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Binding of Ammonium Hexafluorophosphate and Cation-Induced Isolation of Unusual Conformers of a Hexapodal Receptor

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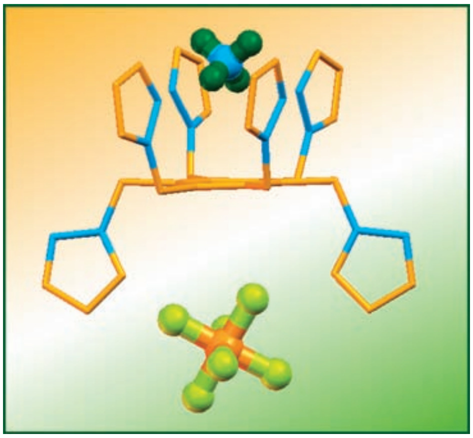
ABSTRACT



The pyrazole-based hexa-host receptor showed the preference of an unusual conformation via 1:1 hydrogen bonding with ammonium hexafluorophosphate over steric gearing. Two different unusual conformers of the receptor are also isolated upon complexation with Cu^{2+} and Cd^{2+} ions.

Molecular recognition by artificial receptors and the construction of supramolecular topologies are important toward a better understanding of the recognition phenomena in nature and their potential applications in separation processes, catalysis, sensing, and biochemical studies.[1] In particular, synthetic receptors for recognition/binding of ion pairs has been a subject of current research interest.[2] Generally, in hexasubstituted benzene derivatives, the arms are directed to project opposite sides of the plane of the benzene ring, resulting in a 1,3,5 vs 2,4,6 facial segregation (steric gearing). Thus, it is not surprising to find this conformational networking used in the design of preorganized receptors with suitably

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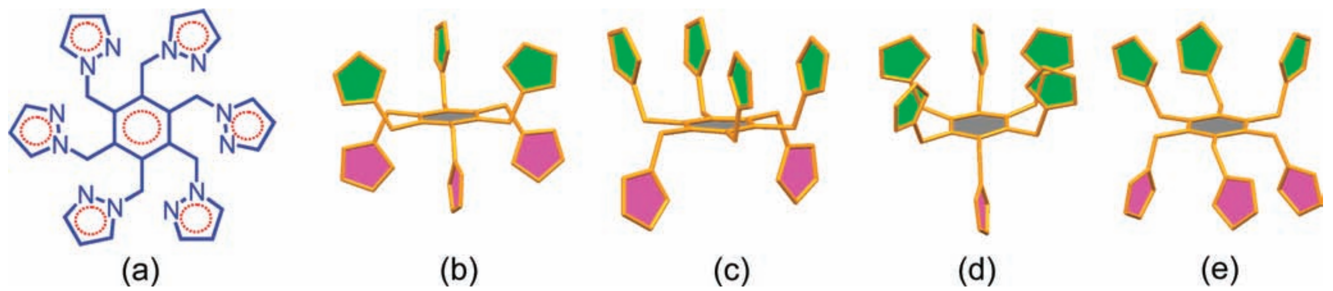

Figure 1. View showing (a) the molecular structure of **L**, (b) *ababab*, (c) *aabaab*, (d) *aaaaab*, and (e) *aaabbb* conformations of **L**. Green and pink pentagons represent the arms extending above and below the central benzene scaffold, respectively.

decorated functional groups, leading to the receptors with great potential to bind guests.[3] Recent reports by Barbour et. al on hexa-host molecules showed the existence of unusual conformations,[4] and on the other hand, we have explored the benzene-based hexamide for the binding of oxyanions in the solid and solution states.[5] In this letter, we demonstrate the binding of the ion pair $NH_4^+PF_6^-$ by an unusual conformer (*aabaab*) of hexakis(pyrazol-1-ylmethyl)benzene, **L** (Figure 1).

Further, we also structurally demonstrate the isolation of two other different unusual conformations *aaaaab* and *aaabbb* (Figure 1) of the hexa-host, **L**, upon complexation with Cu^{2+} and Cd^{2+}, respectively. Our choice of system is a previously reported receptor **L** which consists of a pyrazole chelator connected to the benzene platform through a methylene spacer.[6] The pyrazole moiety can act as a H-bond acceptor for the recognition of ammonium[7] and as a metal chelator.[8] These dual properties might be useful for the development of synthetic receptors having multiple arms for recognition/binding toward ion pairs such as $NH_4^+PF_6^-$.

