Weak Chemical Complexation of PH₃ with Ionic Liquids

Su Chen,[†] **Jiaye Li,**[†] **Chenggang Zhou,**[*,†] **Jinping Wu,**[†] **Daniel J. Tempel,**[‡]
Philip B. Henderson,[‡] **Jeffrey R. Brzozowski,**[‡] **and Hansong Cheng**[*,‡]

Engineering Research Center of Nano-Geomaterials of Ministry of Education and Institute of Theoretical Chemistry and Computational Materials Science, China University of Geosciences, 388 Lumo Road, Wuhan 430074, China, and Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania 18195-1501

We present a combined theoretical and experimental study on weak chemical complexation between PH₃ and a few selected Cu(I)- and Al-based ionic liquids (ILs). PH₃ molecules were found to covalently bind with the cationic sites of the ILs. Effects of cations, anions, ion pairing, and solvents on the binding strength were systematically examined. The weak coordination of PH₃ on the ILs allows the PH₃ gas to be stored at near ambient conditions with a high capacity.

I. Introduction

Liquid phase subatmospheric storage and delivery of gases offers an important advantage over conventional compressed gas sources for highly reactive or environmentally hazardous gases.[1–3] Ionic liquids (ILs) have been shown to have significant potential as carriers of a variety of gas species due to their highly polarized chemical environment, low vapor pressure and wide temperature liquid phase.[4–8] Through careful design of IL structures, storage and delivery of the gas species can be carried out under near ambient conditions. This concept was demonstrated in a recent Communication in which it was shown that the inherent physical properties of ILs are ideally suited for selectively storing large quantities of pure toxic gases, namely PH₃ and BF₃, in a small volume at low pressures.[9] These molecular species interact with ILs via weak chemical complexation. As a consequence, exceptionally high gas storage capacities were achieved.[10,11] In the present work, we conducted a combined theoretical and experimental study to further examine the weak chemical interactions between PH₃ and a few selected Cu(I)- and Al-based ILs. The main purpose is to unveil factors that dictate the interaction strength to aid novel materials development. Understanding these factors will enable us to tune the binding energies of the gas species on the ILs suitable for specific applications by designing or selecting appropriate ILs with maximum gas capacities.

Fundamentally, the weak chemical complexation between PH₃ and the Cu(I)- and Al-based ILs arises from electron transfer from the lone pair of PH₃ to the empty 4s orbital of copper for Cu(I)-based ILs or to the 3s orbital for Al-based ILs in which the Al atom is largely ionized.[9] Ligands and counterions may exert considerable influences on the interaction strength. Many quantum chemical calculations deal with molecular interactions with ILs using only the ions to which the molecular species are attached (in the present case, the anion species), ands the effects of ion pairing and solvent on the binding strength are often ignored.[12–14] Several interesting questions thus arise:

1. What role does the cation play in ILs upon PH₃ coordination?
2. What are the solvent effects on PH₃ reaction energies?
3. How sensitive is PH₃ coordination to the nature of the halide ligands on the anion?
4. What are the effects of ion pairing on the computational accuracy for evaluating molecular binding strength on ILs?

In this paper, we attempt to address these fundamental issues by performing extensive quantum mechanical calculations using density functional theory (DFT). The results are then compared with experimentally observed reaction strengths and capacities. Details of the experimental results will be published separately.

II. Computational Methods

The DFT calculations utilize the Perdew−Wang's exchange-correlation functional (PW91) and a double numerical atomic basis set augmented with polarization functions as implemented in DMol³ package.[15–17] All molecular structures are fully optimized without symmetry constraint with energy and gradient tolerances of 10^{-5} Ha and 0.002 Ha/Å, respectively. Transition state structure search for PH₃ attachment to the Cu(I)/Al complexes was conducted by using the linear synchronous transit method (LST) with the Newton−Raphson algorithm for geometry optimization.[18] Zero point energy corrections were applied to a few selected reaction systems and the effects on the calculated PH₃ reaction energies were found to be marginal largely due to the error cancellation. Calculations on the solvent effects were done using the COSMO continuum model.[19]

The ion pairing energy (IPE) can be calculated using the following equation:

$$\text{IPE} = E_{\text{cation}} + E_{\text{anion}} - E_{\text{ion-pair}} \tag{1}$$

where E_{cation}, E_{anion}, and $E_{\text{ion-pair}}$ represent the total energies of cation, anion and ion-pair, respectively. The PH₃ binding energy is defined by

$$\Delta E = E_{\text{PH}_3-\text{A}} - E_{\text{A}} - E_{\text{PH}_3} \tag{2}$$

where A stands for either an anion or an ion pair. The second binding energy of PH₃ can be evaluated in the same way. Here A represents the first coordination complex.

