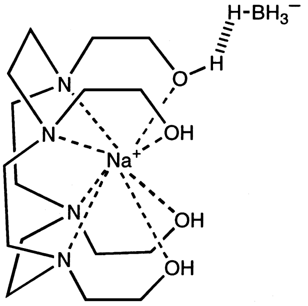
[5] J. D. Carr, L. Lambert, D. E. Hibbs, M. B. Hursthouse, K. M. A. Malik, J. H. R. Tucker, *Chem. Commun.* **1997**, 1649.
[6] F. Garcia-Tellado, S. Goswami, S. K. Chang, S. J. Geib, A. D. Hamilton, *J. Am. Chem. Soc.* **1990**, *112*, 7393; S. P. Lustenberger, E. Martinborough, T. M. Denti, F. Diederich, *J. Chem. Soc. Perkin Trans. 2* **1998**, 747; S. Goswami, K. Ghosh, S. Dasgupta, *J. Org. Chem.* **2000**, *65*, 1907.
[7] M. S. Goodman, A. D. Hamilton, J. Weiss, *J. Am. Chem. Soc.* **1995**, *117*, 8447; I. Prévot-Halter, T. J. Smith, J. Weiss, *J. Org. Chem.* **1997**, *62*, 2186.
[8] M. J. Hynes, *J. Chem. Soc. Dalton Trans.* **1993**, 311.
[9] After the addition of one equivalent of GA, $[\mathbf{2}\text{:GA}]/[\mathbf{2}] = (70 \pm 2)/(30 \pm 2)$ and $[\mathbf{1}]/[\mathbf{1}\text{:GA}] = (89 \pm 2)/(11 \pm 2)$, $K = [\mathbf{2}\text{:GA}][\mathbf{1}]/[\mathbf{2}][\mathbf{1}\text{:GA}] = 19 \pm 5$.
[10] A ^{1}H NMR study revealed that the amide and Cp protons of **1** (1 mM in $CDCl_3$/[D$_6$]DMSO (0.5 %)) underwent very small downfield shifts upon the addition of excess **3** (e.g. H_a, +0.08 ppm) with 50 % complexation only achieved after the addition of six molar equivalents of diacid.
[11] For previous cyclic voltammetry studies with **1** and for experimental conditions, see reference [5].

Toward Crystalline Covalent Solids: Crystal-to-Crystal Dihydrogen to Covalent Bonding Transformation in $NaBH_4 \cdot$ THEC[**]

Radu Custelcean,* Mircea Vlassa, and
James E. Jackson*

The hydridic-to-protonic interaction, or dihydrogen bonding, between negatively charged hydrogen atoms of M–H (M = Al, B, Ga, Ir, Mo, Mn, Os, Re, Ru, W) bonds and conventional proton donors has been extensively studied since 1994.[1] With characteristics similar to those found in classical hydrogen bonding, this unconventional interaction can influence reactivity and stereoselectivity in solution.[2] In the solid state, dihydrogen bonds have the ability to direct crystal packing, thus finding utility in supramolecular synthesis.[3] Along this line, we have employed $O{-}H\cdots H{-}B$ hydrogen bonds in the construction of novel one-, two-, and three-dimensional extended structures with various topologies.[4] More interestingly, some of these systems can react topochemically in the solid state, releasing H_2 and exchanging the weak $O{-}H\cdots H{-}B$ interactions for strong B–O covalent bonds, to form ordered, extended covalent materials.[4] However, due to the cumulative shrinkage of the B–O distances during decomposition, these topochemically assembled solids have shown poor crystallinity. In 1998 we suggested two strategies to circumvent this problem: a) design of cations to form closed loops in coordination with hydride-bearing anions, in which case the lattice distortion accompanying decomposition would not be cumulative, and b) selection of globular cations large enough that their close packing determines the lattice parameters, with the hydridic anions fitting into the interstitial holes, in which bond formation via flexible arms would induce minimal change in the unit cell.[4a] We now describe a dihydrogen-bonded system that satisfies both of these geometrical criteria, leading as a result to a crystalline covalent product, in a crystal-to-crystal thermal decomposition.

