 in Table 2 to D_{25}[22] gives a value of 39.5 kcal, while the experimental value is 45.0 kcal.[35] This exceptional agreement between calculated and experimental D_{25} suggests that the comparative values of D_e in Table 2 are sufficiently reliable for this study.

Also listed in Table 2 are our results for the $AlCl_3$–H_2S complex. As expected, the D_e calculated for this complex is much less than that of $AlCl_3$–NH_3. $AlCl_3$–H_2S has been reported but heat of vaporization measurements indicate that it is completely dissociated in the gas phase,[25] so we have no experimental comparison for the calculated results. Nevertheless calculated structural results obtained for this complex are useful when considering the structure of complex II (*vide infra*).

In modeling the polymeric systems, in order to save CPU time we have used benzothiazole and the benzothiazole complexes shown in Table 2 rather than benzobisthiazole (Figure 2) and its complexes. D_e values were calculated for benzothiazole–*N*–$AlCl_3$ (I) and for benzothiazole–*S*–$AlCl_3$ (II). These structures are too large to allow the force calculation necessary to obtain zero-point corrections. In agreement with prediction from HSAB theory, D_e of I is larger than that of II. For complex III, bisbenzothiazole–*N*,*S*–$(AlCl_3)_2$, no minimum energy structure was found. Successive optimization cycles produced

Table 2. Summary of Calculations (*ab Initio*, 6-31G*)

compound	electronic energy (atomic units)	D_e (kcal)	D_0 (kcal)
NH_3	-56.184356		
H_2S	-398.667323		
$AlCl_3$	-1620.576087		
Al_2Cl_6	-3241.181229		
$AlCl_3$–NH_3	-1676.827050	42.1	38.7
$AlCl_3$–H_2S	-2019.265282	13.7	11.7
Al_2Cl_6–NH_3	-3297.414428	30.6 (to Al_2Cl_6) 7.2 (to $AlCl_3$–NH_3)	
	-719.9518596		
 I	-2340.586087	36.5	
 II	-2340.544189	10.2	
 III	did not converge		
 IV	-3961.173649	25.4 (to Al_2Cl_6) 7.3 (to I and $AlCl_3$)	

longer and longer Al–S bond lengths until the search was terminated at ~8 Å. Our results show then that in the gas phase a first coordination of aluminum chloride to the hard-base N site prevents subsequent coordination by aluminum chloride to the soft-base S site. In the nitro solvents used in the Lewis acid solubilization of PBZT, the effect of solvent would be to add additional base sites to compete with the PBZT base sites. This would further diminish coordination from the weak sulfur site by competition for the Lewis acid.

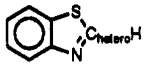
Table 3 contains data which illustrate the major bond length changes which occur when $AlCl_3$ or Al_2Cl_6 complexes to Lewis base sites in the compounds studied here. Agreement between calculated and experimental bond lengths is good, although the experimental structures are not exactly the same as the structures on which calculations were done here. For example, $r_{C_{hetero}\text{-}N}$ and $r_{C_{hetero}\text{-}S}$ quoted for uncomplexed benzothiazole are for 2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole.[26] The $r_{C_{hetero}\text{-}N}$ values given for complexed benzothiazole are for a Pd(II) complex (the range given is due to the fact that the complex in question contains two Pd–benzothiazole moieties). Similar $r_{C_{hetero}\text{-}N}$ values have been obtained for the diphenyldichlorotin(IV) complex of benzothiazole.[28] The agreement between calculated and experimental bond lengths shown in Table 3 indicates that our calculated experimental parameters are reliable, and we believe that changes in the calculated values of the bond distances listed here are indicative of changes in bonding.

On complexation of aluminum by a hard Lewis base, $r_{Al\text{-}Cl}$ in $AlCl_3$ increases by ~0.05 Å. This is reasonable since back-bonding between aluminum and chlorine is diminished when complexation occurs. When aluminum complexes to nitrogen, $r_{Al\text{-}Cl}$ is calculated to lengthen to at least 2.12 Å, whereas when aluminum complexes to sulfur, $r_{Al\text{-}Cl}$ is calculated to lengthen to 2.11 Å. This small difference in lengthening reflects the lesser degree of bonding between aluminum and sulfur versus aluminum and nitrogen.

Table 3. Selected Bond Lengths

bond	compound	r_{calc} (Å)	r_{exp} (Å)
Al–Cl	$AlCl_3$	2.077	2.05 (ref 18)
Al–Cl	$AlCl_3$–NH_3	2.122	2.10 (ref 18)
Al–Cl	$AlCl_3$–H_2S	2.11	
Al–Cl	I	2.13	
Al–Cl	II	2.11	
Al–$Cl_{terminal}$	Al_2Cl_6–NH_3	2.10, 2.11	
$C_{hetero}{}^{c}$–N	benzothiazole	1.265	1.292[a] (ref 26)
C_{hetero}–N	I	1.285	1.299–1.305[b] (ref 27)
C_{hetero}–N	II	1.252	
Al–N	$AlCl_3$–NH_3	2.025	1.996 (ref 18)
Al–N	Al_2Cl_6–NH_3	2.02	
Al–N	I	2.012	
Al–N	IV	1.99	
$C_{hetero}{}^{c}$–S	benzothiazole	1.747	1.758[a] (ref 26)
C_{hetero}–S	I	1.708	1.713–1.737[b] (ref 27)
C_{hetero}–S	II	1.782	
Al–S	$AlCl_3$–H_2S	2.517	
Al–S	II	2.538	

