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Structural Characterization, Infrared Spectroscopy, and Theoretical Calculations for $B(C_6F_5)_3$-Stabilized Benzene–Ammonia and Benzene–Water Complexes**

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Nonconventional hydrogen bonds between X−H donors (X = C, N, O) and the π-electron cloud of an aromatic moiety are a well-documented phenomenon which is of great importance in structural biology.[1] As prototypical models for C−H⋅⋅⋅π, O−H⋅⋅⋅π, and N−H⋅⋅⋅π interactions, benzene–CHX_3 (X = halogen),[2] benzene–water,[3] and benzene–ammonia[4] complexes have been the subject of numerous theoretical and gas-phase experimental studies.[5] However, in these gas-phase experiments, the hydrogen positions were not directly determined. Experimental evidence for X−H⋅⋅⋅π interactions in the solid state is usually based on accurate X-ray crystallographic data, but surprisingly few structurally characterized solid-state structures with C/N/O−H⋅⋅⋅π interactions have been reported. Examples include a calixarene ligand–water complex featuring O−H⋅⋅⋅π interactions, reported in 1991,[6] (mercuracarborand–water)$_2$–benzene complex $\{(C_2B_{10}H_{10}\text{-}Hg)_3{\cdot}H_2O\}_2{\cdot}C_6H_6$, in which the H atoms could not be located accurately because of crystalline disorder,[7] and a hexaanthryl octamino cryptand stabilized chloroform–benzene complex.[8] Reed and co-workers showed that the hydronium ion H_3O^+ forms complexes to three benzene rings in the presence of weakly coordinating anions.[9] These were obtained by the reaction of H(carborane) acids with 1 equiv of water to give well-characterized $[H_3O]$[carborane] salts that are soluble in benzene, dichloromethane, and 1, 2-dichloroethane. The benzene salts have the formula $[H_3O{\cdot}3\,C_6H_6]^+$ [carborane]$^-$ (carborane = $CHB_{11}R_5X_6$; R = H, Me, Cl; X = Cl, Br, I) and the X-ray crystal structure of $[H_3O{\cdot}3\,C_6H_6][CHB_{11}Cl_{11}]{\cdot}C_6H_6$ was determined.[9a] At present, no benzene–ammonia complex has been structurally characterized in the solid state and, apart from the mercuracarborand complex mentioned above, no structurally characterized benzene–water complex has been reported in the solid state. We now report isolation, structures, IR spectra, and calculations for hydrogen-bonded benzene complexes of water or ammonia stabilized by the well-known Lewis acid $B(C_6F_5)_3$,[10] which enhances the Lewis acidic character of H_2O and NH_3. The new complexes $B(C_6F_5)_3{\cdot}H_2O{\cdot}C_6H_6$ (**1**) and $B(C_6F_5)_3{\cdot}NH_3{\cdot}C_6H_6$ (**2**) feature benzene–ammonia and benzene–water interactions with located hydrogen atoms, and therefore permit a straightforward comparison of the spectroscopic and structural consequences of benzene complexation.

Single crystals of benzene complexes **1** and **2** were obtained by recrystallization of $B(C_6F_5)_3{\cdot}H_2O$[11] and $B(C_6F_5)_3{\cdot}NH_3$[12] from benzene. The crystals are fragile and readily decompose under reduced pressure or on exposure in a dry box, which results in evaporative benzene loss. ^1H NMR experiments show that the chemical shifts of complexes in $CDCl_3$ are indistinguishable from those of $B(C_6F_5)_3{\cdot}H_2O$ or $B(C_6F_5)_3{\cdot}NH_3$ and free C_6H_6, which suggests that benzene in **1** and **2** is displaced by the polar solvent $CDCl_3$. Nonetheless, the benzene complexes proved sufficiently stable for IR spectroscopic studies. Figure 1 shows IR spectra for **2** and $B(C_6F_5)_3{\cdot}NH_3$ (for **1** and $B(C_6F_5)_3{\cdot}H_2O$, see Supporting Information) in the N−H stretching region. In comparison to those of $B(C_6F_5)_3{\cdot}H_2O$ and $B(C_6F_5)_3{\cdot}NH_3$,[12] the vibrational bands of the O−H and N−H bonds in **1** and **2** display considerable shifts to lower frequency of up to 87 cm^{-1} for **1**

