Electronic supplementary information

Complexation of Neutral 1,4-Dihalobutanes with Simple Pillar[5]arenes That is Dominated by Dispersion Forces

Xiaoyan Shu, Jiazeng Fan, Jian Li, Xiaoyang Wang, Wei Chen, Xueshun Jia,* and Chunju Li*

cjli@shu.edu.cn

Contents

Copies of $^1$H NMR and $^{13}$C NMR spectra of hosts. S2

$^1$H NMR spectra of guests in the absence and presence of AlkP5As. S6

Crystal structures of DIBu ⊂ BuP5A, DFBu ⊂ BuP5A and DCIBu ⊂ OctP5A S15

complexes.

Job plots. S18
Copies of $^1$H NMR and $^{13}$C NMR spectra of hosts.

Figure S1. $^1$H NMR spectrum (500 MHz) of MeP5A in CDCl$_3$.

Figure S2. $^{13}$C NMR spectrum (125 MHz) of MeP5A in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum (500 MHz) of EtP5A in CDCl$_3$.

Figure S4. $^{13}$C NMR spectrum (125 MHz) of EtP5A in CDCl$_3$. 
**Figure S5.** $^1$H NMR spectrum (500 MHz) of BuP5A in CDCl$_3$.

**Figure S6.** $^{13}$C NMR spectrum (125 MHz) of BuP5A in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum (500 MHz) of OctP5A in CDCl$_3$.

Figure S8. $^{13}$C NMR spectrum (125 MHz) of OctP5A in CDCl$_3$. 
$^1$H NMR spectra of guests in the absence and presence of AlP5As.

**Figure S9.** $^1$H NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + EtP5A, and (c) EtP5A in CD$_3$Cl at 4.2–5.0 mM. The peaks marked with an asterisk are due to water.
Figure S10. $^1$H NMR spectra (500 MHz) of (a) DClBu, (b) DClBu + EtP5A, and (c) EtP5A in CD$_3$Cl at 4.4–5.2 mM. The peaks marked with an asterisk are due to water.
Figure S11. $^1$H NMR spectra (500 MHz) of (a) DFBu, (b) DFBu + EtP5A, and (c) EtP5A in CD$_3$Cl at 4.3–5.2 mM. The peaks marked with an asterisk are due to water.
Figure S12. $^1$H NMR spectra (500 MHz) of (a) DOHBu, (b) DOHBu + EtP5A, and (c) EtP5A in CD$_3$Cl at 4.1–4.7 mM. The peaks marked with an asterisk are due to water.
Figure S13. $^1$H NMR spectra (500 MHz) of (a) DN$_3$Bu, (b) DN$_3$Bu + EtP5A, and (c) EtP5A in CD$_3$Cl at 4.0–4.6 mM. The peaks marked with an asterisk are due to water.
Figure S14. $^1$H NMR spectra (500 MHz) of (a) BrBu, (b) BrBu + Et5P, and (c) Et5P in CD$_3$Cl at 4.0–4.6 mM. The peaks marked with an asterisk are due to water.
Figure S15. $^1$H NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + MeP5A, and (c) MeP5A in CD$_3$Cl at 4.2–4.8 mM. The peaks marked with an asterisk are due to water.
Figure S16. $^1$H NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + BuP5A, and (c) BuP5A in CD$_3$Cl at 4.2–5.0 mM. The peaks marked with an asterisk are due to water.
Figure S17. $^1$H NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + OctP5A, and (c) OctP5A in CD$_3$Cl at 4.2–5.1 mM. The peaks marked with an asterisk are due to water.
Crystal structures of DIBu⊂BuP5A, DFBu⊂BuP5A, and DCIBu⊂OctP5A complexes.

**Figure S18.** Crystal structure of the interpenetrated complex DIBu⊂BuP5A. Hydrogens of the host have been omitted for clarity. BuP5A is green, DIBu is blue, oxygens are red, and iodines are magenta. Dashes represent C−H···π interactions or C−H···I/O hydrogen bonds.

(A) C−H···π parameters: H···ring centre distances (Å), C−H···ring angles (deg) A, 3.15, 156; B, 3.44, 111; C, 3.33, 118; D, 3.18, 144; E, 3.45, 135; F, 2.75, 144; G, 2.81, 176; H, 3.40, 150.

(B) C−H···I hydrogen-bond parameters: H···I distances (Å), C−H···I angles (deg) A, 3.25, 162; B, 3.19, 167; C, 3.47, 135; D, 3.44, 135; E, 3.41, 138; F, 3.34, 168; G, 3.33, 139; H, 3.25, 130; I, 3.43, 123; J, 3.21, 142; K, 3.35, 138; L, 3.29, 154.

(C) C−H···O hydrogen-bond parameters: H···O distances (Å), C−H···O angles (deg) A, 3.09, 155; B, 3.49, 102; C, 3.19, 133; D, 3.30, 135; E, 3.32, 144; F, 3.47, 162.
Figure S19. Crystal structure of the interpenetrated complex DFBu⊂BuP5A. Hydrogens of the host have been omitted for clarity. BuP5A is green, DFBu is blue, oxygens are red, and fluorines are magenta. Dashes represent C−H···π interactions or C−H···F/O hydrogen bonds.

(A) C−H···π parameters: H···ring centre distances (Å), C−H···ring angles (deg) A, 3.17, 150; B, 3.44, 112; C, 3.42, 114; D, 3.14, 144; E, 3.07, 153; F, 2.98, 160.

(B) C−H···F hydrogen-bond parameters: H···F distances (Å), C−H···F angles (deg) A, 3.21, 164; B, 2.90, 145; C, 2.87, 153; D, 3.39, 151; E, 3.48, 138; F, 2.92, 141; G, 3.02, 135; H, 3.11, 159.

(C) C−H···O hydrogen-bond parameters: H···O distances (Å), C−H···O angles (deg) A, 3.39, 128; B, 3.19, 168; C, 3.38, 151; D, 3.35, 167; E, 3.11, 140.
Figure S20. Crystal structure of the interpenetrated complex DClBu⊂OctP5A. Hydrogens of the host have been omitted for clarity. OctP5A is green, DClBu is blue, oxygens are red, and chlorines are magenta. Dashes represent C−H···π interactions or C−H···Cl/O hydrogen bonds.


(B) C−H···Cl hydrogen-bond parameters: H···Cl distances (Å), C−H···Cl angles (deg) A, 3.23, 137; B, 2.84, 147; C, 3.45, 135; D, 3.30, 129; E, 3.03, 132; F, 3.26, 116; G, 3.02, 161; H, 3.11, 163; I, 2.94, 149; J, 3.22, 165; K, 3.05, 160; L, 3.49, 117; M, 3.02, 138.

(C) C−H···O hydrogen-bond parameters: H···O distances (Å), C−H···O angles (deg) A, 3.17, 164; B, 2.89, 165; C, 2.86, 140; D, 3.32, 139; E, 3.23, 159; F, 3.37, 155.
**Job plots.**

**Figure S21.** Left: Job plot showing the 1 : 1 stoichiometry of the complex between DOHBu and EtP5A in CDCl₃ by plotting the Δδ in chemical shift of the guest’s methylene proton H₄ observed by ¹H NMR spectroscopy against the mole fraction of guest (X_{guest}). ([host] + [guest] = 12.0 mM). Right: Job plot showing the 1 : 1 stoichiometry of the complex between BrBu and EtP5A in CDCl₃ by plotting the Δδ in chemical shift of the guest’s methyl proton observed by ¹H NMR spectroscopy against the mole fraction of guest (X_{guest}). ([host] + [guest] = 16.0 mM).