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


# Supplementary Information: Binding of Carboxylate and Water to Monovalent Cations

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## Data Tables and Files

Coordinate files (xyz format) for the optimized geometries are available in a separate zip file (xyzfiles.zip). The files are labeled X_nmk.xyz, where X identifies the cation (Li, Na, or K), and n, m and k are the number of acetates, waters and cations (0 or 1), respectively. For example, K_231.xyz is the file for the complex with 2 acetates, 3 waters and one $K^+$.

The binding free energies are given for the ion-ligand complexes for each ion type in Table S1 and plotted in Fig. 1.

Table S1: Free energies ($\Delta G$ in kcal/mol) for formation of ion-ligand complexes composed of a monovalent cation, $n_{\mathrm{A}}$ acetate ligands and $n_{\mathrm{W}}$ waters.

| $n_{\mathrm{A}}$ | $n_{\mathrm{W}}$ | $\Delta G(\mathrm{Li}^+)$ | $\Delta G(\mathrm{Na}^+)$ | $\Delta G(\mathrm{K}^+)$ |
|---|---|---|---|---|
| 0 | 1 | -25.6 | -16.1 | -10.4 |
| 0 | 2 | -45.9 | -29.9 | -18.7 |
| 0 | 3 | -59.3 | -38.5 | -26.2 |
| 0 | 4 | -67.2 | -44.8 | -28.8 |
| 0 | 5 | -66.0 | -42.0 | -25.7 |
| 0 | 6 | -65.5 | -42.7 | -26.0 |
| 0 | 7 | -68.7 | -44.5 | -28.5 |
| 0 | 8 | -68.7 | -45.9 | -29.9 |
| 1 | 0 | -158.7 | -134.3 | -118.1 |
| 1 | 1 | -166.7 | -141.8 | -123.4 |
| 1 | 2 | -173.1 | -147.5 | -130.5 |
| 1 | 3 | -178.2 | -151.1 | -131.8 |
| 1 | 4 | -179.2 | -152.8 | -133.8 |
| 1 | 5 | -181.3 | -155.6 | -136.0 |
| 1 | 6 | -179.2 | -153.4 | -134.9 |
| 2 | 0 | -198.2 | -172.4 | -154.1 |
| 2 | 1 | -202.3 | -175.6 | -157.4 |
| 2 | 2 | -206.2 | -178.8 | -160.7 |
| 2 | 3 | -209.2 | -182.1 | -163.4 |
| 2 | 4 | -211.6 | -185.5 | -165.9 |
| 2 | 5 | -210.8 | -186.7 | -166.1 |
| 3 | 0 | -145.9 | -120.7 | -104.4 |
| 3 | 1 | -156.2 | -129.0 | -112.4 |
| 3 | 2 | -160.8 | -136.7 | -118.2 |
| 3 | 3 | -166.1 | -142.8 | -123.2 |
| 3 | 4 | -171.7 | -147.1 | -128.5 |
| 4 | 0 | -37.5 | -21.2 | -11.6 |
| 4 | 1 | -51.6 | -32.9 | -20.9 |
| 4 | 2 | -65.3 | -44.5 | -31.3 |
| 4 | 3 | -65.9 | -46.5 | -33.5 |

The basis set superposition error (BSSE) has been calculated for selected cases, including the most optimal structures for each cation. Table S2 lists the BSSE values. For medium sized systems, such as 2 acetates and 2 waters binding to a cation, the BSSE value is between 1 and 2 kcal/mol. For larger systems, BSSE increases above 3 kcal/mol. These values are small compared to the magnitude of $\Delta G$ and the differences between $\Delta G$ for adding or subtracting a ligand. Consequently, they do not affect the dependencies and derived conclusions.

Table S2: The basis set superposition error (BSSE) in kcal/mol for selected cases.

| ion | $n_{\mathrm{A}}$ | $n_{\mathrm{W}}$ | BSSE |
|---|---|---|---|
| Li | 1 | 1 | 0.62 |
| Na | 1 | 1 | 0.76 |
| K | 1 | 1 | 1.05 |
| Li | 2 | 2 | 1.67 |
| Na | 2 | 2 | 1.57 |
| K | 2 | 2 | 1.73 |
| Li | 2 | 4 | 2.80 |
| Na | 2 | 4 | 3.02 |
| K | 2 | 4 | 3.41 |

To test the use of the hybrid $\omega$B97X-D approximation to the exchange-correlation energy, calculations using Moeller-Plesset perturbation theory (MP2) were performed. In Table S3, the values for the MP2 calculations are given, and in Table S4, the values for the $\omega$B97X-D calculations are given. The differences in $\Delta H$ between the two methods are given in Table S5. These differences are larger for $K^+$.