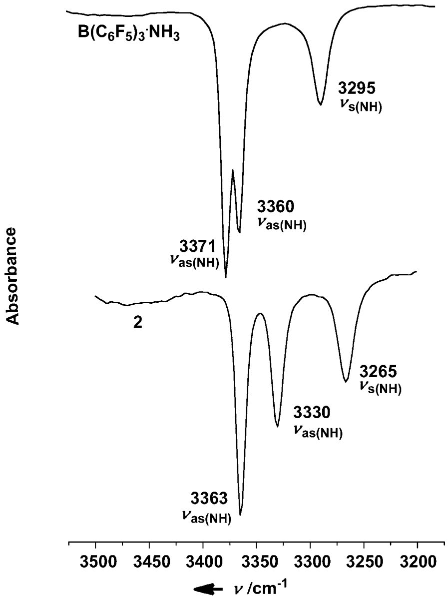

Figure 1. The N−H stretching region of the IR spectra of $B(C_6F_5)_3{\cdot}NH_3$ and **2**.

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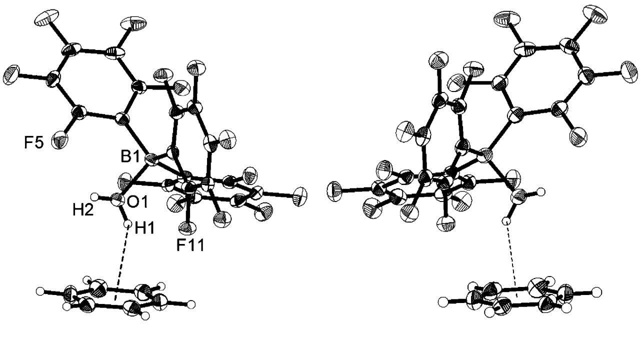
and 30 cm^{-1} for **2**, which indicate significant interactions between H_2O/NH_3 and C_6H_6.

X-ray crystal studies reveal that **1** crystallizes as a racemate of two chiral isomers **1**-*P* and **1**-*M* in space group $P\bar{1}$ (Figure 2) and **2** in space group $P2_1/c$ (Figure 3). In **1** and **2**, water O and ammonia N atoms remain bound directly to boron, and the hydrogen atoms of coordinated water or ammonia were located unambiguously from the difference maps. The $(C_6F_5)_3B{\cdot}H_2O$ and $(C_6F_5)_3B{\cdot}NH_3$ units interact with the benzene rings such that the oxygen and nitrogen atoms are located approximately over the centroids of the benzene rings. One hydrogen atom of water or ammonia is oriented toward the benzene ring. The O(N)···benzene centroid distances, H···benzene centroid separations, and the H-O(N)-H angles in **1** and **2** are listed in Table 1. It is noteworthy that the O···benzene centroid distance of **1** (3.231(3) Å) is longer than that of $\{(C_2B_{10}H_{10}Hg)_3{\cdot}H_2O\}_2{\cdot}C_6H_6$ (2.99(1) Å)[7] but is comparable to the range observed in $[H_3O][CHB_{11}Cl_{11}]{\cdot}3\,C_6H_6$ (3.05–3.16 Å).[9] We attribute the shorter distances in the mercuracarborand complex to the fact that the water molecule is confined within a cavity.[7] The interactions of H_3O^+ with C_6H_6 in the $[H_3O{\cdot}3\,C_6H_6]^+$ complex differ from those in **1** in that the H atoms do not point directly at the center of the C_6H_6 rings but to C−C bonds and afford H···ring plane distances of 2.13, 2.16, and 2.26 Å[9] (cf. H···centroid distances of 2.58 Å in **1**). The O(N)···benzene centroid distances in **1** and **2** are about 0.12 Å (0.31 Å) shorter than those determined spectroscopically for a benzene–water (benzene–ammonia) dimer in the vapor phase.[3,4] There are also $H_{water/ammonia}$···F contacts (H_{water}···F 2.18(6), 2.42(5) Å; $H_{ammonia}$···F 2.26(1) Å; Σ van der Waals radii of H and F = 2.67 Å) while $H_{C_6H_6}$···F contacts are very weak ($H_{C_6H_6}$···F ≥ 2.67 Å in **1** and ≥ 2.61 Å in **2**). The angle between the H-O-H plane and the C_6H_6 plane in **1** is about 59.3(1)° (Figure 4), whereas in the gas-phase water–benzene complex the two planes are perpendicular to each other.[3] The difference in water orientation in **1** from that in gas phase is probably caused by intramolecular O−H···F−C hydrogen-bonding interactions, as the geometry of $B(C_6F_5)_3{\cdot}H_2O$ with the lone pair of oxygen approaching fluorine atoms is highest in energy on the potential-energy surface (see Supporting Information).



