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The nature of interactions between [Cu$_2$Cl$_3$]$^−$-based ionic liquid and thiophene − A theoretical study

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Abstract   In an effort to deepen the understanding of nature of interactions between CuCl-based ionic liquids and thiophene, the electronic and topological properties of interactions between 1-butyl-3-methylimidazolium ([BMIM]$^+$[Cu$_2$Cl$_3$]$^−$) and thiophene (TS) have been investigated by the density functional theory. The occurrence of interactions caused by resonance effects between virtual orbitals of Cu and virtual orbitals of thiophene has been corroborated at the molecular level.

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1. Introduction

The desulfurization of fuel has received worldwide attention because environmental regulation of the sulfur limit for fuels is becoming increasingly stringent. In the past years, ionic liquids have gained an increasing interest due to its unique properties both as extractant and catalyst. Recently, CuCl-based ionic liquids were employed to remove thiophenic compounds from fuel (Huang et al., 2004; Zhang et al., 2005). CuCl-based ionic liquid exhibited remarkable desulfurization ability in the desulfurization of gasoline when used as an extraction absorbent. The effectiveness of sulfur removal was proposed as the π-complexation of Cu(I) with thiophene, which shows promise as an approach for the deep desulfurization of motor fuel (Huang et al., 2004; Zhang et al., 2005).

However, the nature of interactions between ([BMIM]$^+$[Cu$_2$Cl$_3$]$^−$) and thiophene (TS) is still unknown at the molecular level. Therefore, this work reports an analysis of structures of [BMIM]$^+$[Cu$_2$Cl$_3$]$^−$ and [BMIM]$^+$[Cu$_2$Cl$_3$]$^−$-TS complexes using quantum chemical calculations. The theoretical results here will confirm the formation of hydrogen bonds, interactions between virtual orbitals of Cu and virtual orbitals of TS at the molecular level firstly.

2. Computational details

All geometric optimizations reported here were performed with DMol^3 program package (Delley, 1990). The double numerical basis sets plus polarization functional (DNP) was employed. For the exchange correlation term of the energy functional, the generalized gradient corrected functional GGA and PW91 functional as implemented in the DMol^3 program, were used for all the geometry optimizations, which are the most widely

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Table 1 Selected donor–acceptor interactions in [BMIM][Cu$_2$Cl$_3$], [BMIM][Cu$_2$Cl$_3$]-TS and their second order perturbation stabilization energies, $E(2)$ (kcal/mol).

Donor	Acceptor	$E(2)$ (kcal/mol)	Donor	Acceptor	$E(2)$ (kcal/mol)
[BMIM][Cu$_2$Cl$_3$]					
σ(C2–H2)	σ^*(Cl2–Cu1)	0.11	LP(Cu1)	RY*(H81)	0.11
LP(Cu1)	σ^*(C2–H2)	0.17	σ^*(Cl2–Cu1)	RY*(H2)	1.15
σ^*(Cl2–Cu1)	RY*(H81)	4.48	σ^*(Cl2–Cu1)	RY*(H61)	1.46
σ^*(Cl2–Cu1)	σ^*(C2–H2)	0.35	LP(Cl1)	σ^*(C2–H2)	11.85
LP(Cl1)	σ^*(C8–H81)	0.17	LP(Cl1)	σ^*(C6–H61)	1.91
LP(Cl1)	RY*(H81)	2.31	LP(Cl1)	RY*(H61)	0.58
LP(Cl3)	π^*(N1–C2)	1.00	LP(Cl3)	σ^*(C7–H71)	1.33
LP(Cl3)	σ^*(N1–C2)	0.08			
[BMIM][Cu$_2$Cl$_3$]-TS					
π(C4′–C3′)	π^*(C5–C4)	0.05	π(C4′–C3′)	σ^*(C7–H72)	0.15
π(C2′–C1′)	σ^*(C7–H72)	0.10	LP(S)	σ^*(C7–C8)	0.06
LP(S)	σ^*(C7–H71)	0.12	LP(S)	LP*(Cu1)	0.14
LP(Cu2)	σ^*(C2–H2)	0.56	LP*(Cu2)	RY*(N1)	0.40
LP*(Cu2)	RY*(C2)	1.74	LP*(Cu2)	RY*(H71)	3.97
LP*(Cu2)	RY*(C7)	0.22	LP*(Cu2)	RY*(H81)	0.13
LP*(Cu2)	RY*(C4′)	0.15	LP*(Cu2)	RY*(S)	3.14
LP*(Cu2)	RY*(H4′)	0.08	LP*(Cu2)	RY*(C1′)	0.30
LP*(Cu1)	RY*(C4′)	2.45	LP*(Cu1)	RY*(C3′)	0.95
LP*(Cu1)	RY*(S)	1.15	LP*(Cu1)	RY*(H4′)	0.35
LP*(Cu1)	RY*(C1′)	0.13	LP*(Cu1)	σ^*(S–C1′)	0.15
LP(Cl3)	σ^*(C2–H2)	12.87	LP(Cl3)	σ^*(C7–H71)	0.90
LP(Cl3)	σ^*(N3–C2)	0.10	LP(Cl3)	σ^*(C8–H81)	0.05
LP(Cl3)	RY*(S)	0.60	LP(Cl1)	σ^*(C6–H63)	1.70
LP(Cl1)	π^*(N1–C2)	0.22	LP(Cl1)	σ^*(C6–H62)	0.07
LP(Cl1)	σ^*(C4′–H4′)	2.01	LP(Cl1)	σ^{**}(C4′–C3′)	0.06
LP(Cl1)	RY*(C4′)	0.60	LP(Cl1)	RY*(C3′)	0.19
LP(Cl1)	RY*(S)	0.10	LP(Cl1)	RY*(H4′)	0.10
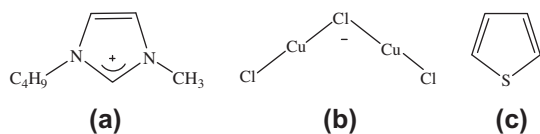
Figure 1 The structures of (a) 1-butyl-3-methylimidazolium ([BMIM]$^+$) (b) [Cu$_2$Cl$_3$]$^-$ (c) thiophene (TS).