N,N′,N″,N‴-tetrakis-(2-hydroxyethyl)cyclen (THEC) and $NaBH_4$ form a 1:1 complex (**1**), which precipitates as a white crystalline solid from 2-propanol.[5]



1

Single crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution of **1** in acetonitrile. The crystal structure is depicted in Figure 1.[6] The THEC adopts a conformation with all hydroxyethyl arms oriented toward the same face of the azacrown ring, as observed in previously reported metal complexes containing this ligand.[7] The nitrogen and oxygen atoms are thus organized in a pseudo-cubic geometry, encapsulating the octacoordinated Na cation. The Na^+THEC units have thus the appropriate geometry for the formation of the desired closed-looped dihydrogen-bonded assembly. Indeed, these cations self-assemble into D_2-symmetrical dimers, held together by four conventional $O(2){-}H\cdots O(1)$ hydrogen bonds, complemented by four orthogonal $O(1){-}H\cdots H{-}B$ proton-hydride interactions involving the borohydride anions (Figure 1 a). There is no hydrogen bonding interconnecting the dimers, which are packed into two-dimensional layers (Figure 1 b). The layers are stacked in a parallel fashion, thus creating one-dimensional channels along the *a* axis, in which the BH_4^- ions reside.

The association in closed loops, as well as the packing mode of the large globular $[Na_2(THEC)_2]^{2+}$ ions, appear to fulfill the two geometrical requirements that we predicted should favor the transfer of crystallinity from dihydrogen- to covalent-bonded networks.[4a] Solid-state decomposition of **1**, induced by heating under an inert atmosphere at 160 °C for 20 h, results in complete elimination of H_2, as indicated by the FT-

---

[*] R. Custelcean, Prof. J. E. Jackson
Department of Chemistry
Michigan State University
East Lansing, MI 48824 (USA)
Fax: (+1) 517-353-1793
E-mail: custelce@cem.msu.edu
jackson@cem.msu.edu

Prof. M. Vlassa
Department of Chemistry
Babes-Bolyai University
11 Arany Janos Str., 3400 Cluj-Napoca (Romania)

[**] The support of the MSU Center for Fundamental Materials Research is gratefully acknowledged. THEC = *N,N′,N″,N‴*-tetrakis-(2-hydroxyethyl)cyclen.