* Corresponding authors. E-mail: C.Z., cgzhoux@gmail.com; C.H., chengh@airproducts.com.
† China University of Geosciences.
‡ Air Products and Chemicals, Inc.

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Cations
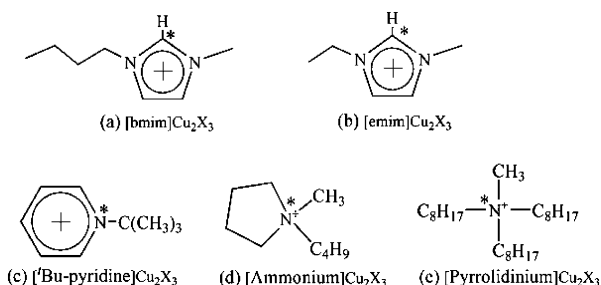
Figure 1. Schematic view of $[Cu_2X_3]^-$ based ionic liquids.

III. Results and Discussion

III.1. Brief Description of Experimental Results. The reaction of equimolar quantities of 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and CuCl yields [bmim][CuCl₂], and the reaction of 2 equivalents of CuCl with [bmim]Cl yields [bmim][Cu₂Cl₃].[20] In addition, we prepared a range of trichlorocuprate salts comprising different cations as well as the chloroaluminate ionic liquids, [bmim][AlCl₄] and [bmim]-[Al₂Cl₇]. Capacities for these ionic liquids were determined by measuring PH₃ uptake at room temperature, and comparisons were made at an equilibrium pressure of 760 Torr. The experimentally measured PH₃ capacities of these ionic liquids are shown in Table 1.

We note that the room temperature ionic liquid, [bmim]-[CuCl₂], has a capacity of only 0.32 mol of PH₃/mol of IL. In contrast, the capacity of [bmim][Cu₂Cl₃], 1.6 mol of PH₃/mol of IL (0.78 mol of PH₃/mol of Cu), is significantly higher under the same conditions. The same trend is observed for the bromocuprate analogs, with slightly higher measured capacities of 0.63 and 1.8 mol of PH₃/mol of IL for [bmim][CuBr₂] and [bmim][Cu₂Br₃], respectively. Note that $Cu_2Cl_3^-$ and $Cu_2Br_3^-$ are only formalisms. The anion likely comprises an equilibrium mixture of chloride and chlorocuprate or bromide and bromocuprate species.[20] Our results suggest that the nitrogen-based ILs (imidazolium, pyrrolidinium, and ammonium salts) all exhibit

approximately the same degree of reactivity (mole ratio capacity) toward PH₃. We found that the Lewis acidic heptachloroaluminate ionic liquid, [bmim][Al₂Cl₇], exhibits a very weak interaction with PH₃, providing a molar capacity of only 0.66 mol of PH₃/mol of IL (0.33 mol of PH₃/mol of Al). The complex with PH₃ was found to be reversible. Finally, the tetrachloroaluminate ionic liquid, [bmim][AlCl₄], was found to have essentially no capacity for PH₃ because it is not Lewis acidic. To help understand the experimental results, we carried out quantum chemical calculations to examine various effects on the binding strength of PH₃ on selected ILs.

III.2. Computational Results on Cu(I) Complexes. For convenience, we first denote the two forms of Cu(I) anions as $Cu_2X_3^-$ and CuX_2^-, where X represents a halide atom. The selected counterions are shown in Figure 1. These cations were selected because they represent classes that have been widely reported in the literature.[20-23] The charge on the cations can be delocalized in the aromatic systems or localized in the aliphatic systems. The side chain length of the aromatic systems may also exert influences on the cation properties. It is also instructive to compare the calculated energies of ion pairing with the relative Coulomb interaction strengths.