used tools for studying the geometric and electronic structures of molecules and have been shown to produce more reliable geometries for hydrogen bonding systems. Although PW91 functional is unable to provide a good description of dispersion interactions, GGA/PW91/DNP can give good results of inter-actions between conjugated systems (Castellano et al., 2011). All the stationary structures have been fully optimized without geometrical constraints. A frequency analysis was performed on all structures to insure the absence of imaginary frequencies. To examine the nature of interactions, the electronic properties for stationary points are illustrated based on the natural bond orbital (NBO) analysis (Reed et al., 1988). These non-local do-nor–acceptor-orbital interactions are associated with the delo-calization of electron density between states i and j in the NBO basis, as given by

$$E(2) = \Delta E_{ij} = n_i \frac{(F_{ij})^2}{\varepsilon_j - \varepsilon_i}$$

where n_i is the donor orbital occupancy, ε_i and ε_j are the diagonal elements, and $F_{i,j}$ is the off-diagonal NBO Fork ma-trix element. Intermolecular interactions such as lone pair $\rightarrow$ -anti-bonding orbital mixtures are representative of donor–acceptor bonding, whereas non-Lewis-type (highly delocal-ized) interactions such as anti-bond $\rightarrow$ anti-bond orbital mix-tures represent effects like resonance stabilization. The AIM analysis was used to analyze the nature of interactions at the B3LYP/6-31 + + G** level by AIM2000 package (Biegler-Kö-nig and Schönbohm, 2002) with the wave functions generated from B3LYP/ 6-31 + + G** results.

3. Results and discussion

The structures of 1-butyl-3-methylimidazolium cation ([BMIM]$^+$), [Cu$_2$Cl$_3$]$^-$, thiophene (TS) are shown in Fig. 1. The [Cu$_2$Cl$_3$]$^-$ anion or/and TS have been gradually placed in different regions around [BMIM]$^+$ cation to form [BMIM]$^+$[Cu$_2$Cl$_3$]$^-$ and [BMIM]$^+$[Cu$_2$Cl$_3$]$^-$-TS for optimization.

The most stable structure of [BMIM]$^+$[Cu$_2$Cl$_3$]$^-$ is shown in Fig. 2a. It can be seen that the most stable structure of [BMIM]$^+$[Cu$_2$Cl$_3$]$^-$ has three Cl···H interactions. The interact-ing distances are 2.387 Å (Cl1···H2), 2.867 Å (Cl1···H61) and 2.900 Å (Cl3···H71), while the sum of Bondi's van der Waals radii of chlorine atom and hydrogen atom (1.75 and 1.20 Å) is 2.95 Å (Bondi, 1964). The short distances of H2-involved interactions may be ascribed to the highly positive H2 due to the withdrawing electron of two nitrogen atoms. The most sta-ble structure of [BMIM]$^+$[Cu$_2$Cl$_3$]$^-$-TS is shown in Fig. 2b. The ring plane of TS and imidazolium ring is parallel to each other. The interacting distances between [BMIM]$^+$[Cu$_2$Cl$_3$]$^-$