1-*P* **1**-*M*

Figure 2. Thermal ellipsoid (50%, 90 K) plot of **1**. Selected bond lengths [Å] and angles [°]: O1−H1 0.78(5), O1−H2 0.83(7), O1−B1 1.630(3), H2−F5 2.18(6), H1−F11 2.42(5), O1···benzene centroid 3.231(3), H1···benzene centroid 2.58(5); H1-O1-H2 103(5).

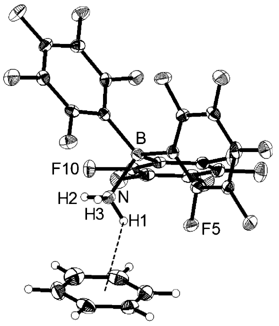


Figure 3. Thermal ellipsoid (50%, 90 K) plot of **2**. Selected bond lengths [Å] and angles [°]: N−H1 0.93(1), N−H2 0.88(1), N−H3 0.90(1), N−B 1.633(1), H2···F10 2.26(1), H1···F5 2.26(1), H1···benzene centroid 2.64(1), N···benzene centroid 3.281(1); H1-N-H2 105(1), H1-N-H3 107(1), H2-N-H3 107(1).

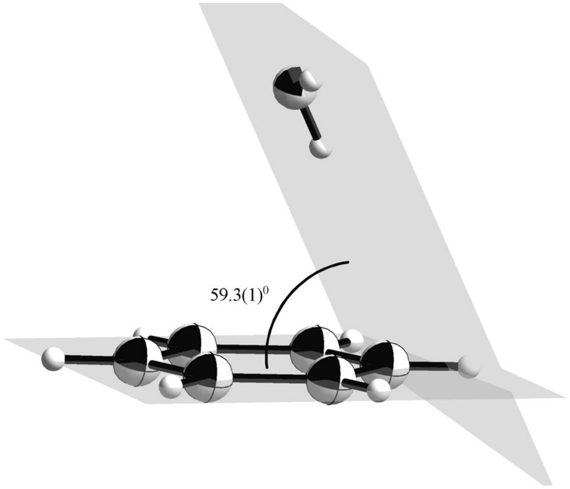


Figure 4. Angle between the H-O-H plane and the C_6H_6 plane in **1**.

To further study the strength of the hydrogen bonds in **1** and **2**, and how they are affected by Lewis acid $B(C_6F_5)_3$, we performed ab initio calculations for model complexes $BH_3{\cdot}H_2O{\cdot}C_6H_6$ (**3**), $H_2O{\cdot}C_6H_6$ (**4**), $BH_3{\cdot}NH_3{\cdot}C_6H_6$ (**5**), and $NH_3{\cdot}C_6H_6$ (**6**).[13] They were found to have energy minima at the HF/6-31G* level, and their geometries were further optimized at the MP2/aug-cc-pVTZ level (Table 1 and

Table 1: Comparison of selected experimental and calculated structural parameters for **1**, **2**, and related complexes.

	1	$H_2O{\cdot}C_6H_6$ spectroscopic[a]	$BH_3{\cdot}H_2O{\cdot}C_6H_6$ (**3**) calculated[b]	$H_2O{\cdot}C_6H_6$ (**4**) calculated[b]	**2**	$NH_3{\cdot}C_6H_6$ spectroscopic[c]	$BH_3{\cdot}NH_3{\cdot}C_6H_6$ (**5**) calculated[b]	$NH_3{\cdot}C_6H_6$ (**6**) calculated[b]
H···centroid [Å]	2.58 (5)	–	2.15	2.71, 2.71	2.64(1)	–	2.13	2.45
O(N)···centroid [Å]	3.231 (3)	3.347(5)	3.028	3.215	3.281(1)	3.590(5)	3.171	3.467
H-O(N)-H [°]	103(5)	–	105	102	106(1)	–	108	106

[a] Ref. [3]. [b] At the MP2/aug-cc-pVTZ level. [c] Ref. [4].