At $n_{\mathrm{A}} = 1$, the optimized structures are similar. The difference is thus due to the energy calculation for the two methods. Therefore, we performed calculations with different combinations of functional and basis set for the $n_{\mathrm{A}}$=1 and $K^+$ complex. Extending the basis set to aug-cc-pvTz, $\Delta H = -128.6$ kcal/mol. Using $\omega$B97X-D and the basis set 6-311+G(2df,2pd), $\Delta H = -127.4$ kcal/mol. Changing the functional to B3LYP with the aug-cc-pvDz basis set yields $\Delta H = -128.0$ kcal/mol. These values are all close to the value in Table S4 for $\omega$B97X-D.

way off!

Table S3: Binding free energies in kcal/mol for MP2 calculations.

| $n_A$ | $\Delta H(Li^+)$ | $\Delta H(Na^+)$ | $\Delta H(K^+)$ |
|---|---|---|---|
| 1 | -166.2 | -140.0 | -111.9 |
| 2 | -217.5 | -188.1 | -161.3 |
| 3 | -177.4 | -148.2 | -123.1 |
| 4 | -85.2 | | -46.0 |

Table S4: Binding free energies in kcal/mol for $\omega$B97XD DFT calculations.

| $n_A$ | $\Delta H(Li^+)$ | $\Delta H(Na^+)$ | $\Delta H(K^+)$ |
|---|---|---|---|
| 1 | -166.5 | -142.0 | -125.1 |
| 2 | -216.7 | -190.8 | -169.7 |
| 3 | -177.2 | -150.7 | -130.9 |
| 4 | -83.1 | -64.4 | -51.2 |

Table S5: Differences in binding free energies in kcal/mol between $\omega$B97XD DFT and MP2.

| $n_A$ | $Li^+$ | $Na^+$ | $K^+$ |
|---|---|---|---|
| 1 | 0.3 | 2.0 | 13.2 |
| 2 | -0.8 | 2.7 | 8.4 |
| 3 | -0.2 | 2.5 | 7.8 |
| 4 | -2.1 | | 5.2 |

Calculations of single point CCSD(T) energies have a similar comparison. Table S6 shows a comparison for $Na^+$ up to 4 acetates. The differences in $\Delta H$ are slightly larger than that found for $Na^+$ interaction with water. For 4 waters and $Na^+$, Soniat et al. calculated $\Delta H = -74.8$ kcal/mol for $\omega$B97X-D vs. -73.3 kcal/mol for CCSD(T), which is a -1.5 kcal/mol difference. For $Na^+$ interacting with acetates, the differences are -2.1, -3.4, -2.7 and -1.9 kcal/mol. Table S7 gives the CCSD(T) data for $K^+$. Like the MP2 data, the differences are larger for $K^+$.

Table S6: Comparison of enthalpies between ωB97X-D DFT and CCSD(T) calculations for $Na^+$. Values in kcal/mol.

| $n_A$ | $H$(wB) | $\Delta H$(wB) | $H$(CCSD) | $\Delta H$(CCSD) |
|---|---|---|---|---|
| 1 | -390.8 | -143.6 | -389.9 | -141.5 |
| 2 | -619.4 | -193.2 | -618.0 | -189.8 |
| 3 | -847.8 | -154.1 | -845.9 | -151.4 |
| 4 | -1076.1 | -68.7 | -1073.8 | -66.8 |

Table S7: Comparison of enthalpies between ωB97X-D DFT and CCSD(T) calculations for $K^+$. Values in kcal/mol.

| $n_A$ | $H$(wB) | $\Delta H$(wB) | $H$(CCSD) | $\Delta H$(CCSD) |
|---|---|---|---|---|
| 1 | -828.4 | -126.3 | -827.2 | -107.0 |
| 2 | -1057.0 | -171.7 | -1055.3 | -161.7 |

Figures S1-S9 provide images of additional geometries of the complexes. Figures S10-12 provide plots of the full ChelpG data.