To gain qualitative understanding on the Coulomb interactions, we define the distance between the charge center of the selected cations and the center of mass of Cu−Cu atoms in $Cu_2X_3^-$ as d. For the selected cations, we chose the atom on which the charge is most positive as the charge center as labeled in Figure 1. Table 2 lists the optimized d values, the calculated ion pairing energies (IPE) with the selected cations and anions, and the net charges of anions. For the same cation, the calculated IPE increases as the halide ligand becomes more polarizable (IPE increases in the order F < Cl < Br < I). The net Mulliken charges on the anions show a gradual decline and the calculated d value increases steadily for the halide series going from F to I, indicating that ion pairing becomes increasingly weaker in energy. For the same anion, the dependence of ion pairing energy on d is not obvious since d reflects only partially the relative Coulomb interaction strength. Nevertheless, the d value

TABLE 1: Experimental PH₃ Capacities for Ionic Liquids at Room Temperature, 760 Torr

ionic liquid	volumetric capacity (mol of PH₃/L of IL)	mole ratio capacity (mol of PH₃/mol of IL)
1-butyl-3-methylimidazolium [CuCl₂]	2.62	0.32
1-butyl-3-methylimidazolium [Cu₂Cl₃]	7.15	1.55
1-ethyl-3-methylimidazolium [Cu₂Cl₃]	6.55	1.32
1-hexyl-3-methylimidazolium [Cu₂Cl₃]	6.32	1.40
1-butyl-2,3-dimethylimidazolium [Cu₂Cl₃]	6.57	1.40
1-butyl-3-methylpyridinium [Cu₂Cl₃]	7.13	1.41
1-butyl-1-methylpyrrolinium [Cu₂Cl₃]	5.38	1.25
1-hexyl-1-methylpyrrolinium [Cu₂Cl₃]	6.66	1.78
methyltrioctylammonium [Cu₂Cl₃]	3.14	1.40
1-butyl-3-methylimidazolium [CuBr₂]	3.21	0.63
1-butyl-3-methylimidazolium [Cu₂Br₃]	7.83	1.80
1-butyl-3-methylimidazolium [AlCl₄]	0.06	0.01
1-butyl-3-methylimidazolium [Al₂Cl₇]	1.80	0.66

TABLE 2: Calculated Distance d (Å), Ion Pairing Energy (IPE, kcal/mol) of $[Cu_2X_3]^-$ Based Ionic Liquids, and the Mulliken Charge of the $[Cu_2X_3]^-$ Anion (Q)

	F			Cl			Br			I		
	d	IPE	Q	d	IPE	Q	d	IPE	Q	d	IPE	Q
(a)	3.345	−80.3	−0.088	3.708	−70.8	−0.097	3.816	−69.7	−0.091	3.839	−68.5	−0.090
(b)	3.348	−83.4	−0.086	3.692	−73.5	−0.303	3.809	−72.9	−0.314	3.954	−72.0	−0.346
(c)	3.661	−96.9	−0.148	4.090	−90.3	−0.292	4.100	−89.1	−0.294	3.425	−88.0	−0.321
(d)	4.113	−86.4	−0.177	4.580	−79.6	−0.308	4.753	−78.4	−0.307	5.056	−76.4	−0.351
(e)	4.025	−82.8	−0.176	4.444	−75.6	−0.308	4.517	−74.4	−0.308	4.750	−72.9	−0.352
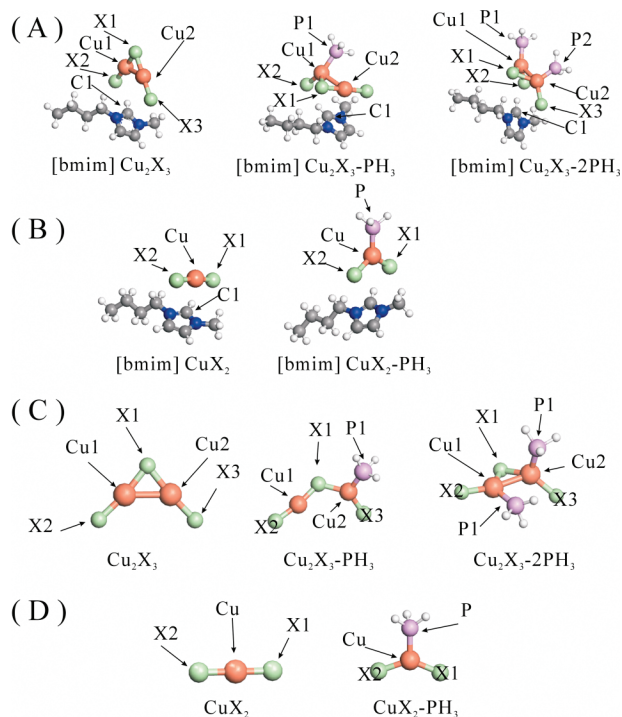
Figure 2. Reaction process of PH$_3$ on (A) [bmim] Cu$_2$X$_3$, (B) [bmim] CuX$_2^-$, (C) Cu$_2$X$_3^-$, and (D) CuX$_2^-$.

may describe qualitatively the relative distance between a cation and an anion.