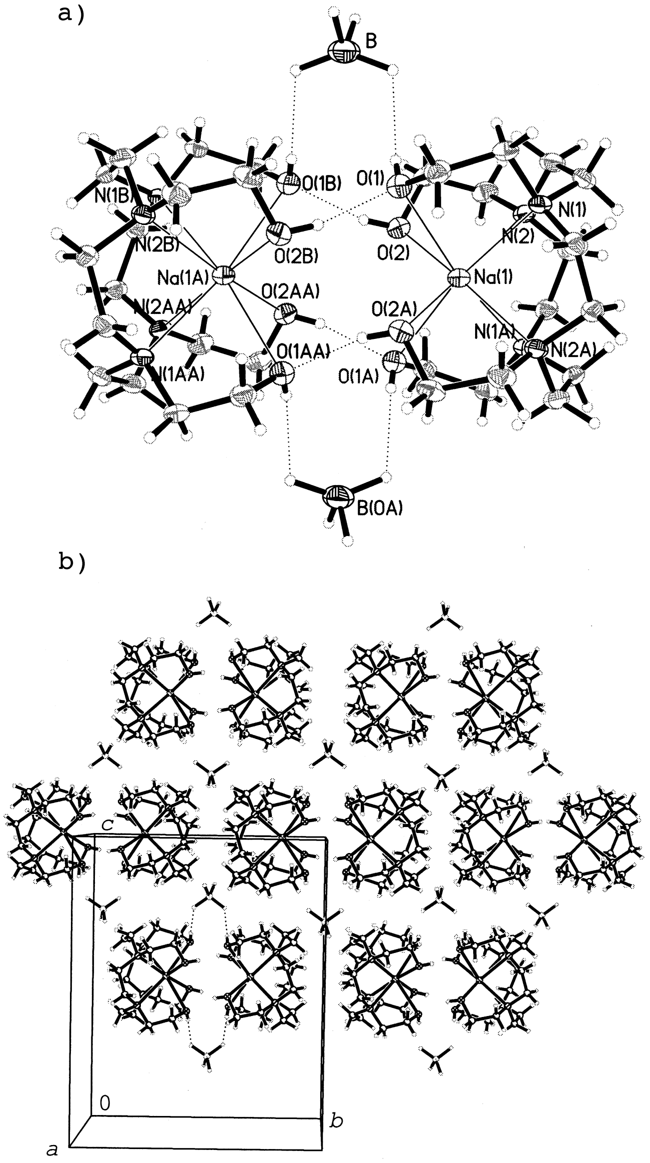


Figure 1. X-ray crystal structure of the dihydrogen-bonded complex **1**: a) self-assembled dimers; selected bond lengths [Å] and angles [°]: O(1)-H 0.72(3), B-H 1.17(2), O(1)H···HB 2.00(5), O(1)···B 3.352(3), O(2)-H 0.88(4), O(2)H···O(1) 1.94(5), O(2)···O(1) 2.801(6), N(1)-Na 2.706(2), N(2)-Na 2.634(2), O(1)-Na 2.690(2), O(2)-Na 2.474(2); O(1)-H-H 151(2), B-H-H 115(3), O(2)-H-O(1) 164(3); b) packing of dimers in layers.

IR and ^{11}B solid-state MAS NMR spectra of the resulting material.[8] Thermogravimetric analysis shows a remarkably sharp 1.88% weight loss between 168.0 and 168.8 °C, which corresponds to 3.63 mol H_2. The solid-state decomposition product (**2**) exhibits high crystallinity, as indicated by microscopic examination, which showed good transparency to polarized light for the decomposed crystals (Figure 2). The reaction appears to be crystallographically homogeneous, in direct contrast to our previously reported dihydrogen-bonded systems, where the covalent product nucleated as a separate phase.[4c] That the solid-state decomposition of **1** is a single-phase transformation is also supported by powder X-ray diffraction analysis, which shows a gradual shift of the diffraction pattern as the reaction progresses.[9] The final covalent product exhibits high crystallinity, in agreement with the microscopic observations (Figure 3). For comparison, an amorphous solid results when **1** is decomposed in the melt at 200 °C for 10 min (Figure 3c).[10] The unit cell parameters for **2**, calculated using powder X-ray diffraction data, are: $a = 8.600(34)$, $b = 13.864(74)$, $c = 16.895(27)$ Å, and $V = 2014(11)$ Å^3. They correspond to 3.3, 2.5, 3.5, and 9.0% shrinkage, respectively, relative to **1**.[11] We also monitored the evolution of unit cell parameters during the solid-state decomposition of **1** at 120 °C. The initial crystal lattice smoothly transforms into the corresponding lattice of **2**, indicating a crystal-to-crystal process (Figure 4).[9]

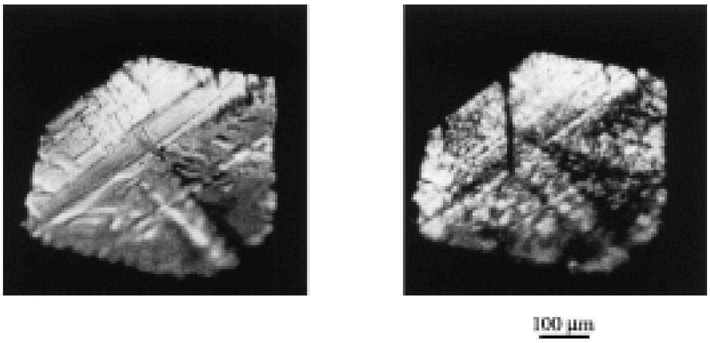


Figure 2. Polarizing microscopic view of $NaBH_4 \cdot$THEC crystal-to-crystal decomposition: left) initial crystal; right) after 20 h at 160 °C. Scale bar = 100 µm.

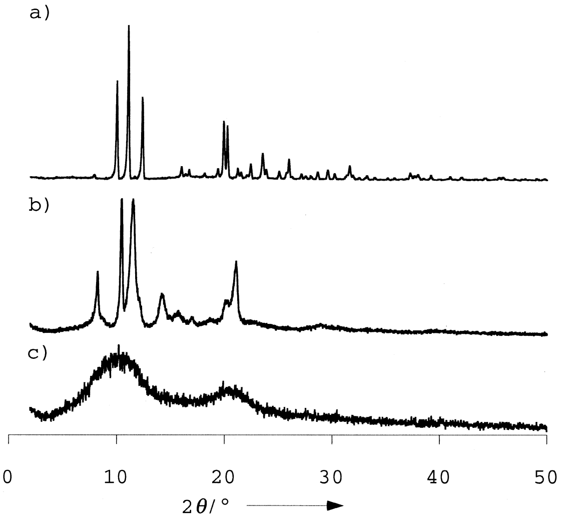


Figure 3. Powder X-ray diffraction patterns for: a) dihydrogen-bonded complex **1**; b) solid-state decomposition product **2**; c) product of decomposition in the melt.

