



Hexapodal pyrazole-based receptors: complexes with ammonium ions and solvent molecules in the solid state



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ABSTRACT

New crystalline complexes of hexapodal pyrazole-based hosts with $\text{NH}_4^+\text{PF}_6^-$ and/or solvent molecules were obtained and detailed analysed. The binding motifs observed between the binding partners give valuable insights into the phenomena of molecular recognition processes. Analyses of the conformations of the hexasubstituted benzene derivatives have shown that both *ababab* as well as *abbabb* and *aaabbb* conformations of the hexapodal compounds **1**–**3** are observed in the crystal structures **1a**–**d**, **2**, **2a**, **3a** and **3b**.

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1. Introduction

Pyrazole-based compounds that enforce tripodal or hexapodal topologies were reported to be effective in the molecular recognition of ions^{1,2} and neutral molecules, such as carbohydrates.³ Tripodal compounds based on a triethylbenzene scaffold were described to be interesting receptors for cations,^{2a,b} whereas the hexapodal compound **1** (Fig. 1) was shown to be an effective receptor in the recognition of ion-pairs.⁴ The potential of pyrazole-based compounds in the complexation of ionic and neutral substrates was evaluated both in the solution and in the solid state.

In this paper we describe new crystalline complexes of hexapodal pyrazole-based compounds with NH_4^+ and/or solvent molecules, showing interesting binding motifs between the binding partners. The analyses of the binding motifs give valuable insights into the phenomena of molecular recognition processes. The interactions of compound **1** with $\text{NH}_4^+\text{PF}_6^-$ and solvent molecules provided four new multi-component crystals **1a**–**d** (see Fig. 1). In addition to compound **1**, the new bromo-substituted analogues **2** and **3** were prepared and used for the crystallographic studies. On

the base of these bromo derivatives three multi-component crystals with $\text{NH}_4^+\text{PF}_6^-$ and/or solvent molecules could be obtained and analysed in detail. Moreover, the solvent-free crystal structure of **2** is described in this work.

Multi-component crystals including solvent molecules are described as solvates, however, this definition is controversial discussed in the literature (for a discussion on the definitions ‘solvate’ and ‘co-crystal’, see Ref. 5). In the case of the complexes of **1** and **3** with $\text{NH}_4^+\text{PF}_6^-$ (crystals **1a**, **1b**, **1c** and **3a**) such solvents as ethanol (**1a**), methanol/water (**1b**), chloroform/acetonitrile (**1c**) and methanol (**3a**) are involved in the crystal structures. Crystals **1d**, **2a** and **3b** represent solvates of **1**, **2** and **3** with acetonitrile, dimethylformamide and toluene, respectively.

It should be noted that solvate formation is of high interest to different research areas. As mentioned by Griesser,⁶ ‘solvate formation opens perspectives for supramolecular chemistry and crystal engineering. Crystal structures of different solvates enable the study of molecular conformations, recurring patterns in hydrophobic aggregation and inclusion as well as molecular recognition phenomena in general’. Furthermore, the formation of solvates is of particular interest to the pharmaceutical industry.⁷

Analyses of the conformations of different hexasubstituted benzene derivatives,⁸ including analyses in solvate inclusion compounds, have been reported in the literature.⁹ Although the *ababab*

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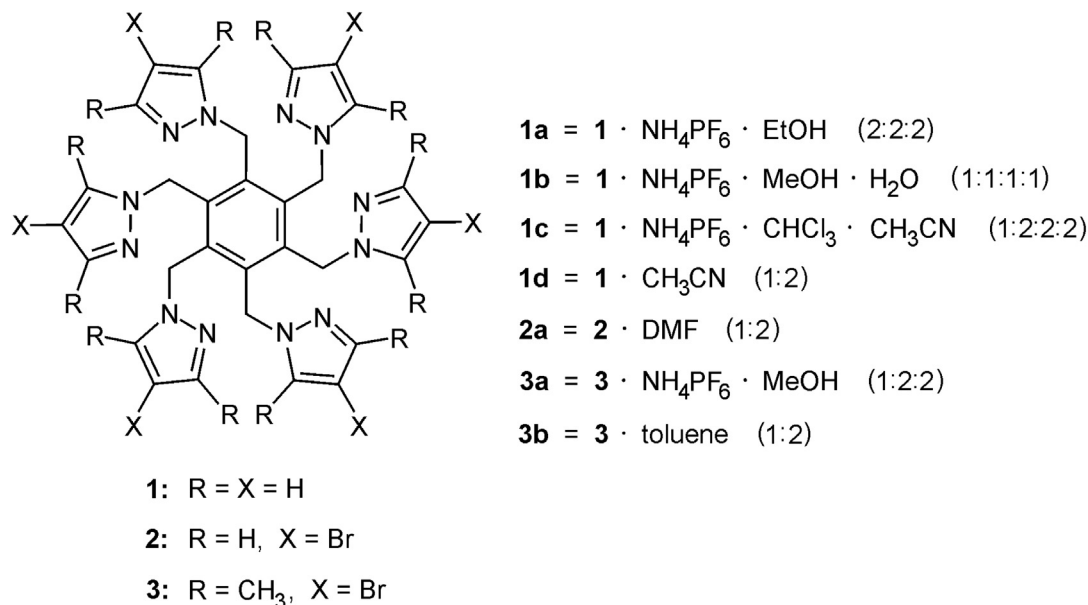


Fig. 1. Structures of compounds 1–3 and the composition of the multi-component molecular crystals 1a–d, 2a, 3a and 3b.

conformation (*a*=above, *b*=below) of the hexapodal molecules is most commonly observed in the crystal structures, unusual conformations such as *aaabbb* and *aaabab* are also described in the literature. Such conformations are, for example, assumed by hexakis(4-cyanophenoxy)benzene in its different solvates.^{9b,c} Substrate-dependent conformational changes (including also the formation of the *aaaaa* conformation) were observed for hexa-substituted benzenes with amide functionalities, designed to recognize anionic substrates.^{9e–h} In the case of the present studies, both the *ababab* as well as the *abbabb* and *aaabbb* conformations of the hexapodal hosts 1–3 are observed in the crystal structures 1a–d, 2, 2a, 3a and 3b.