To simplify the presentation, we will focus our discussions mostly on 1-butyl-3-methylimidazolium [bmim] as the cation, since PH$_3$ interacts directly with the anion and our experimental results indicate that cations are much less influential on the PH$_3$ binding strength through the selected ion pairs (Table 1). We will study PH$_3$ coordination based on two different models. In the first model, the PH$_3$−IL interaction is simplified to a PH$_3$−anion interaction; i.e., only the anionic part of the IL is used to evaluate the interaction strength with PH$_3$, and the cation influence is ignored. In the second model, the ion pair is included. The optimized structures of Cu(I) anions and ion pairs

TABLE 5: Bond Parameters (Å) of the CuX$_2^-$ Anion before and after PH$_3$ Coordination

	CuX$_2$				CuX$_2$−PH$_3$			
	F	Cl	Br	I	F	Cl	Br	I
X1−Cu	1.815	2.146	2.302	2.483	1.904	2.237	2.379	2.560
X2−Cu	1.814	2.146	2.302	2.483	1.905	2.242	2.387	2.571
P−Cu					2.153	2.238	2.238	2.251

TABLE 6: Bond Parameters (Å) of CuX$_2^-$ Based Ionic Liquids before and after PH$_3$ Coordination

	[bmim]CuX$_2$				[bmim]CuX$_2$−PH$_3$			
	F	Cl	Br	I	F	Cl	Br	I
X1−Cu	1.806	2.152	2.303	2.44	1.984	2.269	2.394	2.556
X2−Cu	1.819	2.133	2.297	2.436	1.914	2.26	2.39	2.553
P−Cu					2.116	2.192	2.21	2.23

with and without complexed PH$_3$ are shown schematically in Figure 2. The calculated main structural parameters are listed in Tables 3−6. Significant structural relaxations are observed upon PH$_3$ coordination in all cases. For the anionic species, [Cu$_2$X$_3$]$^-$ (Tables 3 and 4), the Cu dimer structure remains stable prior to and after PH$_3$ coordination with the calculated Cu−Cu distance ranging from 2.5 to 2.7 Å. Coordination of the second PH$_3$ molecule only results in a slightly elongated Cu−Cu bond. The X−Cu bonds in general are elongated upon PH$_3$ coordination. Remarkably, the optimized P−Cu distance varies only in a narrow range from 2.1 to 2.3 Å, indicating that chemical bonds are formed. Our calculations show that the optimized P−Cu distance increases slightly from F to I, reflecting increased interaction strength between PH$_3$ and the IL. The difference in the calculated P−Cu distances between the first and second PH$_3$ coordination is only marginal. However, we note that the P−Cu distance on the pure anion model is slightly smaller than on the ion pair model, indicating the important influence of ion pairing on the chemical complexes. For PH$_3$ coordination with [CuX$_2$]$^-$ (Tables 5 and 6), considerable structural relaxation of anions is again observed with the Cu atom being pulled toward PH$_3$. The optimized bond parameters exhibit similar variations for the halide series as in the case of [Cu$_2$X$_3$]$^-$.

The chemical complexation between PH$_3$ and the selected Cu(I) ILs can be readily understood on the basis of frontier

**TABLE 3: Bond Parameters (Å) of the Cu$_2$X$_3^{2-}$ Anion before and after PH$_3$ Coordination**

	Cu$_2$X$_3$				Cu$_2$X$_3$−PH$_3$				Cu$_2$X$_3$−2PH$_3$			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
X1−Cu1	1.888	2.188	2.336	2.532	1.836	2.172	2.327	2.728	2.098	2.313	2.428	2.657
X2−Cu1	1.795	2.126	2.273	2.461	1.804	2.144	2.294	2.528	1.873	2.223	2.362	2.553
X1−Cu2	1.888	2.188	2.340	2.525	2.267	2.367	2.472	2.579	2.096	2.318	2.486	2.656
X3−Cu2	1.793	2.126	2.275	2.461	1.839	2.216	2.369	2.573	1.874	2.237	2.392	2.554
Cu1−Cu2	2.712	2.722	2.634	2.612	2.756	2.705	2.657	2.213	2.604	2.668	2.569	2.630
P1−Cu1					2.148	2.206	2.227	2.213	2.147	2.220	2.246	2.247
P2−Cu2									2.148	2.229	2.263	2.247

