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Lithium-Mediated Organofluorine Hydrogen Bonding: Structure of Lithium Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate Tetrahydrate

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Recent interest in fluorine-stabilized tetraarylborates has increased due to their proven role as relatively unreactive and weakly coordinating anions.[1] In particular, the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) anion has found utility as counteranion to electrophilic cationic transition metal complexes[1,2a,b] due to its lipophilic character and stability in oxidizing and acidic media.[1c,3] While the identity of the countercation may be varied via solvent partition,[2b,3a,4] LiTFPB·4H_2O was prepared by the method previously reported for NaTFPB·3H_2O.[5]

Clear pale amber crystals, used in the single-crystal X-ray analysis, were recovered by overnight recrystallization of off-white LiTFPB·4H_2O powder[6a] from 3:1 benzotrifluoride−hexanes at −20 °C. Larger crystals, up to 2 mm × 1 mm × 1 mm in size, were isolated by slow evaporation of a benzotrifluoride solution at 23 °C. The monohydrate[6b] was recovered after heating to 100 °C for 24 h at 10^{-4} Torr, while longer treatment (48 h) results in some decomposition.

LiTFPB·4H_2O is soluble in common polar organic solvents,[7] while the monohydrate salt is sparingly soluble in benzotrifluoride and insoluble in methylene chloride. Dehydration of acetonitrile solutions of LiTFPB·H_2O by treatment with activated 3 Å molecular sieves (alumina−silicate, K^+) were unsuccessful, in that ion exchange of K^+ for Li^+ occurred over a 7 day period. Anhydrous K(TFPB) was recovered after heating in vacuo.[6c] The anhydrous sodium salt was similarly prepared by treatment of a NaTFPB·3H_2O acetonitrile solution with activated 4 Å sieves (alumina−silicate, Na^+) for 7 days.[6d]

A single-crystal X-ray study of LiTFPB·4H_2O was carried out to investigate the nature of the interaction(s) of the four water molecules with Li^+ and their polar opposite, the large lipophilic TFPB anion.[1d,8a] As shown in Figure 1, the structure of LiTFPB·4H_2O consists of tetrahedral TFPB anions that surround water molecules coordinated tetrahedrally to lithium cations (Li−O1 = 1.908(4) Å, O1−H = 0.83 Å[8b]). One of the two unique CF_3 groups per phenyl group is in close proximity to one hydrogen atom per water molecule (F′···H = 2.54 Å, F···H = 2.59 Å, F4′−O1 = 2.91 Å). These F···H distances approach the sum of the van der Waals radii of H and F of 2.3−2.5 Å[9a] and lie below the 2.720 Å F···H average for C−F···H−X (X = O, N, C) interactions observed in aromatic ring compounds with CF_3, O, and/or N acceptor groups.[9d] Meaningful F···H distances in C−F···H interactions are generally thought to lie below 3.0 Å, but can be as short as 2.2 Å.[9]

Only the CF_3 groups involved in the hydrogen-bonding interaction are statically disordered.[8c] Two positions, with occupancy factors of $^2/_3$ for CF_3 (unprimed) and $^1/_3$ for CF_3' (primed) are related by a 60° rotation along the aryl−CF_3 bond. The exact nature of the disorder observed in the interacting CF_3 groups remains undetermined. The opposite scenario might be expected, one in which the hydrogen-bonding interaction stabilizes the rapidly spinning CF_3 groups. However, vibrational and/or rotational modes of the coordinated water molecules could contribute to the observed disorder phenomenon.

Figure 2 shows the hydrogen-bonding net formed by the packing of TFPB anions about the hydrated lithium cation.[11] The net features four three-centered hydrogen bonds, formed by the interaction of four CF_3'/CF_3 pairs with four water hydrogen atoms. Each pair of identical three-centered interac-

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(1) For recent accounts on large and weakly coordinating anions see: (a) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025. (b) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1181. (c) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (d) The crystal structure of the TFPB anion is presented in ref 1c.

(2) (a) Gamble, A. S.; Boncella, J. M. *Organometallics* **1993**, *12*, 2814. (b) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151.

(3) (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Koybayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Iwamoto, H. *Tetrahedron Lett.* **1983**, *24*, 4703. (c) Fujuki, F.; Kashiwagi, M.; Miyamoto, H.; Sonoda, A.; Ichikawa, J.; Koybayashi, H.; Takaaki, S. *J. Fluorine Chem.* **1992**, *57*, 307.

(4) AgTFPB·$x$$Et_2O$ ($1 \geq x > 0$) is prepared by shaking an ethereal solution of the Li^+ or Na^+ salt with 1 M $AgNO_3$(aq) in a separatory funnel with exclusion of light. The salt is isolated by solvent removal in vacuo. Extended periods in vacuo lead to decomposition. Preliminary results have shown that AgTFPB·$x$$Et_2O$ can be used to abstract halogens from a variety of substrates.

(5) Gol'dberg, Y. S.; Abele, A. M.; Liepinsh, A. A.; Shimanskaya, M. V. *Zh. Org. Khim.* **1989**, *25*, 1099. $LiBF_4$ was used in place of $NaBF_4$.