L is synthesized from hexakis(bromomethyl)benzene[9] using a newly adopted synthetic procedure in a good yield (Supporting Information). Reaction of **L** with NH_4PF_6, $Cu(ClO_4)_2{\cdot}6H_2O$, and $Cd(ClO_4)_2$ yielded complexes [$\mathbf{L}{\cdot}NH_4PF_6{\cdot}H_2O$] (**1**), [$\mathbf{L}{\cdot}Cu(ClO_4)_2{\cdot}4H_2O$] (**2**), and [$\mathbf{L}{\cdot}Cd(ClO_4)_2{\cdot}5H_2O$] (**3**), respectively, in good yields as crystals suitable for single-crystal X-ray diffraction studies. Crystals of **1** were prepared by allowing a dimethyl formamide solution of **L** to undergo slow evaporation in the presence of NH_4PF_6 and were investigated using single-crystal X- ray diffraction analysis. The structure of **1** revealed the existence of an unusual conformation (*aabaab*) of **L** (Figure 2), where four of the pyrazoles are on the same side of the center benzene ring (upper cleft), and among them two pyrazole units are hydrogen bonded to NH_4^+ via N−H···N interactions (Table 1). On the other hand, the counteranion PF_6^- is located at the lower cleft which is formed by the rest of the two arms of **L**, below the plane of the benzene ring via three C−H···F interactions (Figure S8 and Table S2, Supporting Information). In addition, the recognized ammonium ion at the upper cleft participates in two more hydrogen bonding interactions with two lower cleft pyrazolyls of two different **L** units, resulting in four N−H···N interactions (Figure 2, Table 1). In the case of PF_6^-, four

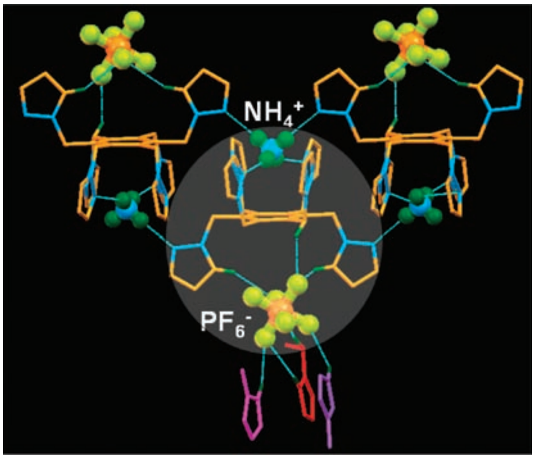

Figure 2. Molecular conformation (*aabaab*) of **L** in complex **1** and the compartmental binding and ditopic recognition of NH_4^+ and PF_6^- in **L**.

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Table 1. Hydrogen Bonding Interactions of NH_4^+ with **L** in **1**[a]

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	∠D−H···A (deg)
N1−H1A···N3^{i}	0.87(2)	2.09(4)	2.927(5)	160(9)
N1−H1B···N44^{ii}	0.86(2)	2.13(2)	2.980(5)	166(4)
N1−H1C···N23^{iii}	0.88(2)	2.13(2)	2.977(5)	164(4)
N1−H1D···N30^{i}	0.86(2)	2.25(4)	2.988(5)	145(5)

[a] Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z$.

additional C−H···F interactions with three pyrazole C−H protons and one methylene proton from three other units of **L** with C−F bond distances ranging from 3.43 to 3.58 Å are observed (Figure S8 and Table S2, Supporting Information). The effect of ion-pair binding in **1** via different hydrogen bonding interactions resulted in the unusual conformation of **L** when compared with the crystal structure of apohost with *ababab* conformation.[6] The conformational flexibility of **L** together with the provision of appropriate hydrogen bonding acceptor sites are important factors that are underlying the ability of **L** to complex with NH_4PF_6.

