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Structure and Ion Exchange Properties of a New Cobalt Borate with a Tunnel Structure “Templated” by Na^+

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The advent of new crystalline networks is of perpetual interest in solid-state chemistry, primarily for the potential unearthing of novel optical, electronic, or magnetic properties. The field remains plagued, however, by the general inability to forecast structure types for new systems of elements. In the specific case of metal borates, prediction is complicated by the flexibility of boron to adopt either trigonal or tetrahedral oxygen coordination. As a result, metal borate crystallography has provided a rich area of research for over 50 years, with a recent resurgence due to interest in luminescent and nonlinear optical materials.[1] Most ternary M−B−O systems have been thoroughly examined wherein certain motifs dominate, including isolated BO_3^{3-} triangles and extended networks containing B_3O_3 six-membered rings.[2] As expected, these common themes also appear in quaternary (and higher) phases, with structural complexity increasing with variety in the metal coordination geometries. The progression toward study of quaternary compounds has already yielded the promising UV laser materials $CsLiB_6O_{10}$,[3] $Sr_2Be_2B_2O_7$,[4] and $K_2Al_2B_2O_7$.[5] Fewer breakthroughs have been reported in the search for metal borates with novel frameworks containing pores or mobile ions; only one synthetic borate with any degree of porosity has been reported,[6] although several zeotypic borophosphates have been made.[7] Our own search for new first-row transition metal borate phases has led us to a remarkable compound containing both exchangeable cations and redox-active metal sites shrouded within a rigid metaborate network. This work represents a new direction in developing non-siliceous frameworks for separations, storage, and heterogeneous catalysis.

The material is formed by reaction of a new cobalt borate, CoB_4O_7, with Borax at high temperatures. To avoid formation of previously characterized compounds, we used flux methods that are often employed for crystallization of phases that melt incongruently. In the Co−B−O system the $Co_3B_2O_6$, $Co_2B_2O_5$, and Co_3BO_5 phases have been structurally characterized,[8] each congruently melting at temperatures in excess of 1000 °C.[9] We find that a source of cobalt(II) (such as oxides, carbonate, nitrate, sulfate, or acetylacetonato complex) forms the CoB_4O_7 phase when fired in air or pure oxygen with excess H_3BO_3 at temperatures below 900 °C. The structural details of this intermediate phase will be discussed elsewhere. More importantly, under optimal conditions[10] “recrystallization” of this vivid purple compound using a Borax ($Na_2B_4O_7 \cdot 10H_2O$) flux results in complete conversion to a paler pink phase. Single-crystal X-ray diffraction[11] revealed the $Na_2Co_2B_{12}O_{21}$ framework shown in Figure 1a. This network is the first infinite borate containing a discernible tunnel structure.

At first glance, it is tempting to say that the oval tunnels within this borate framework have been cast around the rows of sodium ions running parallel to the *b* axis. The templating action of both inorganic and organic agents, either charged or uncharged, is well-known in zeolite synthesis,[13] but the unusual shape of the borate network displayed in Figure 1a is rather enigmatic. The single crystallographically independent sodium ion is coordinated by seven oxygens at less than 2.75 Å, but these are arranged in a very asymmetric configuration, leaving one side virtually exposed. Neighboring Na^+ are found at 4.55 Å along the row and 5.03 Å across the inversion center within the channel. The balance of electrostatics appears to “trestle” the two halves of the tunnel while leaving a significant gap down its center. Whether these ions are indeed necessary for the formation of this structure or simply fill the remaining voids once the borate framework has been assembled is unclear.