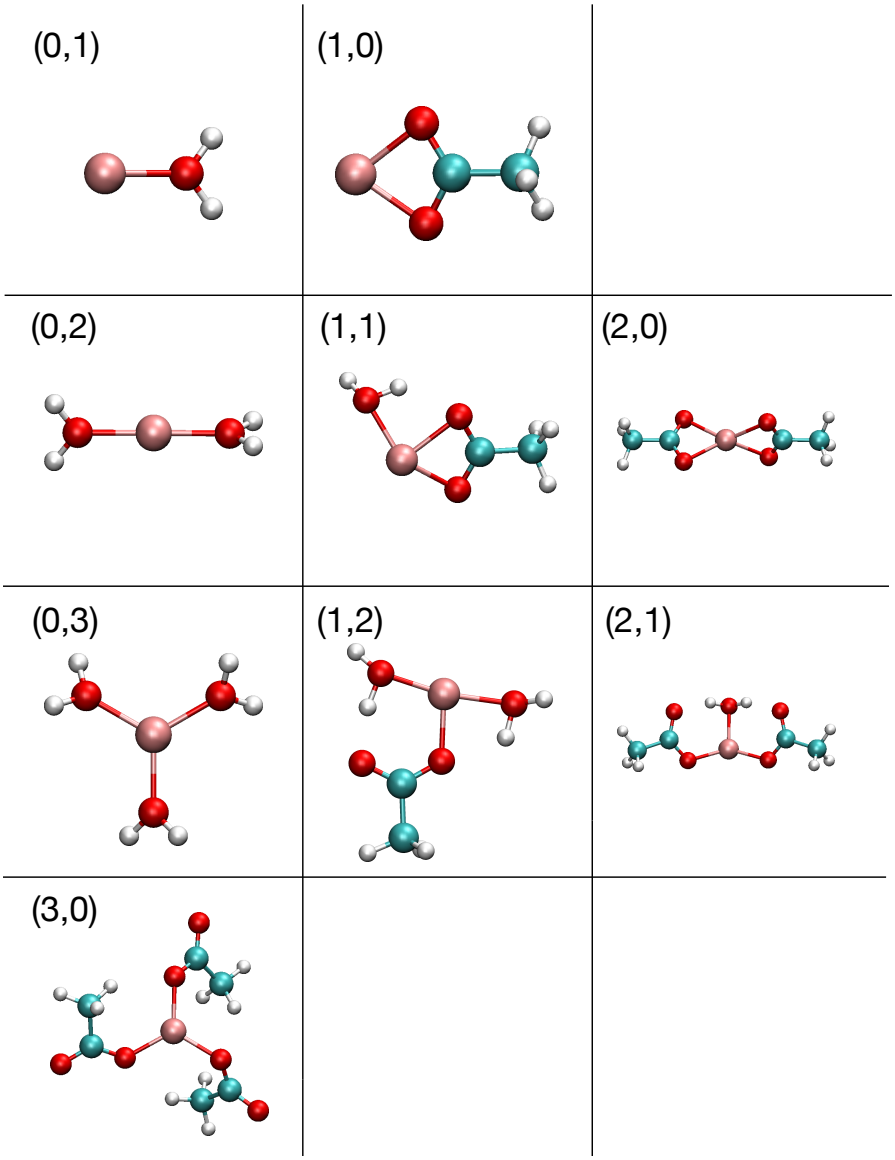


Figure S1: Optimal configurations for $Li^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). In this and all configuration figures: oxygen is red; hydrogen is white; carbon is cyan. Lithium is pink. This figure shows cases for $n_A + n_W = 1$ to 3.