The binding of $NH_4^+PF_6^-$ with **L** in solution is validated by ^{1}H NMR experiments in CD_3CN at 25 °C. Qualitative ^{1}H NMR studies of **L** with NH_4PF_6 showed appreciable downfield chemical shifts in the pyrazolyl protons and the upfield shift of methylene protons which indicated the binding of guests in the solution state. For detailed solution state binding of NH_4PF_6 with **L**, we have carried out ^{1}H NMR titration experiments in CD_3CN at 25 °C. Upon gradual addition of aliquots of NH_4PF_6, changes in chemical shifts are observed for aryl −CH and methylene $-CH_2$ protons of **L** (Figure 3a, Figure S9 of Supporting Information). Considerable change (0.3 ppm) in the chemical shift value is observed for the aryl −CH proton adjacent to the coordinating pyrazolyl nitrogen. The Job's plot for **L** with NH_4PF_6 showed host−guest stoichiometry 1:1 in solution (Figure 3b). This indeed supports the compartmental binding of NH_4^+ and PF_6^- ions in solution. Solution state studies of ion-pair binding with the hexapodal ditopic receptor with both cation and anion binding sites have been recently studied by Roelens et al.[10] As NH_4^+ is in tetrahedral geometry, in the case of 1:1 complexation, the geometry of **L** did not permit all four coordinations by sharing four of its arms. Instead, it allowed only two hydrogen bondings from two arms out of four and two more coordinations from two other units of **L** with the NH_4^+. Upon careful analysis of the corresponding NMR spectra, a huge change in the chemical shifts is observed up to the addition of 1 equiv of NH_4PF_6 to the solution of **L**, and further addition resulted in slight changes in the chemical shift positions (Figure 3c). The association constant for the 1:1 (host:guest) complexation of **L** and NH_4PF_6 is calculated by EQNMR.[11] The association constant log *K* for **L** with $NH_4^+PF_6^-$ is 2.67.

Complexation of **L** with $Cu(ClO_4)_2$ in acetone and water yielded blue crystals of complex **2**. The structure of **2** revealed 1:1 complexation of **L** with $Cu(ClO_4)_2$ resulting in $[Cu(\mathbf{L})(H_2O)_2]{\cdot}2ClO_4{\cdot}4H_2O$ (Figure 4a). Among the six pyrazolyl arms of **L**, three arms participated in coordination with the copper ion with N···Cu bond distances ranging from

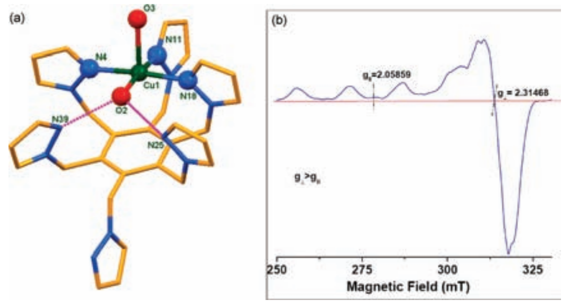

Figure 4. (a) Molecular structure of **2** showing *aaaaab* conformation of **L**. Perchlorate and lattice water molecules are omitted for clarity. (b) EPR spectra of **2**. Color codes: yellow, carbon; blue, nitrogen; red, oxygen; and green, copper.

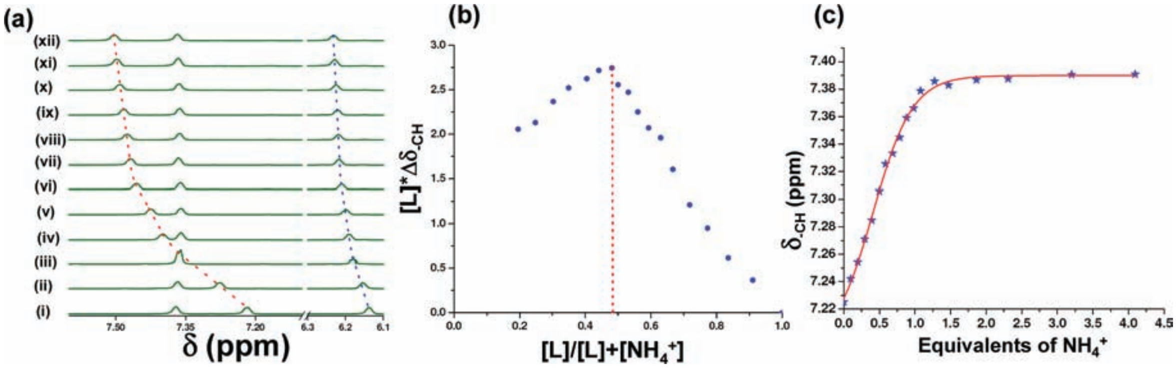

Figure 3. (a) Partial ^{1}H NMR (300 MHz) spectral changes of **L** with added NH_4PF_6 in CD_3CN (25 °C) ($[\mathbf{L}]^0 = 22.13$ mM). Ratio of concentration $[NH_4^+]/[\mathbf{L}]$: (i) 0, (ii) 0.20, (iii) 0.49, (iv) 0.69, (v) 0.89, (vi) 1.08, (vii) 1.28, (viii) 1.47, (ix) 1.86, (x) 2.31, (xi) 3.20, and (xii) 4.09. (b) Job's plot for **L** with NH_4PF_6 in CD_3CN ([**L**] is varied from 22.13 to 11.54 mM by the addition of aliquots of 98.65 mM NH_4PF_6). (c) Plot showing change in chemical shift of the −CH of **L** with increasing amounts of NH_4PF_6 in CD_3CN at 25 °C.