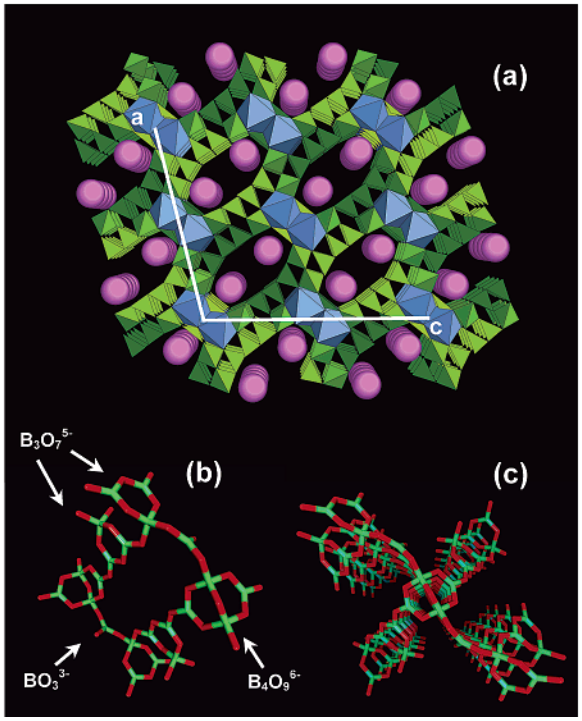

Figure 1. (a) Polyhedral view of the $Na_2Co_2B_{12}O_{21}$ framework perpendicular to the (010) plane with CoO_6 octahedra shown in blue and trigonal BO_3 and tetrahedral BO_4 units in green. Sodium ions (pink spheres) line the oval tunnels of the metaborate network and are shown with a seven-coordinate crystal radius of 1.26 Å.[12] (b) A portion of the metaborate framework, illustrating its construction from several common borate clusters occurring in pairs related by a center of symmetry. Boron and oxygen atoms are represented by green and red pipes, respectively. Stacking of this unit along [010] generates the tunnels. (c) View along a 2-fold axis showing a stack of $B_4O_9^{6-}$ units connected to four helices of $B_3O_7^{5-}$ clusters.

Examination of the network reveals that while as a whole it is entirely novel, it is indeed composed of the common subunits observed in many borate compounds, as illustrated in Figure 1b. A 12-oxygen ring forms the perimeter of the tunnel with atoms lying

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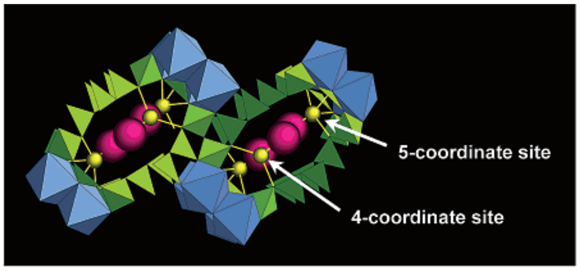

Figure 2. Filling of the tunnels by Li^+ (yellow spheres) and water molecules (red spheres) following ion exchange. The two sites are disordered in a 2:1 ratio over all tunnels. The interstitial species are shown as 75% of their typical sizes for clarity.

nearly planar parallel to approximately (2, −1, 2) or (2, 1, 2). When the connectivity of this spacious structure is extended, we see that the tunnel is bounded by symmetry-related pairs of BO_3^{3-}, $B_3O_7^{5-}$, and $B_4O_9^{6-}$ units. The portions of these units outside the ring's skeleton form part of adjacent rings, and the entire array is stacked along the *b* axis to create the tunnel structure. The cross-sectional dimensions of the tunnel are 4.5 Å × 8.8 Å (atom to atom).

Illustration of the infinite connectivity in this network is provided in Figure 1c. The $B_4O_9^{6-}$ moieties are stacked parallel along *b* and are centered about atom O(1) lying on a 2-fold axis at ($^1/_4$, *y*, $^1/_2$). The four "arms" of these units are then connected, either directly or through BO_3^{3-} triangles, to four chains of $B_3O_7^{5-}$ units also running along the *b* axis. The resulting connectivity is a set of $(-B-O-)_n$ infinite helices adorned with six-membered rings. Connection to adjacent (and inverted) $B_4O_9^{6-}$ stacks in the same manner completes the tunnels, and forms the pockets where the cobalt(II) ions are housed. These sites are found as isolated, edge-shared octahedral dimers that display a prominent axial distortion (four Co−O lengths between 1.998 and 2.064 Å, two at 2.35 Å).

