Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information: Carboxylate Binding to Two Ions

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## Additional Geometries

In Fig. S1 the configuration for $n = 3$ that puts two Na atoms in 4-fold coordination by the O atoms is shown. This structure was created by starting with the optimized structure for a single Na and two acetates with has the single Na in a 4-fold coordination. The midpoint between the two O atoms of the bottom acetate is moved to the origin and the acetate is rotated 90 degrees. The top acetate and Na atom are copied via a mirror image in the z-plane (i.e. z $\rightarrow$ -z). In this way the O atoms and both Na atoms are in the tetrahedral coordination that is optimal for the single Na with two acetates. For this structure $\Delta G = -303$ kcal/mol which is much higher than the -341 kcal/mol of the optimal structural.

The $n = 4$ structure for Na is similar to that for K and Cs, but has 1 3-fold coordinated ion and 1 4-fold coordinated. In Figure S2, which shows the geometry of the Na case with 4 acetates, the O atom labeled 10 in the figure is the key difference. For both Na and K 10 binds to cation atom 16, but for K it also binds to other cation, atom 1. For Na the

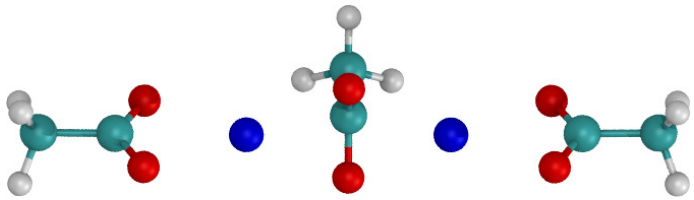

Figure S1: Configuration for two Na atoms (blue) and 3 acetate with both Na atoms having 4 fold coordination with the O atoms.

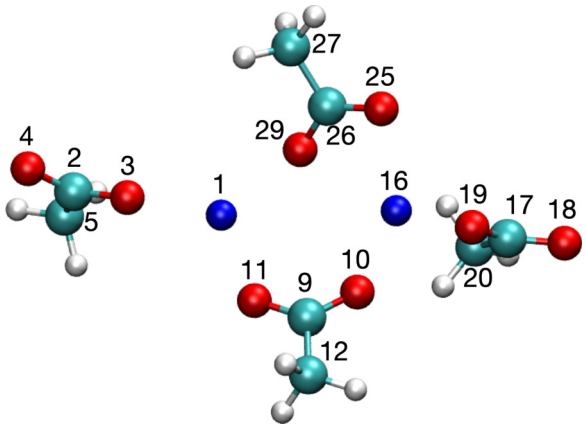


Figure S2: Optimized configuration for four acetates ($n = 4$) for Na. Labels are used for distances in Table S4.

1:10 distance is 3.599Å compared to 2.240Å and 2.283Å for the 1:11 and 10:16 distances, respectively. For the K and Cs $n = 4$ cases, the atoms 1, 29, 16 and 10 almost form a square (it is a coplanar rectangle). In contrast, for Na atoms 1, 29, 16, 10, 11 form a pentagon. For the Na case, a rotation of the ligand containing O atoms 10 and 11, will transform the structure into a structure equivalent to the K structure. However, as stated in the main text, this structure has a higher free energy.

## Data Tables

Table S1: Free energies ($\Delta G$ in kcal/mol) for formation of ion-ligand complexes composed of two monovalent ions and $n$ acetate ligands in a low dielectric environment ($\epsilon = 1$)

| $n$ | Li | Na | K | Cs |
|---|---|---|---|---|
| 1 | -210.1 | -173.9 | -148.1 | -92.1 |
| 2 | -362.9 | -307.0 | -261.7 | -152.8 |
| 3 | -397.0 | -343.1 | -295.0 | -147.0 |
| 4 | -359.0 | -309.8 | -264.6 | -89.1 |

Table S2: Distances (in Å) between atom pairs of types A:B in optimized structures for $n = 1$. X represents cation. Indices are given in Fig. 1.

| indices | A | B | Li | Na | K | Cs |
|---|---|---|---|---|---|---|
| 1:9 | X | X | 5.253 | 5.992 | 6.680 | 7.552 |
| 1:4 | X | O | 1.696 | 2.054 | 2.401 | 2.839 |
| 3:9 | X | O | 1.695 | 2.054 | 2.399 | 2.839 |
| 2:3 | C | O | 1.266 | 1.265 | 1.265 | 1.264 |
| 2:4 | C | O | 1.264 | 1.265 | 1.264 | 1.265 |
| 2:5 | C | C | 1.510 | 1.520 | 1.525 | 1.532 |

Table S3: Distances (in Å) between atom pairs of types A:B in optimized structures for $n = 2$. X represents cation. Indices are given in Fig. 2.