Figure 5). $\mathrm{BH_3{\cdot}H_2O{\cdot}C_6H_6}$ (**3**) has two chiral isomers **3**-*P* and **3**-*M* and a broadly similar structure to that of **1**, except that in **3** the H-O-H plane is perpendicular to that of the benzene ring. The experimentally determined O(N)···centroid distances in **1** and **2** are somewhat longer than those calculated for **3** and **5**, but they are shorter than those spectroscopically determined for $\mathrm{H_2O{\cdot}C_6H_6}$ and $\mathrm{H_3N{\cdot}C_6H_6}$, respectively (Table 1).[3,4] This can be rationalized on the basis that Lewis acids $\mathrm{BH_3}$ and $\mathrm{B(C_6F_5)_3}$ increase the acidities of the hydrogen atoms of water and ammonia in complexes **1**–**3** and **5**, and thus increase the O(N)−H···π hydrogen-bond affinities. Correspondingly the binding energy of $\mathrm{BH_3{\cdot}H_2O}$ ($\mathrm{BH_3{\cdot}NH_3}$) to $\mathrm{C_6H_6}$, corrected for basis set superposition error (BSSE), is about 22.1 $\mathrm{kJ\,mol^{-1}}$ (21.3 $\mathrm{kJ\,mol^{-1}}$) larger than that of $\mathrm{H_2O}$ ($\mathrm{NH_3}$) to $\mathrm{C_6H_6}$, calculated at the MP2/aug-cc-pVTZ level.[13]

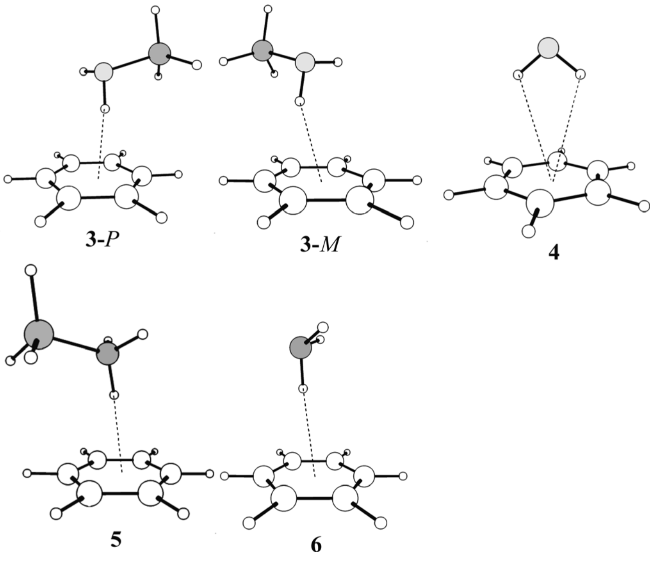


Figure 5. Calculated geometries of complexes **3**–**6**.

Gas-phase and theoretical studies on ammonia–benzene and ammonia–toluene complexes have shown that the electron-donating substituent $\mathrm{CH_3}$ increases the π-electron cloud density of the phenyl ring and thus strengthens the N−H···π hydrogen bonding.[4b] To test this prediction in the solid state, recrystallization of $\mathrm{B(C_6F_5)_3{\cdot}NH_3}$[12] from toluene was carried out, and this afforded single crystals of $\mathrm{B(C_6F_5)_3{\cdot}NH_3{\cdot}C_7H_8}$ (**7**). The structure of **7** (Figure 6) is similar to that of **2** but the N···centroid distance is about 0.075 Å shorter. This is in agreement with spectroscopic and theoretical predictions.[4b]

