

MCuB₇O₁₂·*n*H₂O (M = Na, K): A new copper borate with 14-ring channels†

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The title compounds, which were synthesized in boric acid flux under mild conditions (493 K), contain a 14-member ring borate framework consisting of octahedral (CuO₆), tetrahedral (BO₄) and triangular (BO₃) units.

Microporous materials consist mostly of corner-sharing tetrahedra, and less frequently, of edge-sharing octahedra.^{1–7} Boron is a unique element, which can be coordinated by oxygen with triangular or tetrahedral geometries. Recently, a number of borate open frameworks were reported including, for example, Zn₆B₁₂O₂₄⁸ and Na₂Co₂B₁₂O₂₁,⁹ which contain one-dimensional 8-ring or 12-ring channels formed by ZnO₄ or CoO₆, and tetrahedral BO₄ and triangular BO₃. The sodium cations in the later compound, which are located in the 12-ring channels, are exchangeable. Obviously the geometric flexibility of boron atoms may enrich enormously the topologies of the open frameworks. In this communication, we report a new copper borate, MCuB₇O₁₂·*n*H₂O (M = Na, K), which was synthesized in flux of boric acid,^{7,10} and contains 14-member ring channels.

MCuB₇O₁₂·*n*H₂O (M = Na, K) were synthesized by using boric acid as a flux in closed systems. A typical example for synthesizing NaCuB₇O₁₂·*n*H₂O is to charge C₄H₆O₄Cu·H₂O (5 mmol), Na₂B₄O₇·H₂O (15 mmol), H₃BO₃ (150 mmol) and 8 ml water in a 50 ml Teflon autoclave. After heating at 140 °C for several hours, the volatile components in the system were removed by heating the mixture in an oven at 180 °C. Then 3 g H₃BO₃ was added and the reaction proceeded at 220 °C for 2 days. Phase-pure samples (yield of 90% based on Cu) can be obtained by washing the product with hot water (50 °C). Copper sources and the ratio of the starting materials are not critical for the reaction. One could use, for example, Cu(NO₃)₂·3H₂O or CuSO₄·5H₂O to obtain this compound. KCuB₇O₁₂·*n*H₂O was synthesized by a similar process. The formula of this compound, established by structural analysis and charge consideration, is MCuB₇O₁₂·*n*H₂O in accordance with M : Cu : B ≈ 1 : 1 : 7 found from chemical analysis (ICP).

Because the crystals obtained are too small for a single-crystal structural study, the crystal structure of NaCuB₇O₁₂·*n*H₂O was established and refined using X-ray powder diffraction

techniques.‡ NaCuB₇O₁₂·*n*H₂O crystallizes in the orthorhombic space group *Pnmm*, *a* = 12.73720(8) Å, *b* = 4.69546(3) Å, *c* = 15.17928(9) Å and *V* = 907.83(2) Å³. As shown in Fig. 1a, the structural framework is composed of octahedra (CuO₆), tetrahedra (BO₄) and triangles (BO₃). The CuO₆ octahedra share edges forming an octahedral dimer that further shares all oxygen atoms with borate groups. The borate groups (12BO₃ and 2BO₄), on the other hand, share all corners forming 14-ring one-dimensional channels along the *b*-axis. Na⁺ cations and water molecules are located within the 14-ring channels. In the structure, Cu and O1 occupy the special positions (4*e*) on the two-fold axis, while the B1, O2 and O8 are on the mirror planes (4*g*). The rest of the atoms all occupy general positions. The structure refinement indicated that the occupation factors of Na and O8 are close to unity, therefore, there is approximately one water molecule per formula unit (*n* ≈ 1). The tunnel structure of NaCuB₇O₁₂·*n*H₂O was also studied by using high-resolution TEM imaging (Fig. 1b). To emphasize the framework, the symmetry operations of the structure were included to minimize the noise level of the TEM image. The electron diffraction pattern is also included and the structural model superposed on the HRTEM image further confirms the structure model. KCuB₇O₁₂·*n*H₂O is isostructural with NaCuB₇O₁₂·*n*H₂O, with the cell constants *a* = 12.6406(2) Å, *b* = 4.75296(8) Å, *c* = 15.3850(2) Å and *V* = 924.33 (4) Å³. In comparison with the Na-analogue, the unit cell volume of KCuB₇O₁₂·*n*H₂O increases significantly. However, the expansion of the cell volume is anisotropic; it expands in the *b*- and *c*-directions but shrinks along the *a*-axis.

The basic building block of the structure is a planar [Cu₂B₁₄O₂₈] unit consisting of 4BO₄, 10BO₃ and two square planar CuO₄ components as shown in Fig. 2a. In the structure of NaCuB₇O₁₂·*n*H₂O, the terminal oxygen atom (O4) on the BO₄ connects to the boron atoms at the corner (B2) of neighboring [Cu₂B₁₄O₂₈] units forming a zig-zag net. The oxygen atoms in the structure are all bridged to two boron atoms, so that the linkage of the borate framework is quite saturated like that in zeolites. The octahedron around the Cu atom is distorted due to the Jahn–Teller effect of the Cu²⁺ ion, which has four short Cu–O bonds (1.939(3) to 2.016(3) Å) within the [Cu₂B₁₄O₂₈] unit and two long Cu–O bonds (2.687(3) to 2.707(3) Å) crossing to a neighboring [Cu₂B₁₄O₂₈] unit.

