Kinetics of Ion Transport through Supramolecular Channels in Single Crystals

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Reactions in single crystals of supramolecular assemblies are most often associated with the breaking of the crystals into polycrystalline or amorphous materials, induced by the major transformations and related strain during the reaction. The rare examples in which the single crystallinity is maintained in supramolecular compounds during the reaction are based on the neutral sorption and desorption of guest molecules in robust three-dimensional (3D) metal–organic frameworks (MOFs) or [2+2] photodimerization processes in organic compounds or coordination polymers. Ion-exchange reactions, as reported, for example, for zeolites and polycrystalline MOFs, are often incomplete and determined by methods such as atomic absorption spectroscopy and energy dispersive X-ray spectroscopy. While 3D MOFs have been compared to zeolites, we now show the generation of one-dimensional (1D) channel systems based on crown ether ligands which perform alkali cation transport in analogy to ion channels in biology and synthetic organic channels in membranes. Crown ether complexes with alkali metal ions have been described, yet the number of compounds in which this kind of ligand assembles into 1D stacks is extremely limited. In the current study we used trihalide anions of the type $X_3^-$, $X_2Y$ $^-$, and $XY_2$ $^-$ ($X$ = I, $Y$ = Br) as structural pillars, which induce the stacking of dibenzo[18]-crown-6 molecules (DB[18]C6, Figure 1). Single crystals of the resulting channel systems turned out to allow fast alkali cation exchange. To our knowledge, this is the first time that the activation energy for cation transport could be measured in supramolecular stacks. The crystals are very stable during these experiments as they remain unchanged in form and size.

Compound 1a, $[K_4(DB[18]C_6)_{8}(H_2O)_{8}(I_3)_{4}]$ (Figure 1) was obtained as large rodlike single crystals (monoclinic) from the reaction of KI with DB[18]C6. Amazingly, we observe three types of parallel and differently filled channels made up of DB[18]C6 molecules between quasi-linear chains of triiodide anions running along the b-axis (Figure 1).

Channel type C1 (Figure 2) is filled with linearly arranged, alternating water molecules and K$^+$ ions, the latter being placed in the cavity of the crown ether ligand. In channels of type C2, every second crown ether molecule remains empty, while the first is filled with a K$^+$ ion, to which two water molecules are coordinated in axial positions. A third channel type, C3, contains empty DB[18]C6 units with water molecules in between (Figure 2, left). In the unit cell, the orientation of the phenyl groups of the DB[18]C6 ligands is opposite in the two C2-type channels. Antiparallel stacks, running “up” and “down”, are also observed for channels C1 and C3. The crown ether molecules of channels C2 are almost
perfectly stacked with respect to the phenyl groups, while in C1 and C3 channels, the aromatic rings are offset by roughly 20°.

Compounds isostructural to 1a which also crystallized in the space group P2₁, 1b and 1c, were also obtained with the heterotrihalide ions Br₃⁻ and BrI⁻, respectively (see the Supporting Information). The trihalide ions are all quasi-linear, but tilted by about 12° relative to the b-axis, such that the interaction between the third halide of one anion can form a halogen bond to the first atom of the next trihalide.[9]

Based on the stacking of the crown ether moieties and the resulting channels, the structure of 1 seems to be predestined for cation transport. Thus, single crystals of 1a (results for 1b are given in the Supporting Information) were exposed to NaOH solutions. For example, a single crystal of 1a with dimensions of 0.37 cm × 0.1 cm × 0.1 cm was immersed in 1 M NaOH for 24 h, washed, and—unchanged in appearance—remeasured by single-crystal X-ray diffraction. The space group had changed to orthorhombic, Pccn with almost unmodified unit cell parameters. This is possible as the angle in 1a is very close to the required 90° for an orthorhombic system, allowing a smooth single-crystal-to-single-crystal transition. The new compound is found to be isostructural to 1a, thus, single crystals of 1a were both used, and the kinetic studies on the sodium ion transport gave the same results within the experimental error. The time dependence of the sodium ion concentration in compartment b at 296 K and 323 K, using compound 1b as an example, is shown in Figure 4 for 1a (see the Supporting Information). The conductivity increases linearly with the time, which is in agreement with the zero-order kinetic law. The values are corrected versus the

Figure 3. Device A used to measure Na⁺ conductivity.

We analyzed the transport of monovalent ions in 1a as a pseudo zero-order kinetic because the concentration of sodium ions in compartment a is extremely high, while that in compartment b increases only to a comparatively low value (Figure 3). The single crystals did not dissolve; their shape and their size persisted during the transport measurements. Determination of the rate constants k at two temperatures (k₁ and k₂) allowed the calculation of the activation energy Ɛ by the Arrhenius law [Eq. (1)], where R is the gas constant, E_a is the activation energy needed for ion transport, and A is a constant.

\[ k = Ae^{\frac{E_a}{RT}} \text{ or } \ln k = -\frac{E_a}{RT} + \ln A \]  

Compounds 1a and 1b were both used, and the kinetic studies on the sodium ion transport gave the same results within the experimental error. The time dependence of the sodium ion concentration in compartment b at 296 K and 323 K, using compound 1b as an example, is shown in Figure 4 for 1a (see the Supporting Information). The conductivity increases linearly with the time, which is in agreement with the zero-order kinetic law. The values are corrected versus the
Sodium ion concentration (mg L\(^{-1}\)) of [K\(_2\)(DB[18]C\(_6\)](H\(_2\)O)\(_2\)(Br\(_2\))(H\(_2\)O)]\(_{1\beta}\), showing the time dependence of Na\(^{+}\) conductivity at 296 and 323 K; error bars for three measurements.