Despite our sustained efforts, the detailed structure of **2** has remained elusive to date. The relatively big change in the unit cell accompanying the solid-state decomposition ultimately results in deterioration of the single crystals' quality, precluding their X-ray structural investigation. Also, the unexpected insolubility of **2** in common organic solvents does not allow its recrystallization. Considering the crystal packing of **1**, with no interdimer hydrogen bonding present, formation of discrete molecular cages is expected from the solid-state decomposition. Crosslinking between dimers would require substantial intermolecular rearrangements, which is highly unlikely in a

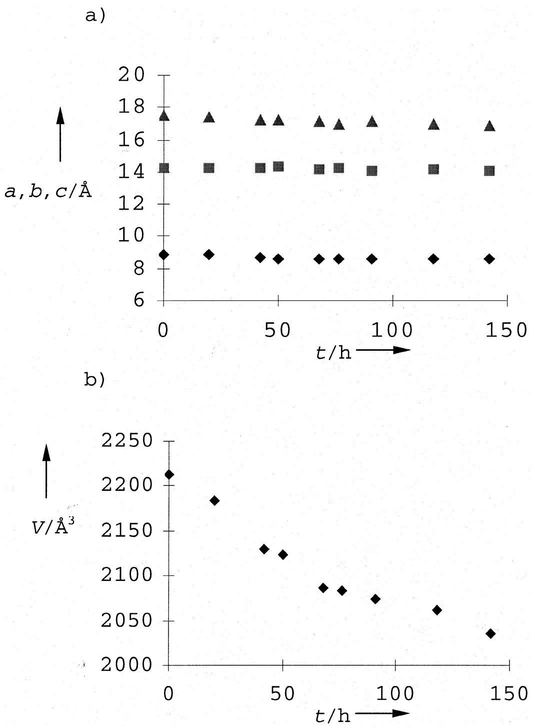


Figure 4. Evolution of unit cell axes (a; a = ◆, b = ■, c = ▲) and volume (b) during the solid-state decomposition of **1** at 120 °C, monitored by powder X-ray diffraction.

crystallographically homogeneous, lattice-controlled transformation. Figure 5 presents a possible structure for the molecular cages in **2**, optimized[12] with the density functional theory (DFT) method at the B3LYP/6-31G* level.[13] No unusual values for the bond lengths and angles were observed in the resulting C_2-symmetrical structure, suggesting minimal strain in these covalent dimers.

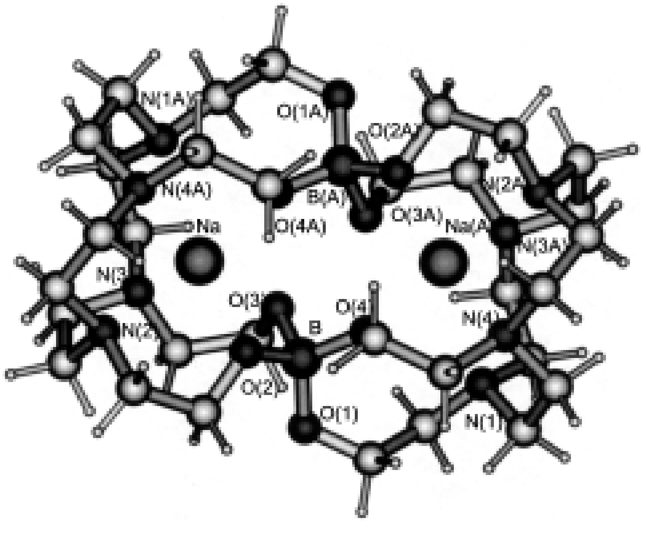


Figure 5. Molecular model of the solid-state decomposition product **2** calculated by using the DFT method at the B3LYP/6-31G* level; selected bond lengths [Å] and angles [°]: B-O(1) 1.458, B-O(2) 1.482, B-O(3) 1.497, B-O(4) 1.474, N(1)-Na(A) 3.003, N(2)-Na 2.714, N(3)-Na 2.435, N(4)-Na(A) 2.565, O(2)-Na 2.670, O(3)-Na 2.276, O(4)-Na(A) 2.228; O(1)-B-O(2) 112.5, O(1)-B-O(3) 109.1, O(1)-B-O(4) 114.6, B-O(1)-C 123.7, B-O(2)-C 122.3, B-O(3)-C 125.9, B-O(4)-C 125.6.