The structure of NaCuB₇O₁₂·*n*H₂O is topologically related to that of Na₂Co₂B₁₂O₂₁.⁹ In Na₂Co₂B₁₂O₂₁, the basic building block is a [Co₂B₁₂O₂₆] unit that contains 4BO₄, 8BO₃ and two square planar CoO₄ components as shown in Fig. 2b. The extended linkage of this asymmetric building unit yields a 12-ring borate framework in a low symmetry (monoclinic) structure. Within the 12-ring channel, only the Na⁺ ions exist.

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† Electronic supplementary information (ESI) available: Rietveld plot, atomic parameters, magnetic susceptibility data, IR spectra, TGA analysis and HRTEM image of NaCuB₇O₁₂·*n*H₂O. See <http://dx.doi.org/10.1039/b506901g>

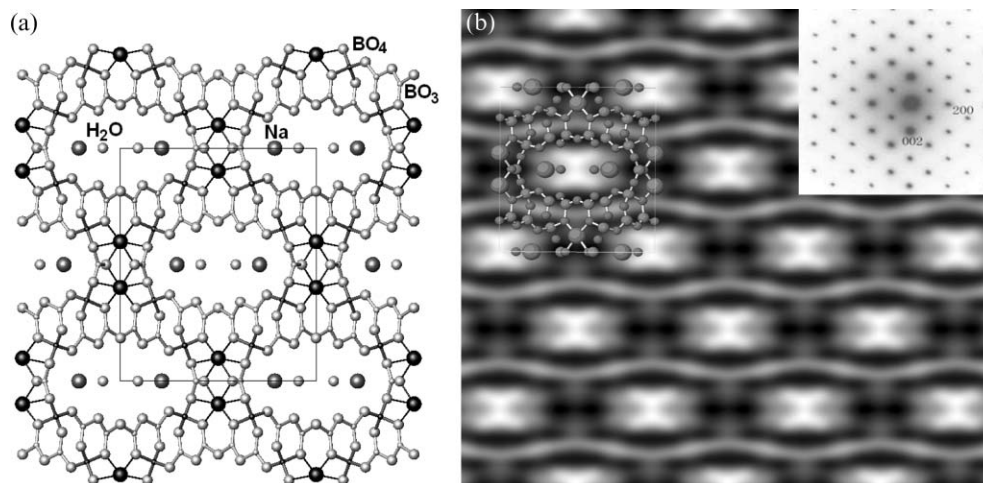


Fig. 1 (a) View of the structure along the b -axis. (Cu^{2+} large black spheres, B^{3+} small black and grey spheres, O^{2-} grey spheres, Na^+ , large grey spheres). The oxygens in the channel represent water molecules. (b) The high-resolution TEM image of $\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ in the 010 zone which have been smoothed and had the symmetry added to the original image. The electron diffraction pattern is shown as an insert in the upper-right corner.

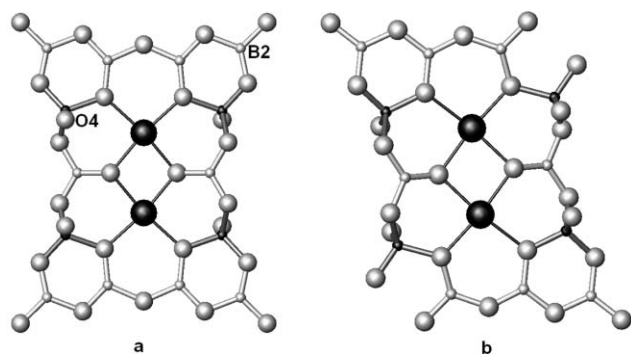


Fig. 2 (a) The basic building block of $\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ which is a planar $[\text{Cu}_2\text{B}_{14}\text{O}_{28}]$ unit consisting of 4BO_4 , 10BO_3 and two square planar CuO_4 components. (b) The topologically related building block of $\text{Na}_2\text{Co}_2\text{B}_{12}\text{O}_{21}$ ⁹ which has a monoclinic cell and one BO_3 less.

The water molecules in the channel can be removed by heating the sample up to $300\text{ }^\circ\text{C}$ (exp. 3.0 wt% and calc. 4.84 wt%). This process is reversible. The anhydrous sample takes up almost completely the water molecules when exposed to air at room temperature for just a few hours. This dehydration and rehydration behavior is confirmed by IR spectra and TGA analysis. The borate framework of $\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ ($M = \text{Na}, \text{K}$) is stable up to $600\text{ }^\circ\text{C}$. High-temperature powder X-ray diffraction studies show that above this temperature $\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ transforms to $\text{M}_2\text{Cu}_2\text{B}_{12}\text{O}_{21}$ ($M = \text{Na}, \text{K}$) and an unknown phase. The phase transformation is irreversible and almost straightforward, and no amorphous intermediate was observed (see the supporting materials[†]), largely due the

topologically related structures of these two phases. Above $800\text{ }^\circ\text{C}$, the borate framework collapses forming CuB_2O_4 and some amorphous materials.

