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Solid State Structural Evidence of Chloroform−Benzene−Chloroform Adduct Trapped in Hexaanthryl Octaaminocryptand Channels

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Complexes of the prototype aromatic π-system proton acceptor, benzene with small molecules that have weak hydrogen-bonding capabilities, have been the subject of numerous experimental and theoretical studies.[1−4] Particularly, in the gas phase, C_6H_6−HCl has been studied by pulsed Fourier transform microwave spectroscopy[3] and by studies on C_6H_6−CHF_3,[4a] C_6H_6−H_2O,[4b] and C_6H_6−NH_3,[4c] where C−H···π, O−H···π, and N−H···π interactions have been characterized through rotational spectroscopy. Structural information of such complexes holds considerable promise for achieving a more accurate description of adducts at a molecular level. In 1991, Atwood et al. showed direct evidence for hydrogen bonding between water and the aromatic π-electrons in the solid state.[1a] To the best of our knowledge, crystallographic corroboration has remained elusive on benzene−ammonia, benzene−chloroform, or benzene−fluoroform in the literature.[5]

Experimental measurements in solution show that benzene forms a complex with chloroform.[6] High-level ab initio calculations of benzene−chloroform/fluoroform complexes have been carried out by Tsuzuki et al.[7] Herein, we report the single-crystal X-ray structural feature of the chloroform−benzene−chloroform adduct stabilized through various nonbonding interactions within the channel of a supramolecular assembly formed via van der Waals stacking of a highly symmetric hexaanthryl-substituted octaaminocryptand, **1** (Figure 1a). This study also shows that the chloroform as a guest has lower thermal stability inside the channel than that of adduct.

The homoditopic cryptand,[8] containing six secondary nitrogen atoms, has been functionalized with six anthryl moieties to have **1** (Figure 1a). The single crystal of complex **1**·C_6H_6·2$CHCl_3$ is grown from ethyl acetate/chloroform/benzene solvents from a light yellow solid of **1**. X-ray crystallography revealed that **1**·C_6H_6·2$CHCl_3$ crystallizes in a trigonal centrosymmetric space group $P\bar{3}1c$ (No. 163). Six molecules of **1** self-assembled together to form a symmetrical organic channel in the solid state, which acts as a host for the $CHCl_3$−C_6H_6−$CHCl_3$ adducts (Figure 1b). The bridgehead nitrogen atoms of these six hexa-anchored cryptand molecules form a ring-like architecture, where the nitrogen atoms (blue) are located at the rim of the circle while being viewed along the [001] plane. A continuous channel is formed along the crystallographic *c*-axis, and the solvent molecules (adduct) are firmly held in the channel via several nonbonding contacts with the host molecule. Interestingly, these channels are propagating through the edges of the unit cell along the *c*-axis in which adducts are trapped to form a porous architecture (Figure 1c). The channels are continuous with a radius of ~4.7 Å, and PLATON[9] calculation reveals a potential solvent-accessible void volume of 1034.2 Å^3. In the asymmetric unit, the bridgehead nitrogen atoms of the cryptand moiety and the carbon atom of the chloroform sit on a crystallographic 3-fold axis. The carbon atom attached to the bridgehead nitrogen is found to be disordered.[10] Two carbon atoms of the solvent benzene sit on a special position with an occupancy factor of 0.5.

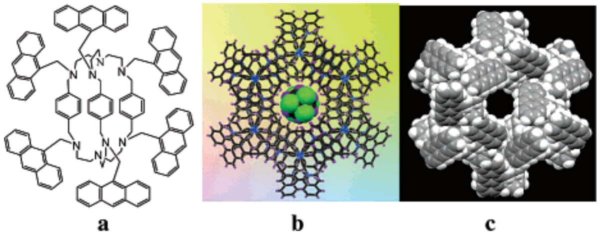

Figure 1. (a) Hexaanthryl octaaminocryptand structure **1**. (b) Self-assembly of six molecules of **1** forming a channel where the adduct (space-filling model) is stabilized. (c) Space-filling model of b without the adduct displaying the porous architecture.

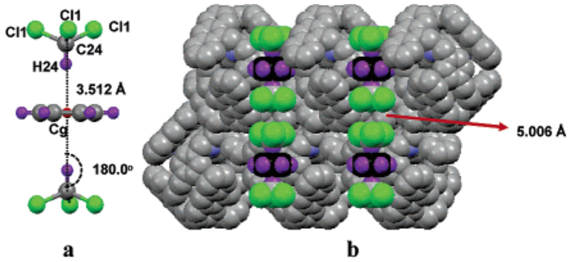

Figure 2. (a) Ball and stick model of the $CHCl_3$−C_6H_6−$CHCl_3$ adduct. (b) Space-filling model showing propagation of adducts; view along *a*-axis.