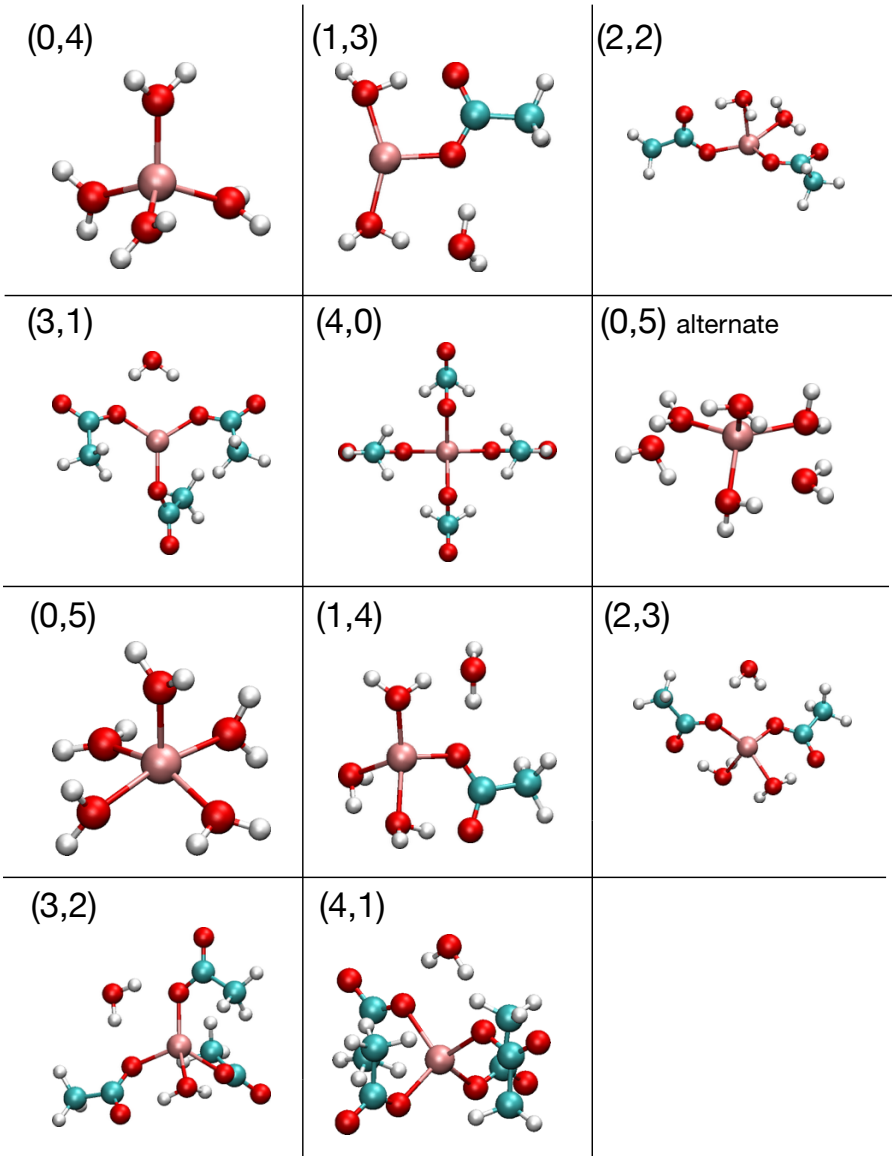


Figure S2: Optimal configurations for $Li^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). This figure shows cases for $n_A + n_W = 4$ to 5.