Importantly, the Na^+ within the tunnels are mobile, and readily exchangeable with preservation of the original crystal morphology. Ion exchange was facilitated by heating the compound in a large excess of molten $LiNO_3$ (4 d at 280 °C), resulting in noticeable darkening. After washing with water, *intact single crystals* with exchanged cations (confirmed by elemental analysis) were recovered for X-ray analysis. Structural refinement[14] revealed that the exchange process is topotactic; the borate network remains unaltered, but the electron density within the tunnels is both decreased and more diffuse. If the ion exchange is performed for a shorter period, weak residues at the original Na^+ sites are apparent in the refinement, providing crystallographic evidence of incomplete exchange. The structure presented here contains no such residues; instead there are atoms located both closer to the walls of the tunnel and nearer to its center. These have been interpreted as a disordered model of Li^+ ions with coordination spheres completed by water molecules, as shown in Figure 2.

As the fields of heterogeneous catalysis and molecular separations continue to specialize, this novel framework should find its niche of applicability. Exchange of the tunnel cations with catalytic metals or by protonation of the tunnel oxygen atoms certainly seems viable, and we have not yet even exploited the redox properties of the cobalt ions. Theoretically, complete evacuation of the tunnels would be accompanied by oxidation of these ions to the +3 state. Replacement of Co^{2+} with an alternate metal is also a work in progress.

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Supporting Information Available: Additional details of the structure refinements for the compounds discussed (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A mixture of $CoCO_3{\cdot}xH_2O$ (Aldrich) and 10 equiv of H_3BO_3 (Baker) was ground in a planetary ball-mill (Fritsch) and fired in air for 2 days at 750 °C. The bright purple cake was then ground with an equal mass of Borax (Aldrich), which was dehydrated at 300 °C after weighing to facilitate better mixing. The resulting mixture (approximate composition $1CoB_4O_7{:}3B_2O_3{:}1.1Na_2B_4O_7$) was fired in a gold crucible by slowly heating to 800 °C, holding for 5 h, and cooling to 600 °C at 2 °C/h, after which the furnace was turned off. The product appeared as pink crystals amidst colorless shards of unreacted flux.

(11) A pink prism of $Na_2Co_2B_{12}O_{21}$ was analyzed at 295 K; monoclinic space group *I*2/*a* with $a = 17.1447(15)$ Å, $b = 4.5530(5)$ Å, $c = 19.4408(15)$ Å, $\beta = 103.212(5)°$, $V = 1477.4(2)$ Å^3, $Z = 4$. This setting of the conventional *C*2/*c* space group was used to bring the β angle closer to orthogonality. Data were collected using graphite-monochromated Mo Kα radiation on a Siemens P4 diffractometer system. A total of 3355 reflections were collected in the range $4.30° < 2\theta < 69.98°$ of which 3261 were independent and 2526 were observed ($I > 2\sigma[I]$). The Bruker SHELXTL program was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the Bruker SHELXTL software package and converged to give $R_1 = 2.65\%$ and $wR_2 = 5.03\%$ ($I > 2\sigma[I]$).

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(14) A bronze prismatic fragment of $Li_2(H_2O)_2Co_2B_{12}O_{21}$ was analyzed at 295 K; monoclinic space group *I*2/*a* with $a = 17.4296(7)$ Å, $b = 4.5518(2)$ Å, $c = 19.5893(8)$ Å, $\beta = 103.9100(10)°$, $V = 1508.56(11)$ Å^3, and $Z = 4$ formula units. Data were collected using graphite-monochromated Mo Kα radiation on a Bruker SMART APEX diffractometer system. A total of 11583 reflections were collected in the range $4.84° < 2\theta < 69.96°$ of which 3264 were independent and 2814 were observed ($I > 2\sigma[I]$). The structure of the framework was solved as in ref 11, while the atoms within the tunnels were modeled using partially occupied sites at appropriate Li−O bond lengths. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the Bruker SHELXTL software package and converged to give $R_1 = 4.2\%$ and $wR_2 = 8.87\%$ ($I > 2\sigma[I]$).

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