In summary, we have shown that water–benzene and ammonia–benzene complexes are stabilized by the Lewis acid $\mathrm{B(C_6F_5)_3}$ and provide rare examples of well-characterized water–benzene and ammonia–benzene complexes in the solid state. The $\mathrm{H_2O/NH_3–C_6H_6}$ interactions in these complexes lead to redshifts of the O−H/N−H stretching vibrations in comparison to those of benzene-free $\mathrm{H_2O}$– or $\mathrm{NH_3}$–borane complexes. In comparison to simple gas-phase water–benzene and ammonia–benzene complexes, the shortened O(N)···centroid distances are consistent with increased H acidities of water and ammonia on coordination to a Lewis acid. The electron-donating substituent $\mathrm{CH_3}$ strengthens the N−H···π hydrogen bonding, which is reflected by a shorter N···phenyl centroid distance in the complex $\mathrm{B(C_6F_5)_3{\cdot}NH_3{\cdot}C_7H_8}$ (**7**). In addition, two chiral isomers are observed as a racemate in **1** and supported by theoretical calculations. A discrete chiral isomer of $\mathrm{BH_3{\cdot}H_2O{\cdot}C_6H_6}$ (**3**) in the gas phase is also possible and might be detected by rotational spectroscopy.[14] Studies on complexes analogous to **1** and **2** involving other aryl rings are under way.

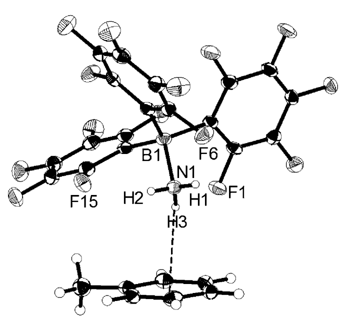


Figure 6. Thermal ellipsoid (50%, 90 K) plot of **7**. Selected bond lengths [Å] and angles [°]: N1−H1 0.83(6), N1−H2 0.76(7), N1−H3 0.90(7), N1−B1 1.633(6), H2···F15 2.22(6), H1···F6 2.19(5), H3···benzene centroid 2.48(6), N1···benzene centroid 3.206(5); H1-N1-H2 111 (6), H1-N1-H3 113(5), H2-N1-H3 109(6).

Experimental Section

Compound **1**: $\mathrm{B(C_6F_5)_3{\cdot}H_2O}$ (0.305 g, 0.576 mmol) was dissolved in benzene (ca. 2 mL). Overnight storage of the solution at about 5 °C afforded colorless X-ray-quality crystals of **1**. IR (KBr, Nujol, $\mathrm{cm^{-1}}$): 3537 (br, ν_{as}(OH)), 3412 (br, ν_s(OH)).

Compound **2**: $\mathrm{B(C_6F_5)_3{\cdot}NH_3}$ (0.331 g, 0.626 mmol) was dissolved in benzene (ca. 2 mL). Overnight storage of the solution at about 5 °C afforded colorless X-ray-quality crystals of **2**. IR (KBr, Nujol): $\tilde{\nu} =$ 3363 (ν_{as}(NH)), 3330 (ν_{as}(NH)), 3265 $\mathrm{cm^{-1}}$ (ν_{as}(NH)).

Compound **7**: $\mathrm{B(C_6F_5)_3{\cdot}NH_3}$ (0.284 g, 0.537 mmol) was dissolved in toluene (ca. 1 mL). Overnight storage of the solution at about −18 °C afforded colorless X-ray-quality crystals of **7**.