$\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ ($M = \text{Na}, \text{K}$) is insoluble in cold water, soluble in concentrated acid solution and slightly soluble in dilute acid and ammonia solutions. In boiling water, $\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ ($M = \text{Na}, \text{K}$) decomposes forming dense CuO on the particle surface (the color changes from light blue to deep grey), which resists further decomposition of the compounds.

The Na and K ions in the channel are mobile and can be partly replaced by Li ions in a melt of LiNO_3 at $285\text{ }^\circ\text{C}$. The lattice constants and chemical analysis of the ion-exchanged samples are listed in Table 1. Interestingly, the substitution of Na and K by Li leads to anisotropic expansion of the unit cell. A similar phenomenon was also observed for $\text{Na}_2\text{Co}_2\text{B}_{12}\text{O}_{21}$.⁹ The reason for the unit cell expansion caused by Li-substitution has not yet been fully understood. However, the structure refinements indicate that the lithium ions prefer the tetrahedral sites near the inner surface of the channel, which might be responsible for this anisotropic unit cell expansion.

The Cu^{2+} ions in $\text{NaCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ are antiferromagnetically coupled and the magnetic susceptibility data show a broad peak at about 50 K. At low temperatures, the magnetic susceptibility increases largely due to a paramagnetic impurity.

In summary, a new copper borate $\text{MCuB}_7\text{O}_{12}\cdot n\text{H}_2\text{O}$ ($M = \text{Na}, \text{K}$) which contains one-dimensional 14-ring channels can be synthesized by using an improved boric acid flux method. The framework is constructed of CuO_6 octahedra and triangular and tetrahedral borate groups, and alkaline metal ions and water molecules are located within the 14-ring channels. Since the linkage

Table 1 The lattice constants and chemical analysis of the ion-exchanged samples

Sample	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	Volume/ \AA^3
$\text{NaCuB}_7\text{O}_{12}$ (as-synthesized)	12.73720	4.69546	15.17928	907.827
$\text{Li}_{0.45}\text{Na}_{0.55}\text{CuB}_7\text{O}_{12}$ (Li^+ exchanged for 2 days)	12.72218	4.68598	15.30243	912.268
$\text{KCuB}_7\text{O}_{12}$ (as-synthesized)	12.64058	4.75296	15.38502	924.334
$\text{Li}_{0.65}\text{K}_{0.35}\text{CuB}_7\text{O}_{12}$ (Li^+ exchanged for 2 days)	12.65487	4.73482	15.47197	927.058

is saturated for all the atoms in the framework, the thermal stability is quite high. The alkali metal ions and water molecules in the channels are exchangeable representing behavior typical of microporous materials. The smaller channel counterpart ($M_2Cu_2B_{12}O_{21}$, $M = Na, K$) can be obtained by heating this phase at high temperature. Further investigation for the catalytic properties of these compounds is under way.

Notes and references

‡ Crystallographic study: The crystallographic study of $NaCuB_7O_{12} \cdot nH_2O$ was performed by X-ray powder diffraction techniques. The powder patterns can be readily indexed in orthorhombic cells by using TREOR90,¹¹ which produce an orthorhombic cell: $a = 12.73720(8) \text{ \AA}$, $b = 4.69546(3) \text{ \AA}$, $c = 15.17928(9) \text{ \AA}$, $V = 907.83(2) \text{ \AA}^3$. The systematic absences narrow the possible space groups to Pmm or $Pmm2$. The structure was established in the space group $Pnmm$ by using *ab initio* methods in TOPAS.¹² All of the atoms can be readily located and the structure was refined by Rietveld techniques. A six-term Chebyshev polynomial and a $1/2\theta$ term were used to model the background. The peak shapes were modeled with the pseudo-Voigt function. Soft restraints were applied to the thermal displacement parameters of the atoms. The final refinement converged to $R_p = 0.038$, $R_{wp} = 0.053$ and $gof = 3.623$, respectively. The structure of the K-analogue was refined by using the atomic parameters of $NaCuB_7O_{12} \cdot nH_2O$ as a starting set. The Rietveld refinement led to $a = 12.6406(2) \text{ \AA}$, $b = 4.75296(8) \text{ \AA}$, $c = 15.3850(2) \text{ \AA}$, $V = 924.33(4) \text{ \AA}^3$, $R_p = 0.0304$ and $R_{wp} = 0.050$. CCDC 273078 and 274697. See <http://dx.doi.org/10.1039/b506901g> for crystallographic data in CIF or other electronic format. The corresponding Rietveld plot and atomic parameters

are presented in the Supporting Materials for the as-synthesized $NaCuB_7O_{12} \cdot nH_2O$.†

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