TABLE 4: Bond Parameters (Å) of Cu$_2$X$_3^{2-}$ Based Ionic Liquids before and after PH$_3$ Coordination

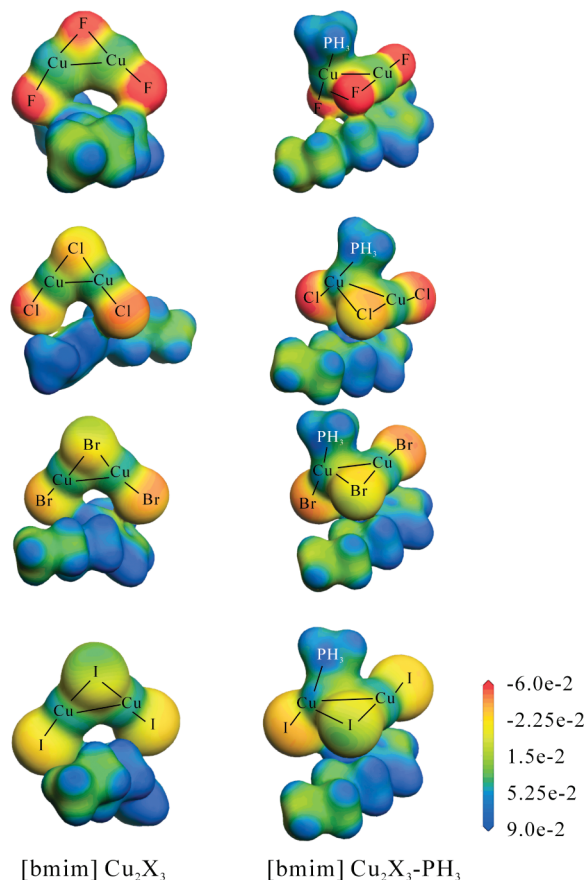|	[bmim]Cu$_2$X$_3$				[bmim]Cu$_2$X$_3$−PH$_3$				[bmim]Cu$_2$X$_3$−2PH$_3$			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
X1−Cu1	1.976	2.176	2.327	2.514	2.285	2.458	2.549	2.699	2.022	2.328	2.457	2.642
X2−Cu1	1.822	2.138	2.284	2.47	1.875	2.216	2.365	2.559	1.918	2.235	2.382	2.567
X1−Cu2	1.885	2.182	2.327	2.515	1.839	2.162	2.312	2.501	2.085	2.331	2.467	2.631
X3−Cu2	1.802	2.131	2.277	2.465	1.799	2.127	2.274	2.465	1.88	2.235	2.385	2.574
Cu1−Cu2	2.585	2.626	2.638	2.634	2.627	2.65	2.67	2.661	2.764	2.709	2.683	2.634
P1−Cu1					2.138	2.196	2.211	2.234	2.121	2.201	2.216	2.237
P2−Cu2									2.127	2.201	2.214	2.238

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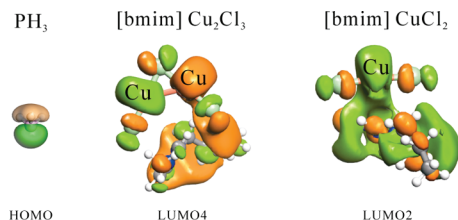
Figure 3. Frontier orbital of (a) PH_3, (b) [bmim] Cu_2Cl_3, and (c) [bmim] $CuCl_2$.

orbital interactions. Figure 3 displays the calculated HOMO of PH_3, the LUMO4 of [bmim][Cu_2Cl_3], and the LUMO2 of [bmim][$CuCl_2$]. The HOMO of PH_3 is occupied by an electron lone pair and the LUMOs of the Cu(I) complexes contain significant 4s orbital character. We note in particular that the difference of orbital energies between the LUMO and the virtual orbitals with strong 4s orbital character in the Cu(I) complexes is relatively small. These virtual orbitals therefore can readily overlap with the HOMO of PH_3, which serves as an electron donor and the Cu(I) serves as an electron acceptor. The partial charge transfer is the dominant mechanism that gives rise to chemical complexation between PH_3 and the ILs.