2. Results and discussion

The crystal structures of four complexes of the hexapodal hosts (receptors) 1 and 3 with NH₄PF₆ and solvent molecules [1 · NH₄PF₆ · EtOH (1:1:1) (1a), 1 · NH₄PF₆ · MeOH · H₂O (1:1:1:1) (1b), 1 · NH₄PF₆ · CHCl₃ · CH₃CN (1:2:2:2) (1c), 3 · NH₄PF₆ · MeOH (1:2:2) (3a)] as well as of the solvate inclusion compounds 1d, 2a and 3b [1 · CH₃CN (1:2) (1d), 2 · DMF (1:2) (2a), 3 · toluene (1:2) (3b)] and the crystal structure of the solvent-free host 2 have been elucidated by X-ray diffraction experiments (basic crystallographic information for the structures is summarized in Table S1).

The conformation of the host molecules may be described best by calculation of dihedral angles, which define the inclination of the pyrazole rings with reference to the plane of the central benzene unit. These parameters together with relevant torsion angles are included in Table S2 while data of possible non-covalent interactions in the crystals are presented in Table S3. The conformations of the host molecules 1–3^{4a,10,11} in the crystal structures 1a–d, 2, 2a, 3a and 3b are given in Fig. 2. As shown in this Figure, the conformation with full up–down alternation of the side-arms (*ababab*) is observed in 1a, 1c, 1d and 3a. Other conformations, such as *abbabb* or *aaabbb*, are observed in 1b, 2a, 2 and 3b. Among the complexes with NH₄PF₆ (1a, 1b, 1c and 3a), only in the case of 1b [1 · NH₄PF₆ · MeOH · H₂O] the conformation of the host molecule differs from the *ababab* conformation. In the case of the solvates 1d, 2a and 3b as well as the solvent-free 2, only 1d [1 · CH₃CN (1:2)] includes host molecule with *ababab* conformation. It should be noted that the conformations differ also in the orientation of the N-

2 of the pyrazole rings; in some cases this nitrogen atom points outwards with respect to the benzene ring, as shown in Fig. 2.

2.1. Complexes 1a–c

The crystal structure of the complex 1 · NH₄PF₆ · EtOH (1:1:1) (1a) reveals the space group *P*-1 with the asymmetric cell unit containing two halves of crystallographically independent host molecules, one NH₄PF₆ and one molecule of solvent. The host molecules exist in a conformation with an alternating arrangement of the pyrazole groups above (*a*) and below (*b*) the plane of the benzene ring (see Figs. 2a and 3a). The pyrazole units are inclined at angles of 78.9(1)–88.7(1)° with respect to the plane of the central benzene ring. An interesting feature of this crystal structure is that only one of the host molecules participates in complexation of two NH₄⁺ ions each bonded in a nearly symmetric fashion by three N–H···N hydrogen bonds¹² (Fig. 3a, see also Table 1) to the nitrogens (N-2 position) of the pyrazole rings [*d*(H···N) 2.03(2)–2.12(2) Å, ∠N–H···N 162(2)–166(2)°].

The remaining hydrogen of NH₄⁺ is used to bind the oxygen of the alcohol molecule [N–H···O 2.00(2) Å, 153(2)°]; the OH hydrogen of the solvent is connected to the F(2) and F(3) of the PF₆⁻ ion [*d*(H···F) 1.99, 2.51 Å, ∠O–H···F 172, 123°]. An ORTEP diagram of the complex is depicted in Fig. 4a. The host molecule excluded from complexation adopts a less symmetric conformation (see Figs. 2a and 4a) as the pyrazole nitrogens of ring *C'* are oriented outward with respect to the benzene ring. As is evident from Table S3 and from the packing excerpt (Fig. S1), the crystal structure is stabilized by a close network of intermolecular interactions comprising C–H···F¹³ [*d*(H···F) 2.49–2.54 Å] and C–H···N [*d*(H···N) 2.49–2.62 Å] hydrogen bonds as well as face-to-face arene interactions¹⁴ between pyrazole rings [Cg(B)···Cg(B')] 4.209(3); Cg(D)···Cg(D') 3.763(3) Å].

The complex 1 · NH₄PF₆ · MeOH · H₂O (1:1:1:1) (1b) crystallizes in the space group *P*-1 (*Z*=2) with the asymmetric part of the unit cell containing one molecule of each crystal component. The pyrazole rings of the receptor molecule are arranged in an unusual *abbabb* pattern around the perimeter of the benzene ring (see Figs. 2b, 3d and 4b and Fig. S2). The four pyrazoles located on one side of the central arene ring create a cavity, which incorporates the NH₄⁺ ion (Fig. 3d). Two of these pyrazoles are connected to the cation via

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