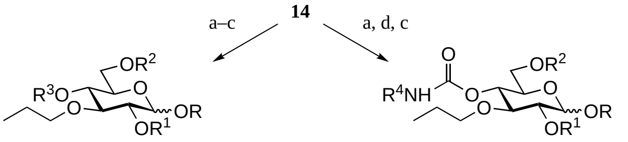

16a, $R^1 = R^3 = Bn$; $R^2 = R = Me$

16b, $R^1 = Bn$; $R^2 = Me$, $R^3 = CH_2COOtBu$, $R = Me$

17a, $R^1 = R^2 = Bn$; $R^4 = 2\text{-}CF_3C_6H_4$; $R = Me$

17b, $R^1 = R^2 = Bn$; $R^4 = 4\text{-}CNC_6H_4$; $R = Me$

Scheme 5. a) MeOH, dioxane, pyridinium-*p*-toluenesulfonate; b) KO*t*Bu, DMF, R^3-X; c) Br_2, CH_2Cl_2, 2,6-di-*tert*-butylpyridine, ROH, Et_4NBr, CH_2Cl_2, cyclohexene; d) R^4-NCO, DMAP, dioxane.

translation of the combinatorial synthesis to stereoisomers of the glucose scaffold (galactose, mannose) are presently under investigation.

Received: March 23, 1998
Supplemented version: June 22, 1998 [Z11622IE]
German version: *Angew. Chem.* **1998**, *110*, 2620–2622

Keywords: carbohydrates · combinatorial chemistry · protecting groups · solid-phase synthesis · thioglycosides

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Evidence for Selective Association of Tetrahedral BO_4 Units with Na^+ and of Trigonal BO_3 Units with H^+ in Dehydrated Zeolite B-ZSM-5 from Solid-State NMR Spectroscopy[**]

Christian Fild, Hellmut Eckert, and Hubert Koller[*]

The study of local structure and bonding in zeolites is of fundamental interest for a better mechanistic understanding of their catalytic function. One of the unresolved questions regards the stabilization of boron in different coordination states in the zeolite framework. Typically, only boron centers tetrahedrally coordinated by O atoms (B[4]) are present in hydrothermally synthesized zeolites, some of which are transformed into trigonally coordinated centers (B[3]) when the organic structure directing agent is removed by calcination.[1–4] The negative charge of the $BO_{4/2}^-$ groups in as-synthesized zeolites is balanced by sodium and quaternary ammonium cations, while the counterions in the calcined zeolite are Na^+ and H^+. Quantum-chemical calculations suggest that the bond between boron and protonated framework oxygen atoms is much weaker than the Al–O bond in Al-O(H)-Si groups; hence, the existence of three-coordinate boron centers in calcined zeolites is plausible.[5]

Here we show that in calcined B-ZSM-5 the B[3] units selectively associate with H^+, and the B[4] units with Na^+ counterions. The zeolites were prepared hydrothermally with tetrapropylammonium (TPA) cations as structure-directing agent. The content of sodium cations in the zeolites was varied by changing the gel composition in the syntheses. The TPA was subsequently removed from the zeolite channels by calcination, and the samples were dehydrated in vacuum at elevated temperature. The ^{11}B MAS NMR spectra of the calcined and dehydrated samples show that the B[4]/B[3] ratio increases with increasing sodium content, and this suggests that sodium cations are associated with B[4] units (MAS = magic angle spinning; rotation of the probe in a magnetic field).

More direct evidence for this association can be obtained on the basis of the heteronuclear dipole interaction between

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[**] We thank Arne Fischer for the ICP/AES analysis and Dr. Leo van Wüllen for valuable discussions. Financial support by the Fonds der Chemischen Industrie, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, and the Deutsche Forschungsgemeinschaft (KO 1817/1-1) is gratefully achkowledged.