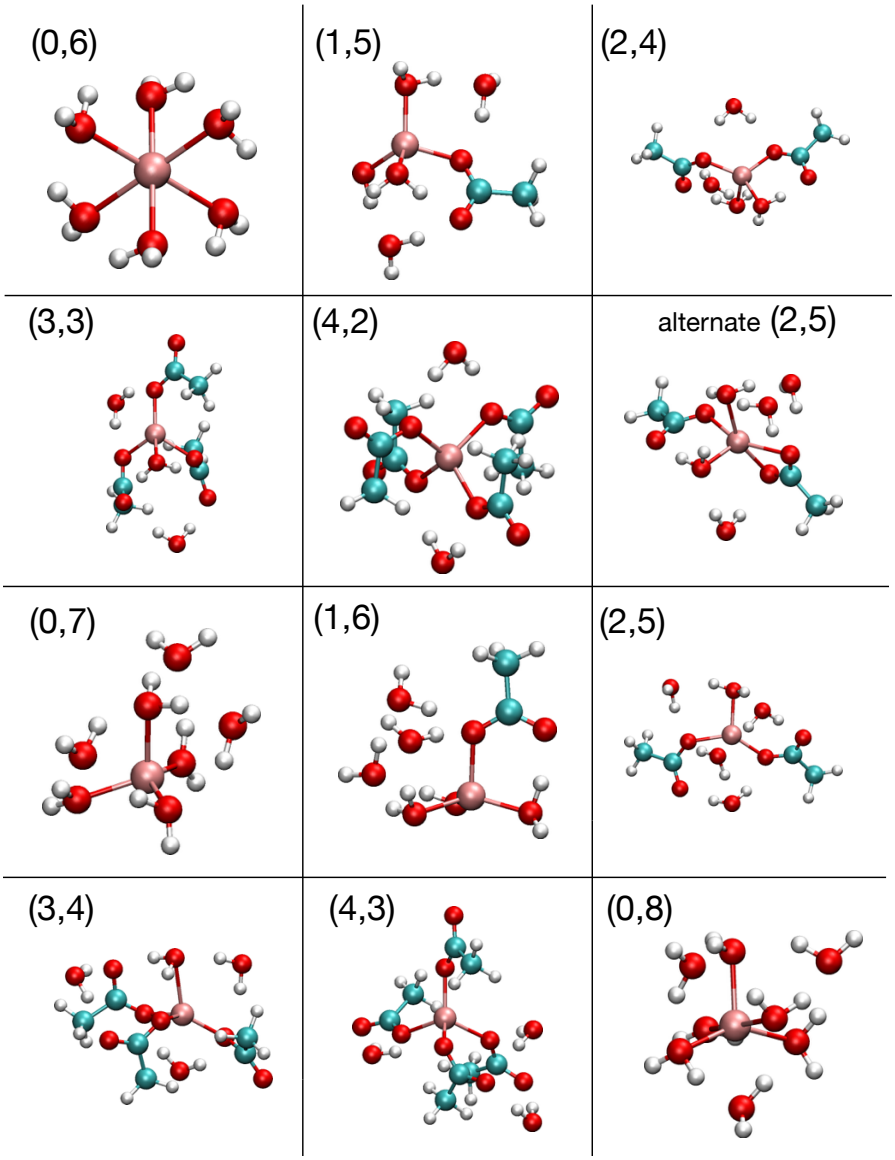


Figure S3: Optimal configurations for $Li^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). This figure shows cases for $n_A + n_W = 6$ to 8.