When **1** was decomposed in DMSO by heating at 120 °C for 48 h, a crystalline product[14] (**3**) precipitated in high yield. X-ray structural analysis of the resulting crystals revealed a centrosymmetric molecular cage very similar to that expected from the solid-state reaction (Figure 6).[6] However, one of the hydroxyethyl arms in each of the two THEC ligands in the dimer does not bind the boron atom, nor does it complex the Na cation, being replaced by an OH group, presumably from the water present in the solvent. Except for the Na, the four N atoms, and C(4) and C(6), all the atoms in the structure are disordered over two sites, with 90.1 and 9.9 % occupancies, respectively. Like **2**, **3** is surprisingly insoluble in common organic solvents, despite its relatively small size, overall neutral charge, and lack of intermolecular hydrogen bonding.

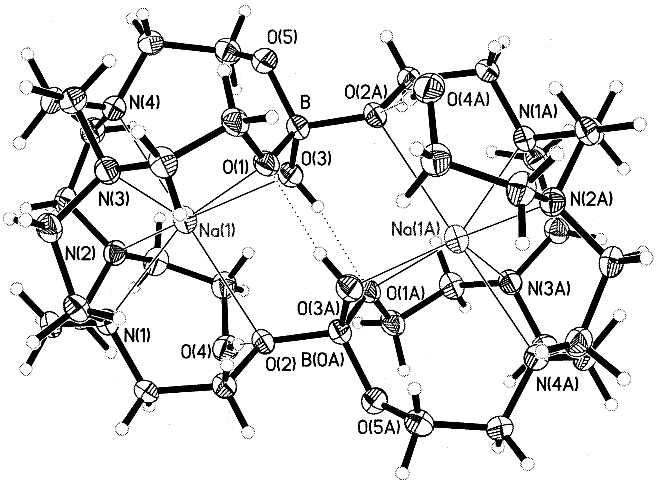


Figure 6. X-ray crystal structure of the major conformation found in the covalent dimer **3**, obtained by decomposing **1** in DMSO; selected bond lengths [Å] and angles [°]: B-O(1) 1.502(2), B-O(2) 1.511(2), B-O(3) 1.450(2), B-O(5) 1.457(2), N(1)-Na 2.519(1), N(2)-Na 2.540(1), N(3)-Na 2.565(1), N(4)-Na 2.682(1), O(1)-Na 2.371(1), O(2)-Na 2.796(1), O(3)-Na 2.391(1); O(1)-B-O(5) 111.6(1), O(2)-B-O(5) 109.8(1), O(3)-B-O(5) 111.6(1), B-O(1)-C 121.7(1), B-O(2)-C 113.2(1), B-O(5)-C 122.8(1).

In summary, we report here the first deliberate crystal-to-crystal dihydrogen to covalent bonding transformation.[15] Judicious engineering of dihydrogen-bonded crystals permits transfer of crystallinity to the covalent products resulting from their solid-state decompositions. Further elaboration of the dihydrogen-bonded building blocks described herein may ultimately lead to low-temperature, rational construction of extended crystalline covalent solids, a class of compounds to which few purposeful synthetic paths exist.

Received: May 2, 2000 [Z15065]

---

[1] a) A. J. Lough, S. Park, R. Ramachandran, R. H. Morris, *J. Am. Chem. Soc.* **1994**, *116*, 8356–8357; b) R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res.* **1996**, *29*, 348–354; c) E. S. Shubina, N. V. Belkova, L. M. Epstein, *J. Organomet. Chem.* **1997**, *536–537*, 17–29; d) I. Alkorta, I. Rozas, J. Elguero, *Chem. Soc. Rev.* **1998**, *27*, 163–170; e) D. Braga, P. De Leonardis, F. Grepioni, E. Tedesco, M. J. Calhorda, *Inorg. Chem.* **1998**, *37*, 3337–3348; f) G. Orlova, S. Scheiner, *J. Phys. Chem. A* **1998**, *102*, 260–269; g) M. J. Calhorda, *Chem. Commun.* **2000**, 801–809.
[2] a) S. Gatling, J. E. Jackson, *J. Am. Chem. Soc.* **1999**, *121*, 8655–8656; b) J. C. Lee, E. Peris, A. L. Rheingold, R. H. Crabtree, *J. Am. Chem.