1.99 to 2.06 Å. In addition, Cu(II) is coordinated with two water molecules with Cu•••O bond distances of 1.98 and 2.23 Å. Detailed bond parameters are given in Tables S3 and S4 of Supporting Information. Thus, in complex **2**, Cu(II) adopted a slightly distorted square pyramidal geometry ($\tau = 0.05$)[12] as shown in Figure 4a. The metal-bound basal water molecule is further hydrogen bonded to two pyrazole units of the same molecule of **L** which orient these two arms in the direction of the metal bound arms. Thus, coordination of the metal ion and hydrogen bonding interactions with the water molecule, **L**, favors highly unfavorable *aaaaab* conformation in **2**. The coordination geometry of the Cu(II)−**L** complex in solution is also established by analyzing the X-band EPR and electronic spectral data of **2**. The EPR spectrum of **2** (1.2×10^{-3} mol dm^{-3}) in acetone−toluene glass (150 K) is shown in Figure 4b. The EPR signals and parameters ($g_{\|} = 2.31468$, $g_{\perp} = 2.05594$, $A_{\|} = 0.14607$ mT, and $A_{\perp} = 0.01206$ mT values) of **2** are consistent with a distorted square pyramidal geometry of Cu(II) with $d_{x2\text{-}y2}$ ground state. Similarly, the optical spectrum of **2** in acetone showed a d−d transition band at 624 nm ($\varepsilon = 35$ M^{-1} cm^{-1}) and a shoulder at 698 nm (Figure S11, Supporting Information). The observed ligand-field band position and its intensity of **2** are similar to those obtained for a Cu(II) where the coordination geometry is distorted square pyramidal.[13] The solution spectral data are in perfect agreement with the solid-state single-crystal X-ray structure of **2**.

Complexation of **L** with Cd(ClO_4)$_2$ in acetone−water yielded colorless crystals of complex **3** in good yield. Single-crystal X-ray structural analysis of **3** revealed 1:1 binding of host to metal (Figure 5). Interestingly, in this case, **L** adopted *aaabbb* conformation like Figure 1e. A similar type of conformation of hexa-host receptors was recently reported by us and others.[4,5] The mode of coordination of cadmium with **L** is shown in Figure 5. The Cd atom adopts a slightly distorted octahedral geometry in which the equatorial plane is formed by four water molecules and the axial positions are occupied by pyrazolyl nitrogen atoms of two different ligands and forms a infinite 1D network.

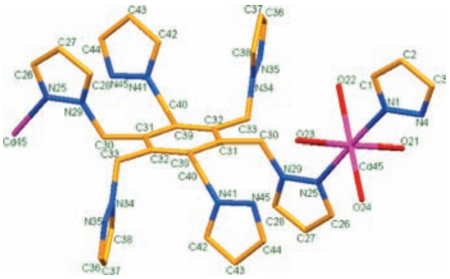

Figure 5. (a) 1D-network of *aaabbb* conformer of **L** in **3**. Color codes: yellow, C; blue, N; red, O; pink, Cd.

In conclusion, we have structurally demonstrated the 1:1 compartmental recognition of ammonium hexafluorophosphate in a hexapodal receptor. The ^{1}H NMR titration experiment also revealed 1:1 binding of $NH_4^+PF_6^-$ in solution. Binding of this salt resulted in *aabaab* conformation purely by hydrogen bonding interactions of guests with the receptor. On the other hand, copper and cadmium ion coordination favored the isolation of different unusual conformations of a hexapodal unit. In the copper complex, the receptor adopted *aaaaab* conformation due to the combined effect of coordination bond and hydrogen bonding interactions, whereas the cadmium complex adopted the *aaabbb* conformation exclusively based on the coordination bond with the metal ion. We are presently working on recognition and sensing of ions and molecules with hexasubstituted arene-based receptors.

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Supporting Information Available: Synthetic procedures, characterization data, crystallographic information file, crystallographic refinement details, ^{1}H NMR titration data, and UV−vis spectra of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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