Crystal data for **1**, **2**, and **7** at 90(2) K with $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å). **1**: $\mathrm{C_{24}H_8BF_{15}O}$, $M = 608.11$, triclinic, space group $P\bar{1}$, $Z = 4$, $\mu = 0.197\ \mathrm{mm^{-1}}$, $a = 10.630(1)$, $b = 13.656(1)$, $c = 15.388(1)$ Å, $\alpha = 87.260(1)$, $\beta = 86.322(1)$, $\gamma = 86.413(2)$°, $V = 2222.6(4)$ Å^3, $R1 = 0.0468$ for 8725 ($I > 2\sigma(I)$) reflections, $wR2 = 0.1421$ (all data). **2**: $\mathrm{C_{24}H_9BF_{15}N}$, $M = 607.13$, monoclinic, space group $P2_1/c$, $Z = 8$, $\mu = 0.194\ \mathrm{mm^{-1}}$, $a = 13.6490(7)$, $b = 18.910(9)$, $c = 17.9196(9)$ Å, $\beta = 90.474(1)$, $V = 4449.1(4)$ Å^3, $R1 = 0.0266$ for 6998 ($I > 2\sigma(I)$) reflections, $wR2 = 0.0727$ (all data). **7**: $\mathrm{C_{25}H_{11}BF_{15}N}$, $M = 621.16$, triclinic, space group $P\bar{1}$, $Z = 4$, $\mu = 0.189\ \mathrm{mm^{-1}}$, $a = 10.536(2)$, $b = 13.795(3)$, $c = 15.992(3)$ Å, $\alpha = 86.281(3)$, $\beta = 89.170(2)$, $\gamma = 87.176(2)$°, $V = 2316.5(8)$ Å^3, $R1 = 0.0715$ for 6635 ($I > 2\sigma(I)$) reflections, $wR2 = 0.2319$ (all data). For **1**, **2**, and **7**, all H atoms were found in difference maps, and those attached to oxygen or nitrogen were refined freely. The other H atoms were refined by using a riding model. CCDC 810110 (**1**), 810111 (**2**) and 810112 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244–1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250; b) O. Takahashi, Y. Kohno, M. Nishio, *Chem. Rev.* **2010**, *110*, 6049–6076.

[2] a) J. C. López, W. Caminati, J. L. Alonso, *Angew. Chem.* **2006**, *118*, 296–299; *Angew. Chem. Int. Ed.* **2006**, *45*, 290–293; b) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Phys. Chem. A* **2002**, *106*, 4423–4428.

[3] a) S. Suzuki, P. G. Green, R. E. Bumgarner, S. Dasgupta, W. A. Goddard III, G. A. Blake, *Science* **1992**, *257*, 942–945; b) R. N. Pribble, T. S. Zwier, *Science* **1994**, *265*, 75–79.

[4] a) D. A. Rodham, S. Suzuki, R. D. Suenram, F. J. Lovas, S. Dasgupta, W. A. Goddard III, G. A. Blake, *Nature* **1993**, *362*, 735–737; b) S. Vaupel, B. Brutschy, P. Tarakeshwar, K. S. Kim, *J. Am. Chem. Soc.* **2006**, *128*, 5416–5426.

[5] For more references, see: a) B. Brutschy, *Chem. Rev.* **2000**, *100*, 3891–3920; b) K. S. Kim, P. Tarakeshwar, J. Y. Lee, *Chem. Rev.* **2000**, *100*, 4145–4155; c) T. S. Zwier, *Annu. Rev. Phys. Chem.* **1996**, *47*, 205–241; d) R. J. Saykally, G. A. Blake, *Science* **1993**, *259*, 1570–1575.

[6] J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr, R. L. Vincent, *Nature* **1991**, *349*, 683–684.

[7] H. Lee, C. B. Knobler, M. F. Hawthorne, *Angew. Chem.* **2001**, *113*, 3148–3150; *Angew. Chem. Int. Ed.* **2001**, *40*, 3058–3060.

[8] P. S. Lakshminarayanan, D. K. Kumar, P. Ghosh, *J. Am. Chem. Soc.* **2006**, *128*, 9600–9601.

[9] a) E. S. Stoyanov, S. P. Hoffmann, K. Kim, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2005**, *127*, 7664–7665; b) E. S. Stoyanov, K. Kim, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 1948–1958.

[10] W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345–354.

[11] C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2000**, *122*, 10581–10590.

[12] A. J. Mountford, S. J. Lancaster, S. J. Coles, P. N. Horton, D. L. Hughes, M. B. Hursthouse, M. E. Light, *Inorg. Chem.* **2005**, *44*, 5921–5933.

[13] Theoretical calculations were performed with the Gaussian03 package. Energy corrections were determined by using HF/6-31G* harmonic vibrational frequencies. BSSE corrections were carried out by the counterpoise method at the MP2/aug-cc-pVTZ level. For citation see Supporting Information.

[14] For chiral hydrogen-bonded compounds and their applications, see: M. S. Taylor, E. N. Jacobsen, *Angew. Chem.* **2006**, *118*, 1550–1573; *Angew. Chem. Int. Ed.* **2006**, *45*, 1520–1543.