NMR nuclei. Fast magic angle spinning usually averages this interaction. However, it can be reintroduced by means of the rotational echo double resonance (REDOR) experiment.[6] A rotor-synchronized spin echo signal (pulse sequence: $\pi/2-\tau-\pi-\tau-$acquire) is recorded for nuclei I, and perturbation π pulses are applied to nuclei S within the echo period τ. The π(S) pulse inverts the sign of the I–S heterodipolar coupling constant. This results in an additional decrease in the phase coherence and hence reduced echo signal intensity. Experimentally, one measures the normalized difference $\Delta S/S_0$ of the echo signal of spins I in the absence and presence of π(S) pulses. $\Delta S/S_0$ is measured as a function of the dipolar evolution time $N \cdot T_r$, where N is the number of rotor cycles and T_r the rotor period. For an isolated I–S spin pair, the internuclear distance can be directly determined from this curve. In the case of multiple-spin interactions, the curvature of this function at short evolution times is proportional to an average dipole–dipole coupling constant.

For these REDOR studies we chose a B-ZSM-5 sample with 1.23 sodium cations and 1.32 boron atoms per unit cell (ICP/AES elemental analysis), resulting in a Si/B ratio of 72:1. This low concentration ensures isolated boron sites. A fraction of the Na$^+$ ions is associated with defect sites, as observed by ^{29}Si MAS NMR spectroscopy. Figure 1a shows the ^{11}B spin echo MAS NMR spectrum of dehydrated zeolite B-ZSM-5. A sharp signal at $\delta = -3.7$ is observed for the B[4] units, while the B[3] units give rise to a MAS powder spectrum with second-order quadrupole interaction. Lineshape simulation yields a quadrupole coupling constant C_q of 2.5 MHz, an asymmetry parameter η of 0.1, and a chemical shift δ_{cs} of 9.7. Figure 1b shows the corresponding ^{11}B{^{23}Na} REDOR spectrum (^{11}B observed, perturbation pulses on ^{23}Na) at an evolution time of 12.8 ms. From the difference spectrum (Figure 1c) and the corresponding plot of $\Delta S/S_0$ versus $N \cdot T_r$ (Figure 1d), it is apparent that only the B[4] units exhibit a REDOR effect. These results show that the B[4] units are closely associated with sodium ions, while the B[3] units are not. That trigonal boron is located in the zeolite framework is indicated by the ^{11}B isotropic chemical shift of $\delta = 9.7 \pm 0.3$, which is typical of BO$_{3/2}$ groups connected to three silicon atoms, as in borosilicate glasses.[7] Secondly, ^{11}B spin echo decay experiments[8] reveal that the homodipolar ^{11}B–^{11}B interactions are very weak. The resulting second moment value of $0.8 \times 10^6\,\mathrm{rad^{-2}\,s^{-2}}$ is only consistent with isolated BO$_{3/2}$ sites and the absence of B-O-B linkages.

The interaction between the H$^+$ counterions and the B[3] units was probed by complementary ^{1}H{^{11}B} and ^{11}B{^{1}H} REDOR experiments. Figure 2a shows the rotor-synchron-