(6) (a) LiTFPB·4H_2O: Anal. Calcd for $C_{32}H_{20}BF_{24}LiO_4$: C, 40.79; H, 2.14. Found: C, 40.61; H, 1.94. IR (KBr, Nujol): 3706, 3638, 2923, 1358, 1283, 1145, 888, 711 cm^{-1}. ^1H NMR (200 MHz, acetone-d_6): δ 7.78 (s, 8 H, H_o), 7.67 (s, 4 H, H_p), 3.19−3.16 (d, 8.6 H, H_2O). ^{19}F NMR (200 MHz, acetone-d_6, external reference $CFCl_3$): δ −58.37 (s, 24 F, −CF_3). ^7Li solid state NMR (116.6 MHz, external reference 1.0 M LiCl(aq)): δ 0.0 (s, 1 Li^+). (b) LiTFPB·H_2O: ^1H NMR (200 MHz, acetone-d_6): δ 7.78 (s, 8 H, H_o), 7.66 (s, 4 H, H_p), 3.95 (s, 2 H, H_2O). (c) K(TFPB): ^1H NMR (200 MHz, acetone-d_6): δ 7.78 (s, 8 H, H_o), 7.66 (s, 4 H, H_p). No ^7Li NMR signal was detected for K(TFPB) isolated from sieve ion exchange. (d) ^1H NMR data for NaTFPB are identical to those for K(TFPB).

(7) Solubility tests were conducted with dry and freshly distilled solvents in an argon-filled inert box or via Schlenk techniques with an inert-vacuum line. LiTFPB·4H_2O is soluble in acetone, acetonitrile, benzotrifluoride, 1,3-bis(trifluoromethyl)benzene, diethyl ether, ethanol, tetrahydrofuran, and methylene chloride.

(8) (a) Crystal data for $C_{23}H_{20}BF_{24}LiO_4$: tetragonal, space group $I4_1/a$, a = 16.004(2) Å, c = 14.988(3) Å, α = 90°, V = 3838 Å^3, Z = 4, d_c = 1.63 g/cm^3. X-ray diffraction intensity data were collected at −100 °C using Mo Kα (0.710 73 Å) radiation from a crystal with the approximate dimensions of 0.4 × 0.4 × 0.5 mm. The structure was solved by a combination of direct methods (SHELX-86) and Fourier techniques and refined (SHELX-93) using the full-matrix least-squares routine with anisotropic displacement parameters for non-hydrogen atoms and riding motion constraints for hydrogen atoms. The hydrogen atoms were located from the difference Fourier map. Final refinement gave residuals of $R(F) = 0.0556$ and $R_w(F^2) = 0.1326$ for all 1543 reflections. The weighted R index based on $F_o{}^2$ is typically twice the conventional R index based on F_o using SHELX-93. $R(F) = \Sigma(|\Delta F|)/\Sigma|F_o|$; $R_w(F^2) = [\Sigma w(|\Delta F|)^2)/\Sigma w(|F_o|)^2]^{1/2}$. (b) In this study, O−H bond lengths were not normalized to the "standard" neutron diffraction value of 0.97 Å, as outlined in ref 10c, pp 107−110. (c) The structural model obtained from data collected at 23 °C differed insignificantly from the final structural model obtained from data collected at −100 °C. (d) The diameter of the TFPB anion was estimated by inscription of the tetrahedral anion in a cube and calculation of the van der Waals radius of the entire molecule.

(9) For accounts on organofluorine hydrogen bonding, see: (a) Murray-Rust, P.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 3206. (b) Karipides, A.; Miller, C. *J. Am. Chem. Soc.* **1984**, *106*, 1494 and references therein. (c) Karipides, A.; White, C. *Acta Crystallogr.* **1993**, *C49*, 1920. (d) For a recent Cambridge Structural Database survey of C−F···H−X interactions see: Shimoni, L.; Glusker, J. P. *Struct. Chem.*, in press.

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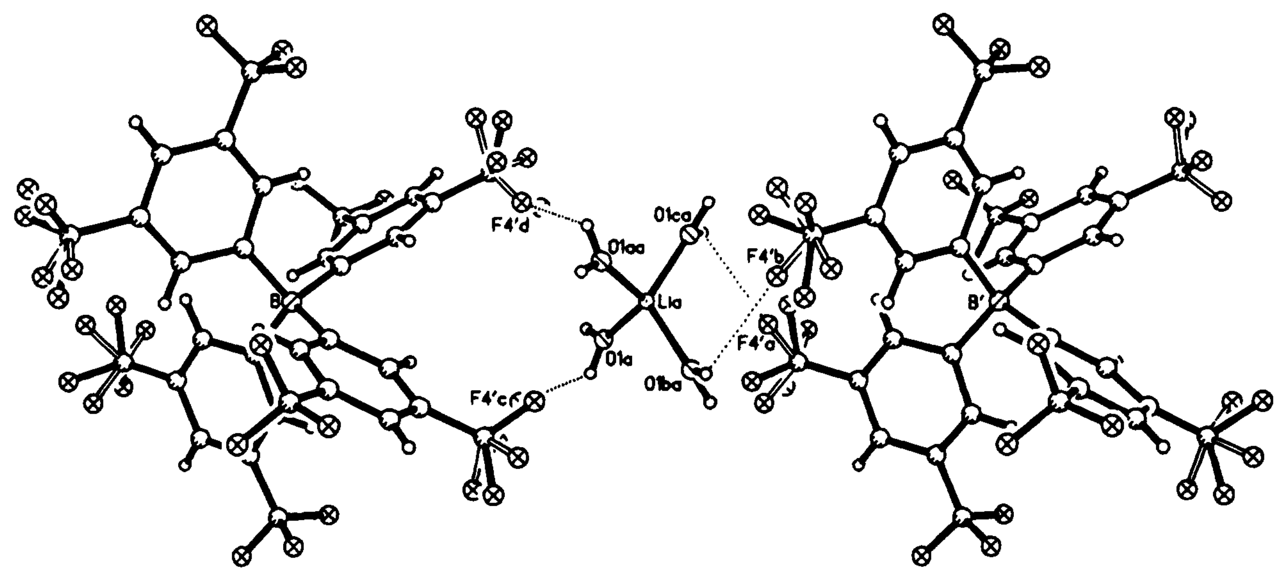