The calculated reaction energies of PH_3 with [bmim][Cu_2X_3], [Cu_2X_3]⁻, [bmim][CuX_2], and [CuX_2]⁻ are shown in Table 7. It is worth noting that the reaction energies on the ion pair IL models are significantly higher than on the corresponding anion models. This is largely due to the fact that the cations in the ion pair models pull electron density from the anions and thus facilitate the electron transfer from the lone pair of PH_3 to the 4s orbital of Cu in the anionic species. For the ion pair models, the calculated first reaction energies on [bmim][Cu_2X_3] are considerably higher than on [bmim][CuX_2] but the second reaction energies on [bmim][Cu_2X_3] are much lower than on [bmim][CuX_2], although the average of the two reaction energies on [bmim][Cu_2X_3] coincide with that of [bmim][CuX_2] very well. For the pure anionic model, the PH_3 binding energy of a given anion is generally smaller than that of the corresponding ion pair due to the charge removal from the anion to the cation, which allows Cu(I) to be more receptive to PH_3. This is consistent with the calculated P−Cu distances, which are slightly shorter in the ion pairs (Tables 3 and 4). On average, the PH_3 binding strength for both [bmim][Cu_2X_3] and [Cu_2X_3]⁻ as well as [bmim][CuX_2] increases slightly from F to I, which agrees well with the experimental observations (Table 1).

Figure 4 displays the calculated electrostatic potentials of [bmim][Cu_2X_3] and [bmim][Cu_2X_3]−PH_3, respectively. It shows clearly that from F to I the anion gradually becomes less polarized and the ion pairing leads to increasingly less basic anions. The Mulliken population analysis on the anionic species of [bmim][Cu_2X_3] gives a negative charge on the anions of approximately −0.1e in all cases. Upon PH_3 coordination, the [Cu_2X_3] species are further pushed slightly toward [bmim]. We note in particular that the calculated PH_3 reaction energies on [bmim][Cu_2Cl_3] are in good agreement with the experimentally measured heats of reaction that we recently reported.[11] The

Figure 4. Electrostatic potential of [bmim] Cu_2X_3 and [bmim] Cu_2X_3−PH_3. X = F, Cl, Br, and I.

results indicate that, for PH_3 coordination with ILs, it is the ion pair model rather than the anionic model that must be used for accurate evaluation of energies.

We next examined the effects of cations on the PH_3 binding strength on the selected ILs only with the calculated average reaction energies. Table 8 displays the calculated values with various cations. For the same halide, the influence of different quaternary ammonium cations on PH_3 reaction energies appears to be relatively small. For the same cation, the calculated binding energy of PH_3 increases modestly from F to I. In all cases, the ion pairs allow PH_3 to be stably coordinated. We further performed population analysis on selected atoms of the ILs with [bmim] as the cation. The results are shown in Tables 9 and 10. For the halide atoms on the anions, the bridge atom gains less charge from the Cu atoms than from the terminal atoms. The electron loss of the Cu atoms decreases from F to I as the anions become less polarized.

Finally, we examined the influence of solvents on IL binding properties with PH_3 since various solvents are sometimes mixed with ILs for practical applications. We selected several conventional solvents with various polarizabilities using the COS-MO continuum model to calculate the reaction energies of PH_3

TABLE 7: Reaction Energies (kcal/mol) of PH₃ on [bmim]Cu₂X₃, [bmim]CuX₂, Cu₂X₃²⁻, and CuX₂⁻

ΔE_r	[bmim][Cu₂X₃]			[Cu₂X₃]⁻			[bmim]CuX₂	CuX₂⁻
	first	second	average	first	second	average		
F	−15.7	−5.1	−10.4	−8.1	−4.6	−6.4	−9.8	2.1
Cl	−12.7	−7.5	−10.1	−9.3	−5.0	−7.2	−10.3	−2.0
Br	−13.8	−9.8	−11.8	−11.6	−6.6	−9.1	−11.8	−4.1
I	−15.2	−10.7	−12.9	−8.0	−14.0	−11.0	−12.8	−5.8