The solvent molecules form a molecular adduct, which is composed of benzene/chloroform (1:2) (Figure 2a). In this adduct, the hydrogen atom of chloroform is located at the centroid of the acceptor benzene ring (C24−H24···benzene$_{\mathrm{centroid}}$ (Cg); C24···Cg = 3.512 Å, ∠C24−H24···Cg = 180°) (Figure 2a).

Recently, Tsuzuki et al. performed theoretical calculations,[7] which suggest that the MP2/cc-pVTZ potential of C_6H_6−$CHCl_3$ has minima when the intermolecular separation (the distance between the center of benzene and the carbon atom of chloroform) is 3.2 Å, which is much shorter than that of the C_6H_6−CH_4 complex (3.8 Å), suggesting the larger attraction in the case of C_6H_6−$CHCl_3$. However, crystallographic separation between the center of benzene and the carbon atom of chloroform in the $CHCl_3$−C_6H_6−$CHCl_3$ adduct (3.512 Å) is in reasonable agreement with the above calculations. Inter-adducts distance is 5.006 Å, as shown in the Figure 2b, where adducts are propagated along the *c*-axis within the channel of the crystal lattice without any inter-adduct interactions.

In the 3-D network, the host molecules are propagated through several nonbonding interactions. For example, Figure 3a depicts that each anthryl moiety is involved in complementary CH···π contacts resulting in 12 such contacts. Each anthryl moiety simultaneously behaves as a proton donor as well as a π-system proton acceptor. Figure 3b shows that the hydrogen atom (red) in

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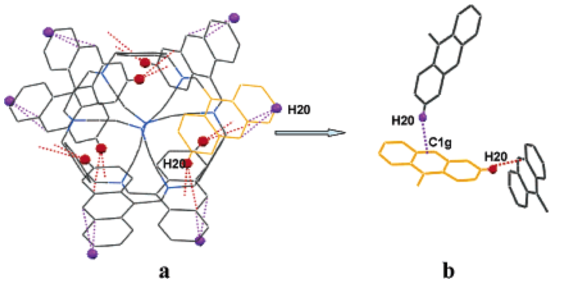

Figure 3. (a) Illustration of the 12 intermolecular CH/π short contacts in **1**; (b) highlighted anthryl moiety showing complementary CH/π interactions among the hydrogen atoms (purple and red) and the π cloud.

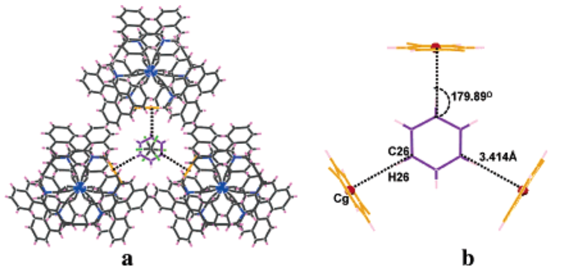

Figure 4. (a) Interactions of the adduct with the host **1**; (b) edge-to-face-type CH···π short contacts between hydrogen atoms (pink) of the adduct benzene and the benzene centroid (red) of three molecules of **1**.

the highlighted anthryl moiety is acting as a proton donor to the edge of the anthryl ring of the adjacent molecule, whereas the edge of the highlighted anthryl ring is acting as a proton acceptor for the hydrogen atom (violet) of the anthryl moiety from the other molecule. This CH/π contact (C20···C1g; centroid (C16 and C17) = 3.544 Å, ∠C20−H20−C1g = 156.51°) among anthryl rings presented here is within the normal range.[11]

The benzene/chloroform (1:2) adducts are stabilized inside the hexaanthryl cryptand channel via various nonbonded interactions with the wall of the channels. Figure 4 shows short contacts between the benzene of the adduct and the phenyl moiety of the cryptand unit. Three alternate hydrogen atoms of the benzene molecule of the adduct are in strong edge-to-face CH···π contacts with the centroid of the acceptor phenyl ring of three host molecules (C26−H26···Cg; C26···Cg = 3.414 Å, ∠C26−H26−Cg = 179.89°). The benzene molecule of the adduct is symmetrically hooked with three phenyl moieties of the host channel through CH···π contacts.