Figure 1. View perpendicular to the four-bar axis of rotation showing interaction (dotted lines) of $^{1}/_{3}$ occupancy CF_3' groups with hydrogen atoms of water molecules tetrahedrally coordinated to Li^+. TFPB anions, with interacting $^{2}/_{3}$ occupancy CF_3 groups above and below the page, have been omitted for clarity.

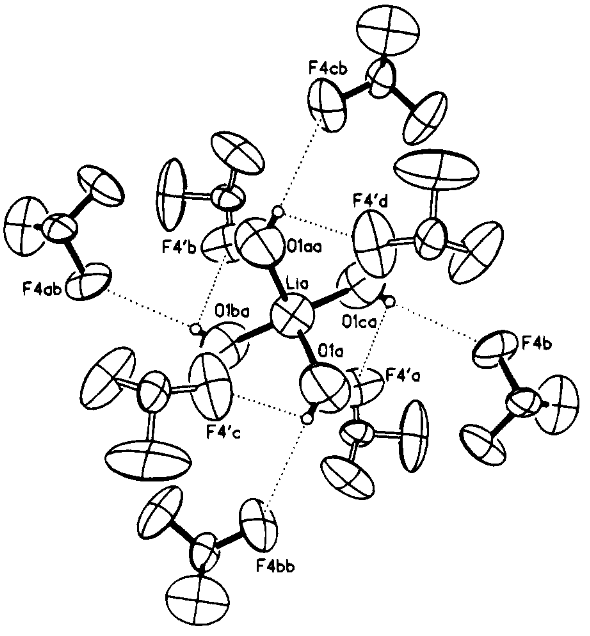

Figure 2. Perspective along the four-bar axis of rotation, with TFPB anions omitted for clarity, showing four symmetry related three-centered hydrogen bonding interactions formed by four CF_3'/CF_3 pairs with water hydrogen atoms.

tions, related by a $\bar{4}$ axis, are approximately planar; i.e., the sum of the angles equals 350°. This arrangement is consistent with the criteria established for three-centered hydrogen bonding,[10] in which the sum of the angles in the three-center interaction is approximately 360° and where the hydrogen atom resides in or close to the plane as defined by the oxygen and the two fluorine atoms.

The crystal structure of $LiTFPB{\cdot}4H_2O$ provides insight into the contributions made by steric and repulsive forces to crystalline network energetics.[12a,c] For example, the Li^+ ionic radius is 0.60 Å,[11] while the TFPB anion radius of 6.5 Å is ca. 10 times larger.[8d] If Li^+ was tetracoordinated by water molecules,[11] its radius would increase to ca. 3.40 Å,[12b] a factor of less than 2 with respect to the TFPB anion. The smaller size differential should reduce adjacent anionic steric demands, resulting in more favorable crystal packing. The effect of the countercation with or without waters of hydration on the solubility of the alkali metal salts of the TFPB anion in organic solvents remains open to question. On the basis of the high solvation energy of Li^+,[11] one might expect the anhydrous and/or monohydrate salts to be more soluble in polar and semipolar organic solvents. Since both salts remain insoluble in both CH_2Cl_2 and benzotrifluoride, it is possible that the lithium cation may be bound to a CF_3 group in a hard–hard Lewis acid–base interaction.[13] This interaction could decrease the ability of a less polar solvent (CH_2Cl_2, benzotrifluoride) to enter the lithium solvation sphere and thus dissolve an interacting $Li^+{\cdots}F_3C$ contact pair.[9b,14c]

In conclusion, while interactions of the type $C{-}F{\cdots}H{-}X$ ($X = O$, N) have become more common in the recent literature reports, metal cation mediated interactions of the form $C{-}F{\cdots}H{-}O(H){-}M^{n+}$ ($n = 1, 2$) continue to be relatively rare.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths, bond angles, hydrogen atom coordinates, and isotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

Registry Number (supplied by authors): TFPB anion, 79230-20-9.

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