| indices | A | B | Li | Na | K | Cs |
|---|---|---|---|---|---|---|
| 1:9 | X | X | 2.794 | 3.130 | 3.797 | 4.575 |
| 1:4 | X | O | 1.767 | 2.153 | 2.517 | 2.967 |
| 1:11 | X | O | 1.808 | 2.239 | 2.604 | 3.047 |
| 1:12 | X | O | 2.859 | 2.410 | 2.745 | 3.228 |
| 2:3 | C | O | 1.288 | 1.283 | 1.258 | 1.278 |
| 2:4 | C | O | 1.255 | 1.259 | 1.282 | 1.258 |
| 2:5 | C | C | 1.511 | 1.519 | 1.525 | 1.532 |
| 9:3 | X | O | 1.909 | 2.239 | 2.604 | 3.047 |
| 9:4 | X | O | 2.142 | 2.410 | 2.745 | 3.228 |
| 9:12 | X | O | 1.809 | 2.153 | 2.517 | 2.967 |
| 10:11 | C | O | 1.271 | 1.259 | 1.258 | 1.258 |
| 10:12 | C | O | 1.269 | 1.283 | 1.282 | 1.278 |
| 10:13 | C | C | 1.516 | 1.519 | 1.525 | 1.532 |

Table S4: Distances (in Å) between atom pairs of types A:B in optimized structures for $n = 3$. X represents cation. Indices are given in Fig. 3.

| indices | A | B | Li | Na | K | Cs |
|---|---|---|---|---|---|---|
| 1:16 | X | X | 5.025 | 3.286 | 3.883 | 4.628 |
| 1:3 | X | O | 1.972 | 2.351 | 2.695 | 3.157 |
| 1:4 | X | O | 1.973 | 2.302 | 2.665 | 3.114 |
| 1:11 | X | O | 1.829 | 2.303 | 2.666 | 3.114 |
| 1:10 | X | O | | 2.351 | 2.696 | 3.157 |
| 3:16 | X | O | | 2.289 | 2.672 | 3.143 |
| 16:10 | X | O | 1.803 | 2.289 | 2.676 | 3.143 |
| 16:18 | X | O | 1.970 | 2.333 | 2.684 | 3.141 |
| 16:19 | X | O | 1.970 | 2.333 | 2.684 | 3.141 |
| 2:3 | C | O | 1.270 | 1.272 | 1.273 | 1.272 |
| 2:4 | C | O | 1.270 | 1.265 | 1.263 | 1.263 |
| 2:5 | C | C | 1.526 | 1.527 | 1.532 | 1.537 |
| 9:10 | C | O | 1.262 | 1.272 | 1.273 | 1.272 |
| 9:11 | C | O | 1.261 | 1.265 | 1.263 | 1.263 |
| 9:12 | C | C | 1.529 | 1.527 | 1.532 | 1.537 |
| 17:18 | C | O | 1.271 | 1.267 | 1.267 | 1.266 |
| 17:19 | C | O | 1.270 | 1.267 | 1.267 | 1.266 |
| 17:20 | C | C | 1.525 | 1.535 | 1.539 | 1.543 |

Table S5: Distances (in Å) between atom pairs of types A:B in optimized structures for $n = 4$. X represents cation. Indices are given in Fig. 4.

| indices | A | B | Li | Na | K | Cs |
|---|---|---|---|---|---|---|
| 1:16 | X | X | 3.919 | 3.822 | 4.111 | 4.914 |
| 1:3 | X | O | 1.871 | 2.178 | 2.559 | 3.021 |
| 1:11 | X | O | 1.894 | 2.240 | 2.761 | 3.216 |
| 1:29 | X | O | 1.904 | 2.245 | 2.662 | 3.109 |
| 1:10 | X | O | | 3.597 | 2.840 | 3.346 |
| 16:10 | X | O | 1.893 | 2.283 | 2.662 | 3.106 |
| 16:19 | X | O | 1.872 | 2.207 | 2.559 | 3.022 |
| 16:25 | X | O | 1.904 | 2.407 | 2.760 | 3.338 |
| 16:29 | X | O | | 2.490 | 2.841 | 3.217 |
| 2:3 | C | O | 1.275 | 1.271 | 1.271 | 1.269 |
| 2:4 | C | O | 1.252 | 1.252 | 1.254 | 1.255 |
| 2:5 | C | C | 1.545 | 1.549 | 1.550 | 1.552 |
| 9:10 | C | O | 1.262 | 1.258 | 1.271 | 1.270 |
| 9:11 | C | O | 1.261 | 1.266 | 1.260 | 1.260 |
| 9:12 | C | C | 1.539 | 1.541 | 1.539 | 1.543 |
| 17:18 | C | O | 1.253 | 1.254 | 1.254 | 1.255 |
| 17:19 | C | O | 1.274 | 1.269 | 1.271 | 1.269 |
| 17:20 | C | C | 1.545 | 1.550 | 1.550 | 1.552 |
| 26:25 | C | O | 1.261 | 1.257 | 1.260 | 1.260 |
| 26:29 | C | O | 1.261 | 1.274 | 1.271 | 1.270 |
| 26:27 | C | C | 1.539 | 1.535 | 1.539 | 1.543 |

[a] top structure in Fig. 4, lowest $G$.
[b] bottom structure in Fig. 4.