The single crystal of compound **1** grown from ethyl acetate/chloroform solvents revealed that **1**·3$CHCl_3$ also crystallizes in a trigonal centrosymmetric space group $P\bar{3}1c$ (No. 163). **1** also forms a channel similar to that in complex **1**·2$CHCl_3$·C_6H_6, which acts as a host for the chloroform guest. After repeated data collection at 100 K on different crystals, modeling the excess electron densities arising from the solvent were unsuccessful, presumably due to the stacking of chloroform molecules in a head-to-tail fashion. This polar orientation of chloroform molecules may violate the centrosymmetric nature of the channel. PLATON/SQUEEZE[12] is performed to refine the host framework, indicating the presence of a 370 e/unit cell. This may be attributed to six chloroform molecules per unit cell. Since the unit cell comprises two host molecules, the host:guest ratio is 1:3. This result is in good agreement with the thermal analysis data performed on the crystals.[10] It is important to note that, in the case of **1**·C_6H_6·2$CHCl_3$, the chloroform/benzene adduct is stabilized via nonbonded interactions between the benzene of the adduct and the phenyl moieties of the host.

Thermal analysis of **1**·C_6H_6·2$CHCl_3$ shows that total loss takes place in the temperature range of 105−235 °C and is 15.1677%, corresponding to the loss of 0.98 of the $CHCl_3$−C_6H_6−$CHCl_3$ adduct.[10] Removal of the adduct at elevated temperature confirms that the trapped complex within the channel of **1** has interaction with the host as observed in single-crystal X-ray studies. In the case of **1**·3$CHCl_3$, weight loss starts at a relatively lower temperature, 50 °C, and first loss is complete at 175 °C. Total loss in this temperature range is 17.3947%, corresponding to the loss of 3.06 $CHCl_3$ molecules.[10] Removal of the guest from **1**·3$CHCl_3$ at a relatively lower temperature than that of **1**·C_6H_6·2$CHCl_3$ may be due to an absence of C_6H_6−C_6H_6 nonbonding interactions in the **1**·3$CHCl_3$ complex.

In summary, we have shown unique single-crystal structural evidence of 1:2 benzene/chloroform adducts. This adduct formation through nonbonding interactions is trapped within the organic channel formed by supramolecular aggregation of an aromatically substituted aminocryptand through van der Waals stacking. Thermal analysis confirms that the chloroform−benzene−chloroform adduct as a guest has better thermal stability than that of the chloroform guest within the channel.

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Supporting Information Available: Synthesis, thermal analyses plot, X-ray data in CIF format for **1**·C_6H_6·2$CHCl_3$ and **1**·3$CHCl_3$. This material is available free of charge via Internet at http://pubs.acs.org.

References

(1) (a) Atwood, J. L.; Hamada, F.; Robinson, K. D.; Orr, G. W.; Vincent, R. L. *Nature* **1991**, *349*, 683. (b) Evans, D. R.; Fackler, N. L. P.; Xie, Z.; Rickard, C. E. F.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 8466. (c) Tsunoda, M.; Gabba, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 8335. (d) Zheng, J.; Kwak, K.; Asbury, J.; Chen, X.; Piletic, I. R.; Fayer, M. D. *Science* **2005**, *309*, 1338.
(2) (a) Brédas, J. L.; Street, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7001. (b) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 3746. (c) Bryantsey, V. S.; Hay, B. P. *J. Am. Chem. Soc.* **2005**, *127*, 8282.
(3) Read, W. G.; Cambell, E. J.; Henderson, G.; Flygare, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7670.
(4) (a) López, J. C.; Caminati, W.; Alonso, J. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 290. (b) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942. (c) Rodham, D. A.; Suzuki, S.; Suenram, R. D.; Lovas, F. D.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Nature* **1993**, *362*, 735.
(5) A CSD (version 5.27, November 2005) search was performed for the adduct of benzene with small molecules, such as water, ammonia, chloroform, and fluoroform. Search was performed by searching only benzene and the corresponding compounds and filtered using *R* factor <10%, no errors and not disordered. Search results show that in the case of benzene and water adduct there are 9 reports which show adduct formation out of 108 hits, whereas there are no reports on benzene and ammonia (8 hits), benzene and chloroform (9 hits), or benzene and fluoroform (0 hits) adduct formation.
(6) (a) Reeves, L. W.; Schneider, W. G. *Can J. Chem.* **1957**, *35*, 251. (b) Zurcher, R. F. *Helv. Chim. Acta* **1961**, *44*, 1380.
(7) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Phys. Chem. A* **2002**, *106*, 4423.
(8) Chen, D.; Martell, A. E. *Tetrahedron Lett.* **1991**, *47*, 6895.
(9) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.
(10) See Supporting Information.
(11) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction: Evidence, Nature and Consequences*; Wiley-VCH: New York, 1998.
(12) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

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