[a] 2,6-Diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole. [b] Pd(II) complex containing two Pd–benzothiazole moieties within each molecule. [c] C_{hetero} is shown in the following structure:



When benzothiazole complexes to aluminum chloride through the nitrogen atom (complex I), the calculated $r_{C_{hetero}\text{-}N}$ lengthens by 0.02 Å, while $r_{C_{hetero}\text{-}S}$ shortens by 0.039 Å. These results are consistent with the experimental data in Table 3 and presumably indicate a combination of charge redistribution and orbital overlap changes on complexation. When benzothiazole complexes to aluminum chloride through the sulfur atom (complex II), the calculated $r_{C_{hetero}\text{-}S}$ lengthens by 0.035 Å and $r_{C_{hetero}\text{-}N}$ shortens by 0.010 Å. Bond length changes are slightly smaller in the case of sulfur complexation, which is consistent with this being the weaker coordinate bond.

A consideration of the bond length changes which occur on complexation as well as charge-transfer effects (*vide infra*) provides insight into why the bis aluminum chloride complex proved to be unstable. Complexation of aluminum chloride to nitrogen caused a lengthening of $r_{C_{hetero}\text{-}N}$ and a shortening of $r_{C_{hetero}\text{-}S}$ (*vide supra*). Complexation of aluminum chloride to sulfur caused exactly the opposite effect, i.e., a shortening of $r_{C_{hetero}\text{-}N}$ and a lengthening of $r_{C_{hetero}\text{-}S}$. Of course, it is not possible for both of these effects to occur simultaneously. In terms of structural changes, the only way that the bisbenzothiazole–*N*,*S*–$(AlCl_3)_2$ complex could be stable is if the above bond length changes were somehow averaged. Such averaging would weaken both coordinate bonds at the same time. Apparently, the energy of such a structure with two weak coordinate bonds is higher than the energy of complex 1 with the second aluminum chloride completely dissociated.

Atomic charge calculations indicate that 0.136 atomic charge is transferred from benzothiazole to aluminum chloride in complex I (similarly 0.139 atomic charge is transferred to $AlCl_3$ in $AlCl_3$–NH_3) while 0.200 atomic charge is transferred to aluminum chloride in complex II. This difference in charge transfer is consistent with the greater polarizability of sulfur versus nitrogen, but more importantly it indicates that charge must be transferred to aluminum chloride for *each* coordinate bond formed. The formation of two such coordinate bonds by the same heterocyclic system may simply require that too much

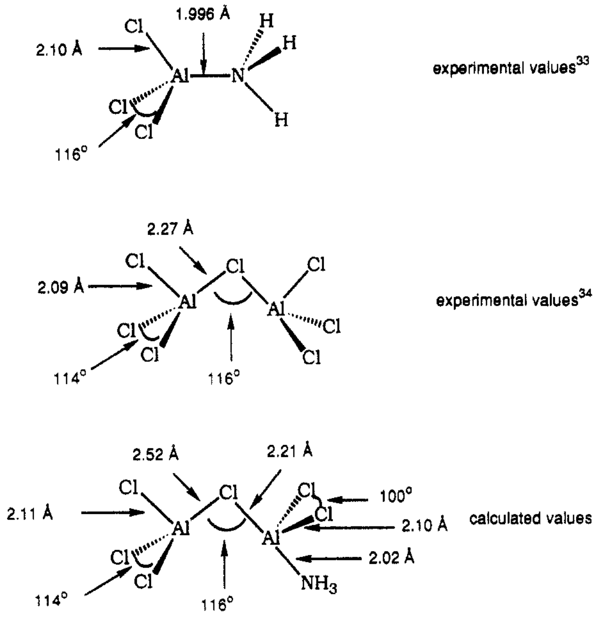


Figure 4. Structural features of $AlCl_3$–NH_3, $Al_2Cl_7^-$, and Al_2Cl_6–NH_3.

charge transfer from the heterocyclic group, particularly since the charge must be transferred in nearly opposite directions.

In view of these results we have considered another possibility for the 4:1 aluminum chloride–PBZT (repeat unit) ratio which has been observed in PBZT solutions. To wit, a complex mixture of polymeric anions, $Al_2X_7^-$, $Al_3X_{10}^-$, ... (X = halogen), exists in melts prepared from halide salts and AlX_3.[29] In fact, $Al_2X_7^-$ can be formed even in nonpolar solution; e.g., when HCl is bubbled into a 1:2 suspension of $AlCl_3$:aromatic hydrocarbon, a solution is produced containing ArH^+ and $Al_2Cl_7^-$.[30] The anion $Al_2X_7^-$ has been characterized in solution with vibrational spectroscopy[30] and crystallographically[31] in the solid state. *Ab initio* molecular orbital calculations give the lowest energy minimum to the singly bridged $Al_2Cl_7^-$ structure, similar to the structure shown in Figure 4, although calculations with the STO-3G basis set gave better structural results than those with the 3-21G basis set.[32]