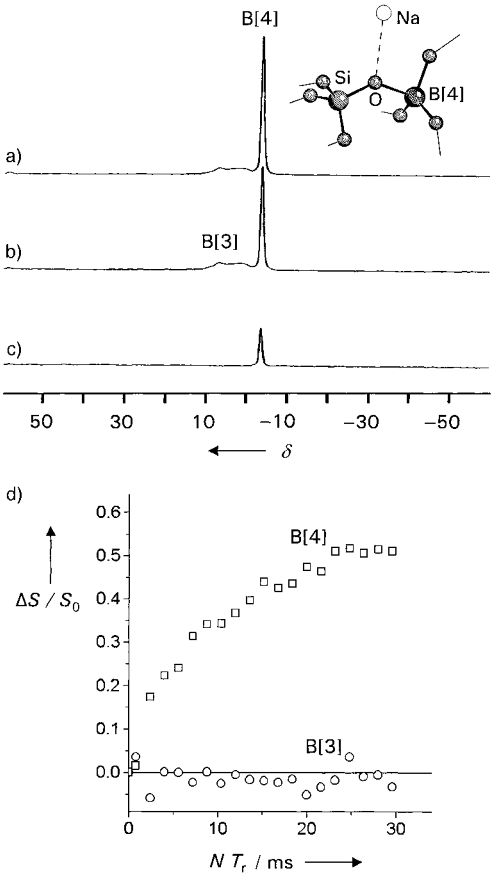

Figure 1. View of the local environment of a B[4] unit (top right) and ^{11}B spin echo MAS NMR spectra (rotation 10 kHz, relaxation delay 5 s, $\pi/2$ pulse length 3 µs) of B-ZSM-5 for 128 rotor cycles between the $\pi/2$ pulse and data acquisition. a) ^{11}B spin echo spectrum; b) ^{11}B{^{23}Na} REDOR spectrum, π pulse on decoupler 9.5 µs; c) difference spectrum; d) ^{11}B{^{23}Na} REDOR curves for B[3] and B[4] (rotation 10 kHz, relaxation delay 5 s, $\pi/2$ pulse length 3 µs, π pulse on decoupler 7.7 µs).

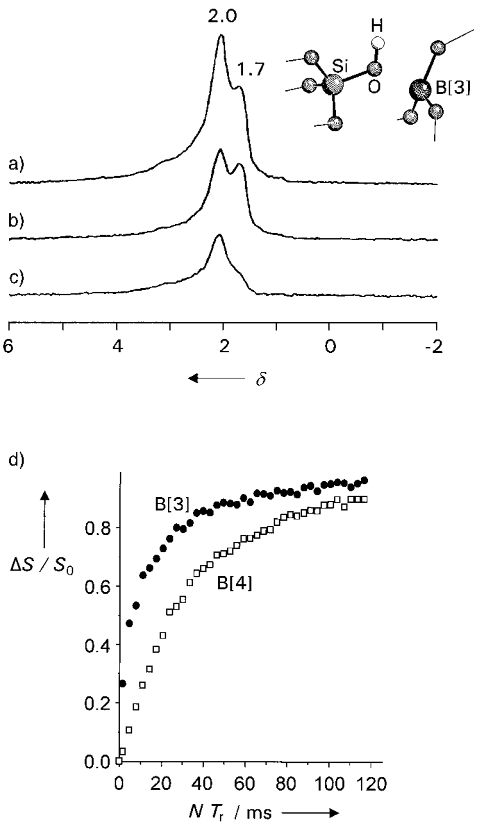

Figure 2. View of the local environment of a B[3] unit (top right) and ^{1}H MAS spin-echo NMR spectra of B-ZSM-5 (rotation frequency 10 kHz, relaxation delay 16 s, $\pi/2$ pulse length 5.2 µs): a) Rotor-synchronized spin echo experiment; b) ^{1}H{^{11}B} REDOR spectrum with 168 rotor cycles, π pulse on decoupler 8.8 µs; c) difference spectrum; d) ^{11}B{^{1}H} REDOR curves for B[3] and B[4] (rotation frequency 10 k Hz, relaxation delay 5 s, $\pi/2$ pulse length 3 µs, π pulse on decoupler 7.7 µs).

ized ^{1}H MAS spin-echo NMR spectrum of B-ZSM-5, which exhibits two maxima at $\delta = 1.7$ and 2.0 and a broad shoulder at $\delta = 3.0$. The corresponding $^{1}\mathrm{H}\{^{11}\mathrm{B}\}$ REDOR spectrum (evolution time 16.8 ms) is displayed in Figure 2b and shows a substantial decrease in the intensity of the maximum at $\delta = 2.0$ and the shoulder at $\delta = 3.0$. This is also evident in the difference spectrum (Figure 2c), in which the relatively weak change in the intensity of the signal at $\delta = 1.7$ can be seen. Although further work is necessary to clarify the detailed assignment of these three signals, it is clear that they arise from protons near to ($\delta = 3.0$, 2.0) or remote from ($\delta = 1.7$) framework boron atoms. We assign the signal at $\delta = 1.7$ to defect silanol groups, and the signals at $\delta = 3.0$ and $\delta = 2.0$ to the SiOH$\cdots$B[3] groups in the zeolite framework. The observation of two different chemical shifts for these sites is similar to findings for analogous zeolites that contain aluminum instead of boron.[9] The weak REDOR effect of the defect silanol groups is explained by their remoteness from boron atoms in the next nearest tetrahedral framework positions (B[3] or B[4]). Consistent with this model, we expect the B[3] units to be closely associated with the protons, since the charge of the B[4] units is balanced by sodium cations (see above). This conjecture is confirmed by the $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$ REDOR curve in Figure 2d. The initial slope of the curve for B[3] is much steeper than for B[4], and this proves that the B[3] units are significantly closer to protons than the B[4] units. This suggests the formation of SiOH$\cdots$B[3] groups, whereas the B[4] units are fairly remote from protons. Although it should be possible in principle to estimate an approximate B–H distance from such experiments, we refrain from doing so here, because the presence of long-range interactions means that no isolated spin pairs are present.