Soc. **1994**, *116*, 11014–11019; c) J. A. Ayllon, C. Gervaux, S. Sabo-Etienne, B. Chaudret, B. Hessen, *Organometallics* **1997**, *16*, 2000–2002; d) S. Aime, R. Gobetto, E. Valls, *Organometallics* **1997**, *16*, 5140–5141; e) H. S. Chu, C. P. Lau, K. Y. Wong, W. T. Wong, *Organometallics* **1998**, *17*, 2768–2777; f) A. Cabalero, F. A. Jalon, B. R. Manzano, *Chem. Commun.* **1998**, 1879–1880.

[3] a) J. P. Campbell, J. W. Hwang, V. G. Young, R. B. Von Dreele, C. J. Cramer, W. L. Gladfelter, *J. Am. Chem. Soc.* **1998**, *120*, 521–531; b) K. Abdur-Rashid, D. G. Gusev, A. L. Lough, R. H. Morris, *Organometallics* **2000**, *19*, 834–843.

[4] a) R. Custelcean, J. E. Jackson, *J. Am. Chem. Soc.* **1998**, *120*, 12935–12941; b) R. Custelcean, J. E. Jackson, *Angew. Chem.* **1999**, *111*, 1748–1751; *Angew. Chem. Int. Ed.* **1999**, *38*, 1661–1663; c) R. Custelcean, J. E. Jackson, *J. Am. Chem. Soc.* **2000**, *122*, 5251–5257.

[5] Spectroscopic data for **1**: ^{1}H NMR (300.1 MHz, C_5D_5N, 25 °C): $\delta = 6.03$ (br.s, 4H; OH), 3.85 (t, $J = 4.5$ Hz, 8H; OCH_2), 2.49, 2.41 (br., 24H; NCH_2), 1.51 (q, $J = 81.3$ Hz, 4H; BH_4); ^{13}C NMR (75.4 MHz, CD_3CN, 25 °C): $\delta = 51.17$ (NCH_2), 56.45 (NCH_2), 58.96 (OCH_2); ^{11}B NMR (96.23 MHz, CD_3CN, 25 °C, $B(OCH_3)_3$): $\delta = -54.21$ (quintet, $J = 81.4$ Hz; BH_4); ^{11}B MAS NMR (128.33 MHz, 4013 Hz, 25 °C, $B(OH)_3$): $\delta = -45.4$ ($\Delta\nu_{1/2} = 2198$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6028 Hz, 25 °C, NaCl): $\delta = -12.3$ ($\Delta\nu_{1/2} = 1440$ Hz); IR (KBr): $\tilde{\nu} = 2298$, 2225 cm^{-1} (B–H); elemental analysis calcd for $C_{16}H_{40}N_4O_4BNa$ (%): C 49.74, H 10.36, N 14.51; found: C 49.37, H 10.87, N 14.80; m.p. 180–181 °C.

[6] A Siemens SMART CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$) was used for the X-ray single-crystal analyses in this study. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL package (Structure Analysis Program 5.1, Brucker AXS, Inc., Madison, WI, **1997**). Absorption corrections were applied using SADABS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference Fourier maps and refined isotropically. For the borohydride ions in **1**, however, only the hydridic hydrogen atoms involved in dihydrogen bonding could be found; the remaining H atoms from BH_4^- were calculated and placed in idealized positions. The observed O–H and B–H distances appear typically shorter than the ideal values of 0.96 and 1.21 Å, and were not corrected. Crystal data for **1**: crystal dimensions: $0.23 \times 0.18 \times 0.13$ mm; $T = 173$ K; orthorombic, I_{222}; $a = 8.8240(3)$, $b = 14.1344(6)$, $c = 17.3533(7)$ Å, $V = 2164.34(15)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.186$ g cm^{-3}; $2\theta_{max} = 56.4°$; 12854 reflections collected, 2608 unique; 200 parameters; $R_1 = 0.0487$, $wR_2 = 0.1221$ for $I > 2\sigma(I)$; residual electron density: 0.488 e Å^3. Crystal data for **3**: crystal dimensions: $0.47 \times 0.39 \times 0.29$ mm; $T = 173$ K; monoclinic, $P2_1/n$; $a = 8.7696(1)$, $b = 13.0571(1)$, $c = 17.7724(2)$ Å, $\beta = 96.36°$, $V = 2022.50(4)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.301$ g cm^{-3}; $2\theta_{max} = 56.5°$; 20248 reflections collected, 4840 unique; 462 parameters; $R_1 = 0.0352$, $wR_2 = 0.0921$ for $I > 2\sigma(I)$; residual electron density: 0.261 e Å^3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143751 and CCDC-143752. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] a) S. Buoen, J. Dale, J. Krane, *J. Chem. Soc. Chem. Commun.* **1982**, 1172–1174; b) S. L. Whitbread, S. Politis, A. K. W. Stephens, J. B. Lucas, R. S. Dhilon, S. F. Lincoln, K. P. Wainwright, *J. Chem. Soc. Dalton Trans.* **1996**, 1379–1384.