The calculated structural details of Al_2Cl_6–NH_3, compared with experimental structural information for $AlCl_3$–NH_3[33] and $Al_2Cl_7^-$,[31] are shown in Figure 4. As can be seen, the calculated bond lengths and angles in Al_2Cl_6–NH_3, excepting the longer $r_{\mathrm{Al-Cl_{bridge}}}$ appear to be normal. While $Al_2Cl_7^-$ is a symmetrical structure, Al_2Cl_6–NH_3 is not; i.e., the two Al–Cl_{bridge} bond lengths are not the same. The shorter $r_{\mathrm{Al-Cl_{bridge}}}$ is calculated to be 2.21 Å, which is close to the experimental value of 2.27 Å in $Al_2Cl_7^-$. The longer $r_{\mathrm{Al-Cl_{bridge}}}$ is calculated to be 2.52 Å. This disparity in bond lengths suggests that Al_2Cl_6–NH_3 might be described as $AlCl_3$–NH_3 weakly attached to a second $AlCl_3$ group. Indeed, D_e calculated for Al_2Cl_6–NH_3 dissociating into Al_2Cl_6 and NH_3 is 30.6 kcal/mol, while D_e for its dissociation into $AlCl_3$–NH_3 and $AlCl_3$ is 7.2 kcal/mol. Atomic charge calculations indicate that 0.143 electronic charge is transferred from ammonia to the Al_2Cl_6 group in this complex. This is approximately the same charge which is transferred from ammonia to $AlCl_3$ in $AlCl_3$–NH_3 (*vide supra*).

Finally, we have calculated the optimized structure of benzothiazole-*N*-Al_2Cl_6 (complex IV), shown in Figure 5. The bond parameters are very similar to those obtained for Al_2Cl_6–NH_3; i.e., the calculated $r_{\mathrm{Al-N}}$ is 1.99 Å, $r_{\mathrm{Al-Cl_{terminal}}}$ are all 2.11 Å, and the Al–Cl–Al bridge is unsymmetrical, with the two distances being 2.22 and 2.54 Å. D_e for dissociation to complex I and $AlCl_3$ is 7.2 kcal/mol (vs 25.4 kcal/mol for dissociation into benzothiazole and Al_2Cl_6). Thus complex IV appears to be a weak complex of complex I and $AlCl_3$. Atomic charge calculations indicate that 0.145 electronic charge is transferred from benzothiazole to the Al_2Cl_6 group, similar to the result obtained with Al_2Cl_6–NH_3. The important conclusion from these calculations is that when complex I approaches $AlCl_3$, it is energetically more advantageous for the $AlCl_3$ to complex at a chlorine atom of a bound $AlCl_3$ rather than at a heterocyclic sulfur atom. The diminished charge transfer which occurs on complexation at chlorine plus the contradictory bond length changes necessary to form complex III would appear to be the dominant factors.

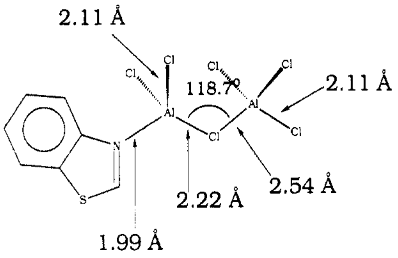


Figure 5. Calculated structural features of IV.

Conclusion

The results reported here show that it is energetically more feasible for Al_2Cl_6 to bind to the nitrogen atom in benzothiazole than for one $AlCl_3$ to bind to the nitrogen and another to bind to the sulfur. If solvent effects do not radically change the energetics of Lewis acid–base interaction, our results suggest that PBZT binds hard Lewis acids exclusively through its nitrogen atoms and that the 4:1 ratio of Lewis acid to PBZT repeat unit results from the dimerization of the Lewis acid. Care should be taken in attempting to generalize our results. For example, gallium chloride is the most effective Lewis acid at promoting solubilization of rigid rod polymers. While Ga_2Cl_6 does exist, gallium chloride is somewhat softer than aluminum chloride,[34] and it is not certain that our results with aluminum chloride apply to gallium chloride containing solutions. Also, since PBO and BBL contain only hard-base heteroatoms, it is not certain that they behave like PBZT toward hard Lewis acids. Further calculations are planned to investigate this latter point.

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(35) The experimental value is obtained using the following thermochemical cycle:

$$NH_{3(g)} + AlCl_{3(g)} \rightarrow AlCl_3\text{–}NH_{3(s)};\quad \Delta H_{rxn} = -62.4\ \text{kcal}^{23}$$

$$AlCl_3\text{–}NH_{3(s)} \rightarrow AlCl_3\text{–}NH_{3(g)};\quad \Delta H_{vap} = 17.4\ \text{kcal}^{24}$$

$$AlCl_3\text{–}NH_{3(g)} \rightarrow NH_{3(g)} + AlCl_{3(g)};\quad \Delta H_{rxn} = 45.0\ \text{kcal}$$