Our $^{11}\mathrm{B}\{^{23}\mathrm{Na}\}$, $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$, and $^{1}\mathrm{H}\{^{11}\mathrm{B}\}$ REDOR results provide the first direct evidence that tetrahedral B[4] units are associated with charge-balancing sodium cations in dehydrated B-ZSM-5. Trigonal B[3] units are located in SiOH$\cdots$B[3] groups, as predicted by the theoretical calculations of Sauer.[5] Two proton NMR signals at $\delta = 2.0$ and 3.0 are observed for these sites. The results from experiments with other Na/H ratios are consistent with the data presented here.

Experimental Section

Zeolite B-ZSM-5 was hydrothermally crystallized at 423 K from a gel of molar composition H_3BO_3:NaOH:TPABr:TPAOH:H_2O:SiO_2 = 0.084:0.08:0.06:0.04:36:1. Calcination was carried out in air at 923 K, and the resulting zeolite powder was carefully dehydrated in vacuum at 623 K. The sample was initially heated to 353 K at 5 K min^{-1} and held at this temperature for 2 h. Subsequently the temperature was raised at 10 K min^{-1} to 623 K and kept at this temperature for 4 h. Solid-state double resonance NMR experiments on the dry samples were carried out on a Bruker DSX-500 spectrometer with a 4 mm triple resonance probe operating at 10 kHz spinning speed. The rotor speed was maintained by a standard automatic control unit. The resonance frequencies for ^{1}H, ^{11}B, and ^{23}Na are 500.11, 160.45, and 132.29 MHz, respectively.

Received: May 13, 1998 [Z11852IE]
German version: *Angew. Chem.* **1998**, *110*, 2654–2656

Keywords: boron · coordination modes · NMR spectroscopy · zeolites

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An Unexpected Layered Structure in Inorganic Cyanide Clusters: $[\mathbf{Cu_4(\mu_3\text{-}OH)_4}][\mathbf{Re_4(\mu_3\text{-}Te)_4(CN)_{12}}]$**

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Cyanide compounds have been known for nearly three centuries.[1–3] New complex transition metal cyanides have been described recently that promise to have a variety of useful applications.[4–7] Complex cyanides demonstrate unique structures, properties, and reactivity.[1–7] The ambidentate nature of the CN$^-$ ligand, its terminal and bridging binding modes, its wide variety of coordination number, and arrangement of metal centers favor the formation of amazing and unusual structures both for binary and for complex cyanides of transition metals. The last few years have made available the cyanide clusters.[8–14] The availability of these compounds gave us the possibility to begin the study of their chemistry systematically.

We have recently prepared and structurally characterized caesium and potassium salts containing the new cyanide cluster anion $[Re_4(\mu_3\text{-}Te)_4(CN)_{12}]^{4-}$.[13, 14] Here we report the new complex, polymeric inorganic cluster compound $[Cu_4(\mu_3\text{-}OH)_4][Re_4(\mu_3\text{-}Te)_4(CN)_{12}]$ (**1**) built from these cluster anions.

Compound **1** was prepared by adding a solution of $CuCl_2$ to $K_4[Re_4Te_4(CN)_{12}]$ in silica gel at about pH 7. The structure of **1** was solved by X-ray single-crystal analysis.[15] The structure consists of layers built from the tetranuclear copper(II) cations

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[**] This research was supported by the Russian Foundation of Basic Research (N96-03-32955) and INTAS (N96-2705ext.). The authors thank Dr. V. N. Ikorskii for the magnetic measurements.