TABLE 8: Average Reaction Energies (kcal/mol) of PH₃ in Various Cation Based [Cu₂X₃]⁻ Ionic Liquids

ΔE_r	[bmim]Cu₂X₃	[^{t}Bu−pyridine]Cu₂X₃	[ammonium]Cu₂X₃	[Emim]Cu₂X₃	[pyrrolidinium]Cu₂X₃
F	−10.40	−9.55	−10.36	−9.3	−10.88
Cl	−10.10	−8.52	−9.26	−9.2	−9.43
Br	−11.78	−10.09	−10.09	−11.43	−10.54
I	−12.94	−10.61	−12.28	−13.46	−11.81

TABLE 9: Muliken Charge Distribution of Cu₂X₃²⁻ Based Ionic Liquids before and after PH₃ Coordination

	[bmim]Cu₂X₃				[bmim]Cu₂X₃−PH₃				[bmim]Cu₂X₃−2PH₃			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
X1	−0.517	−0.246	−0.224	−0.109	−0.554	−0.351	−0.331	−0.227	−0.583	−0.432	−0.423	−0.326
X2	−0.599	−0.459	−0.447	−0.366	−0.611	−0.527	−0.528	−0.472	−0.627	−0.534	−0.533	−0.469
X3	−0.602	−0.449	−0.441	−0.36	−0.597	−0.437	−0.432	−0.361	−0.357	−0.535	−0.539	−0.476
Cu1	0.429	0.149	0.139	0.019	0.293	0.152	0.153	0.068	0.327	0.144	0.142	0.055
Cu2	0.435	0.141	0.133	0.015	0.414	0.102	0.098	−0.015	0.357	0.157	0.151	0.051
P1					0.222	0.198	0.196	0.196	0.183	0.172	0.174	0.172
P2									0.189	0.197	0.207	0.212

TABLE 10: Mulliken Charge Distribution of CuX₂⁻ Based Ionic Liquids before and after PH₃ Coordination

	[bmim]CuX₂				[bmim]CuX₂−PH₃			
	F	Cl	Br	I	F	Cl	Br	I
X1	−0.596	−0.456	−0.456	−0.391	−0.639	−0.553	−0.557	−0.506
X2	−0.599	−0.466	−0.459	−0.392	−0.636	−0.568	−0.566	−0.495
Cu	0.454	0.093	0.089	0.025	0.341	0.142	0.144	0.053
P					0.184	0.184	0.188	0.184

**TABLE 11: Average Reaction Energies (kcal/mol) of PH₃ on [bmim][Cu₂X₃] in Different Media**

ΔE_r	H₂O ($k = 78.54$)	ethanol ($k = 24.3$)	cyclohexane ($k = 2.05$)	gas phase
F	1.19	−0.87	−5.34	−10.40
Cl	0.11	−3.93	−8.29	−10.09
Br	−0.41	−0.40	−9.31	−11.78
I	−2.31	−0.04	−10.46	−12.94

in [bmim][Cu₂X₃]. The results are shown in Table 11. Radically smaller reaction energies are observed due to the solvation effects. Even with a nonpolar solvent like cyclohexane, the significant reduction of reaction energy is obvious, suggesting profound influence of solvent on IL coordination properties.

III.3. Al-Based Complexes. To gain further insight into the influence of anions on the coordination properties of PH₃, we performed calculations on PH₃ coordination in the aluminate ionic liquids, [bmim][Al₂Cl₇], and [bmim][AlCl₄]. Experimentally, we observed that the heptachloroaluminate ionic liquid has a small but reversible capacity for PH₃, but the tetrachloroaluminate ionic liquid has essentially no capacity (Table 1). To understand this behavior, we performed structural optimizations on the coordination structures in the selected ILs. On [bmim][AlCl₄], we found that the PH₃ molecule is repelled from the [AlCl₄]⁻ anion. The P atom of PH₃ is directed away from the IL and two H atoms form weak H-bonds with the Cl atoms of the anion. The closest H−Cl distance is 3.346 Å. As expected, the calculated PH₃ coordination energy on [bmim][AlCl₄] is only −3.0 kcal/mol, significantly weaker than what was found for PH₃ on [bmim][CuX₂].