Ionic conductivities obtained by using measurements in which the two reservoirs a and b contain ultrapure water. The conductivity at 323 K increased as expected more rapidly than that at 296 K. From the slopes (conductivity versus time), rate constants of \((1.8 \pm 0.2) \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}\) at 296 K and \((4.8 \pm 0.5) \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}\) at 323 K can be calculated for 1b. This leads to a ratio of \(k_1/k_2\) of 2.6 \pm 0.4. The ratio of the Na\(^{+}\) concentrations measured in compartment b after 7 h at both temperatures (Table 1) confirms this. For compound 1a, a value of 2.4 \pm 0.9 was obtained. The \(E_a\) value could therefore be determined to \((27 \pm 4) \text{ kJ mol}^{-1}\).[12] This fast sodium ion transport from water through a crystal of 1 is in accord with the low activation free energies of Na\(^{+}\) (log \(K = 1.16\)) and of K\(^{+}\) (log \(K = 1.67\))[13] for DB[18]C\(_6\) monomers in water as solvent. We interpret the ion-exchange reaction 1 → 2 as a gliding/hopping process of the ions through the channels of the single crystals with a low energy barrier between the individual cation sites inside the channels of the crystal lattice.

Interestingly, Na\(^{+}\) transport through the K\(^{+}\)-containing crystal of 1 is much faster than K\(^{+}\) transport through the Na\(^{+}\)-containing crystal 2. Using 1M KOH in compartment a of device A (Figure 3) leads to an ion-transport rate through crystal 2 of only ca. \(1 \times 10^{-6} \text{ mol L}^{-1} \text{s}^{-1}\) at 296 K (see the Supporting Information). This can be explained by the fact that in compound 1 three different channel types are present in the unit cell, one of which contains no cations and which can, in the initial step, bind sodium ions on the side where the single crystal is immersed in NaOH. This has to be the case as in the final structure of 2 no cation-free channels remain. Following this first binding of sodium ions, excess positive charge has to be eliminated. This is more likely to occur on the other end of the single crystal where ions are hydrated by pure H\(_2\)O rather than at the NaOH-containing side where they would compete with Na\(^{+}\), and hence a directed ion transport through the channels is induced. The K\(^{+}\) transport through 2 to give 1 is disfavored as all channels contain ions, out of which 25\% would have to become ion free. Thus, the different structures of the K\(^{+}\)-containing crystal 1 and the Na\(^{+}\)-containing crystal 2 explain the extremely different rates (factor 180 at 296 K) for the cation exchange.

The question arises whether lithium ions can also be transported/conducted through single crystals of the compound series 1, 2, and 3. Exposure of any of these single crystals to LiI or LiOH solutions either by immersion or by use of device A, however, led to decomposition of the single crystals into a white powder, most of which was identified as LiI and crown ether. This is mostly because the small cation Li\(^{+}\) destabilizes the trihalides and hence the pillars, which are apparently needed to maintain the solid-state scaffold structure. If these pillars are destroyed, the crown ether moieties no longer stack and the supramolecular assembly falls apart.

Conclusion: Trihalide ions can be used as structural pillars to assemble three differently filled supramolecular channels based on DB[18]C\(_6\). The K\(^{+}\)-containing single crystals of type 1 have a robust sublattice of crown ether stacks for Na\(^{+}\) exchange. Kinetic experiments at different temperatures show that these supramolecular crystals are excellent ion conductors.

### Table 1: Sodium ion concentration (mg L\(^{-1}\)) in compartment b after 7 h of sodium transfer through a single crystal of 1a and 1b (0.7 cm × 0.1 cm × 0.1 cm).

<table>
<thead>
<tr>
<th>Compound</th>
<th>296 K</th>
<th>323 K</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>0.30 ± 0.04</td>
<td>0.48 ± 0.05</td>
</tr>
<tr>
<td>1b</td>
<td>0.22 ± 0.04</td>
<td>0.58 ± 0.01</td>
</tr>
</tbody>
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[8] Under the same conditions Chekhlov obtained a compound described as [K(DB[18]C6)(H2O)]I3 with an orthorhombic space group Pccn, which we could not confirm. A. N. Chekhlov, Zh. Neorg. Khim. 2009, 54, 516 – 520. When we solved the structure of 1a, the orthorhombic space group was also proposed, but the monoclinic space group gives the best results. In addition, cautious heating of single crystals of 1a to 180°C for 2 h yields water-free crystals of 1a’, [K1(DB[18]C6)] (D8h), containing K+ ions and DB[18]C6 units as well as empty ones, thus indirectly confirming the initial presence of three channel types in 1a.


[10] The origin of the unit cell for 2a is now on the central halogen atom of the trihalide while it was on a K+ ion in 1a.