[8] ^{11}B MAS NMR (128.33 MHz, 4038 Hz, 25 °C, $B(OH)_3$): $\delta = -8.0$ ($\Delta\nu_{1/2} = 2462$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6001 Hz, 25 °C, NaCl): $\delta = -15.6$ ($\Delta\nu_{1/2} = 3421$ Hz).

[9] a) T. Suzuki, T. Fukushima, Y. Yamashita, T. Miyashi, *J. Am. Chem. Soc.* **1994**, *116*, 2793–2803; b) K. Tashiro, T. Kamae, M. Kobayashi, A. Matsumoto, K. Yokoi, S. Aoki, *Macromolecules* **1999**, *32*, 2449–2454.

[10] ^{11}B MAS NMR (128.33 MHz, 6000 Hz, 25 °C, $B(OH)_3$): $\delta = -6.9$ ($\Delta\nu_{1/2} = 1745$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6000 Hz, 25 °C, NaCl): $\delta = -8.9$ ($\Delta\nu_{1/2} = 2704$ Hz).

[11] For this comparison, the following unit cell parameters derived from powder X-ray diffraction data at room temperature were used for **1**: $a = 8.894(7)$, $b = 14.214(13)$, $c = 17.509(17)$ Å, $V = 2214(3)$ Å^3.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, A. D. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Thomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian Inc., Pittsburgh PA, **1998**.

[13] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[14] ^{11}B MAS NMR (128.33 MHz, 6060 Hz, 25 °C, $B(OH)_3$): $\delta = -7.5$ ($\Delta\nu_{1/2} = 1880$ Hz); ^{23}Na MAS NMR (105.81 MHz, 6058 Hz, 25 °C, NaCl): $\delta = -9.0$ ($\Delta\nu_{1/2} = 2476$ Hz).

[15] A topochemical dihydrogen to covalent bonding transformation has been previously reported to occur in the solid-state conversion of cyclotrigallazane to nanocrystalline gallium nitride. However, initial loss of H_2 at 150 °C resulted in an amorphous GaN phase, and subsequent annealing at 600 °C was required to convert it into the final crystalline product. See: J.-W. Hwang, J. P. Campbell, J. Kozubowski, S. A. Hanson, J. F. Evans, W. L. Gladfelter, *Chem. Mater.* **1995**, *7*, 517–525.

NMR and Theoretical Study of Acid Sites Formed by Adsorption of SO_3 onto Oxide Surfaces[**]

Jinhua Zhang, John B. Nicholas,[*] and James F. Haw[*]

The structure and function of acid sites formed by the treatment of oxide surfaces with sulfur compounds is a current problem in heterogeneous catalysis.[1] While many studies have considered hydrogen sulfate surface complexes as the locus of solid acidity in such materials, other acidic surface sites have also been proposed, including those formed from adsorbed SO_3. Haase and Sauer recently reported a periodic ab initio theoretical study of sulfuric acid adsorbed on low-index surfaces of ZrO_2.[2] One of the stable structures they found on $ZrO_2(001)$ was a tridentate-adsorbed SO_3 species. This conclusion was consistent with an experimental study of Babou and co-workers, who on the basis of infrared studies

---

[*] Prof. J. F. Haw
Loker Hydrocarbon Research Institute
and Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661 (USA)
Fax: (+1) 213-740-6679
E-mail: haw@methyl.usc.edu

Dr. J. B. Nicholas
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
Richland, WA 99352 (USA)
Fax: (+1) 509-375-6631
E-mail: john.nicholas@pnl.gov

J. Zhang
Department of Chemistry
Texas A&M University
Austin, TX (USA)

[**] This work was supported by the US NSF.