For [bmim][Al₂Cl₇], two sequentially bound PH₃ molecules were examined. The fully optimized structures are shown in Figure 5. Initially, the Al atoms adopt an sp³ configuration and the two Al atoms in the anion are bridged by a shared Cl atom. Upon the coordination with the first PH₃ molecule, [Al₂Cl₇]⁻ dissociates considerably, forming essentially two weakly bound species: AlCl₃ with a planar configuration and AlCl₄⁻. The calculated distances between Al and the bridge Cl are 2.516

and 2.277 Å, respectively. The P atom of PH₃ is directed toward the Al atom of the AlCl₃ species with a distance of 2.644 Å, indicative of a modest bond strength. The calculated coordination energy is −2.9 kcal/mol, again, much weaker than the value found in [bmim][Cu₂X₃]. We then added a second PH₃ molecule to the system and carried out an energy minimization. We found that the PH₃ molecule is repelled from the PH₃·[bmim][Al₂Cl₇] species. The second PH₃ molecule interacts with the metastable [AlCl₄]⁻, which resulted from coordination of the first PH₃ molecule (PH₃···AlCl₃···AlCl₄). Consequently, the second PH₃ is unable to interact with [AlCl₄]⁻ effectively, similar to the case of [bmim][AlCl₄]. The calculated binding energy for coordination of the second PH₃ is −4.5 kcal/mol. The higher binding energy should not be surprising due to the metastable structure of PH₃·[bmim][Al₂Cl₇]. On average, the binding energy of PH₃ on [bmim][Al₂Cl₇] is −3.7 kcal/mol, slightly higher than the value on [bmim][AlCl₄]. Qualitatively, we found that PH₃ coordination on the Al-based ILs is significantly weaker than on the Cu(I)-based ILs, consistent with what was observed in our experiments.
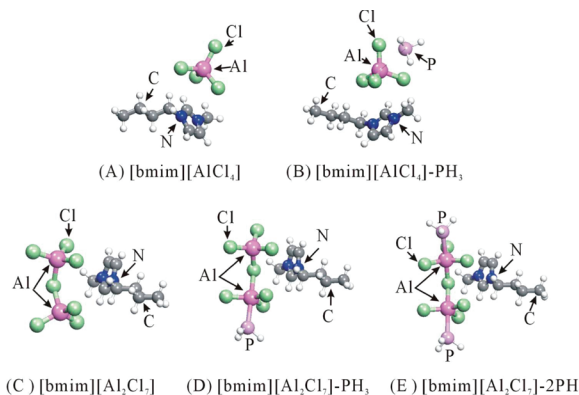
Figure 5. [AlCl₄] and [Al₂Cl₇] based ILs and their reaction processes with PH₃: (A) [bmim] [AlCl₄]; (B) [bmim] [AlCl₄]−PH₃; (C) [bmim][Al₂Cl₇]; (D) [bmim][Al₂Cl₇]−PH₃; (E) [bmim][Al₂Cl₇]−2PH₃.

Complexation of PH₃ with Ionic Liquids

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IV. Summary

Ionic liquids represent an important class of materials that exhibit novel physicochemical properties with great potential as molecular gas carriers. We have experimentally prepared a range of novel ILs used as potential carriers for the toxic gas, PH₃. The volumetric capacities of these ILs were determined by measuring PH₃ uptake at room temperature. Using first principles quantum mechanical methods, we attempted to address several critical issues that may influence PH₃ binding strength in these ILs. Both our experimental and theoretical studies have shown that Cu(I)-based ILs are capable of binding with PH₃ with a suitable strength that allows reversible chemical complexation to be carried out at near ambient conditions.

We have examined the role of cations in enhancing the interaction between PH₃ and ILs. It was found that different cations, either aromatic or aliphatic based, do not significantly affect the interaction strength. This provides a wide and judicious choice of cationic species for ILs suitable for specific applications. We further explored the effects of solvents with small to large dielectric constants on PH₃ complexation with [bmim][Cu₂X₃]. We found that they can radically reduce the binding strength even in the case of nonpolar solvent due to the reduction of the positive charge on Cu(I). Our results indicate that the change of ligands from F to I can moderately increase the PH₃ binding on [bmim][Cu₂X₃]. This is in good agreement with our experimental observations. Finally, we found that it is necessary to use the ion pairing model, rather than the anionic model, to represent the ILs in order to accurately describe the PH₃ interaction strength with the selected ILs.

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