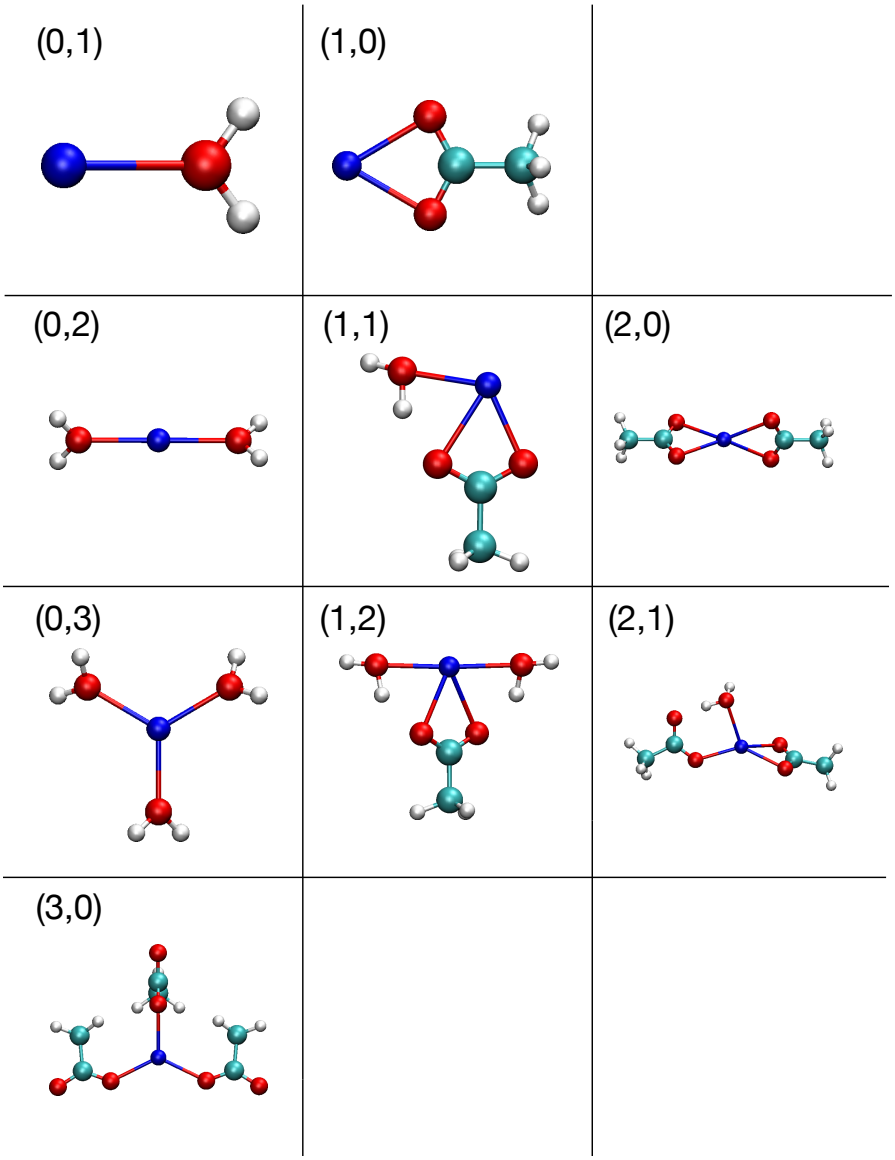


Figure S4: Optimal configurations for $Na^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). Sodium is blue. This figure shows cases for $n_A + n_W = 1$ to 3.

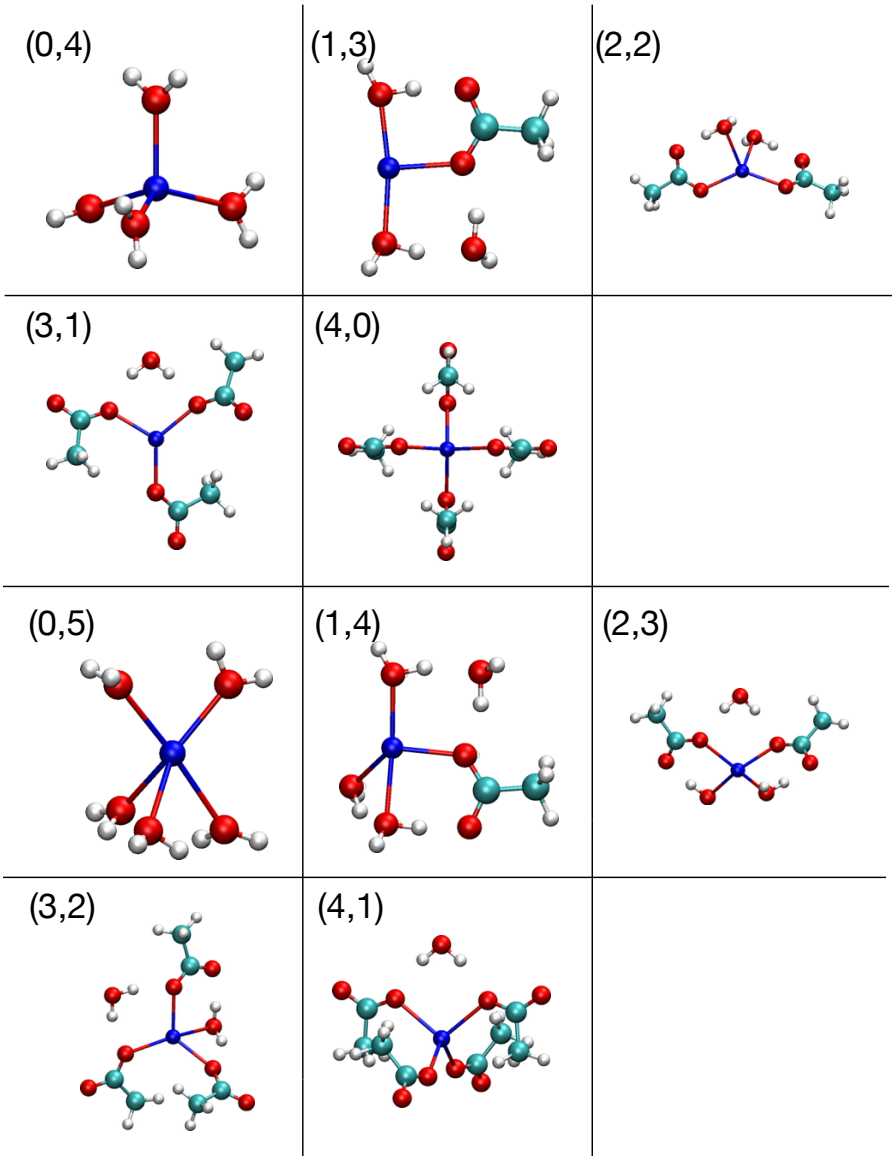


Figure S5: Optimal configurations for $Na^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). This figure shows cases for $n_A + n_W = 4$ to 5.

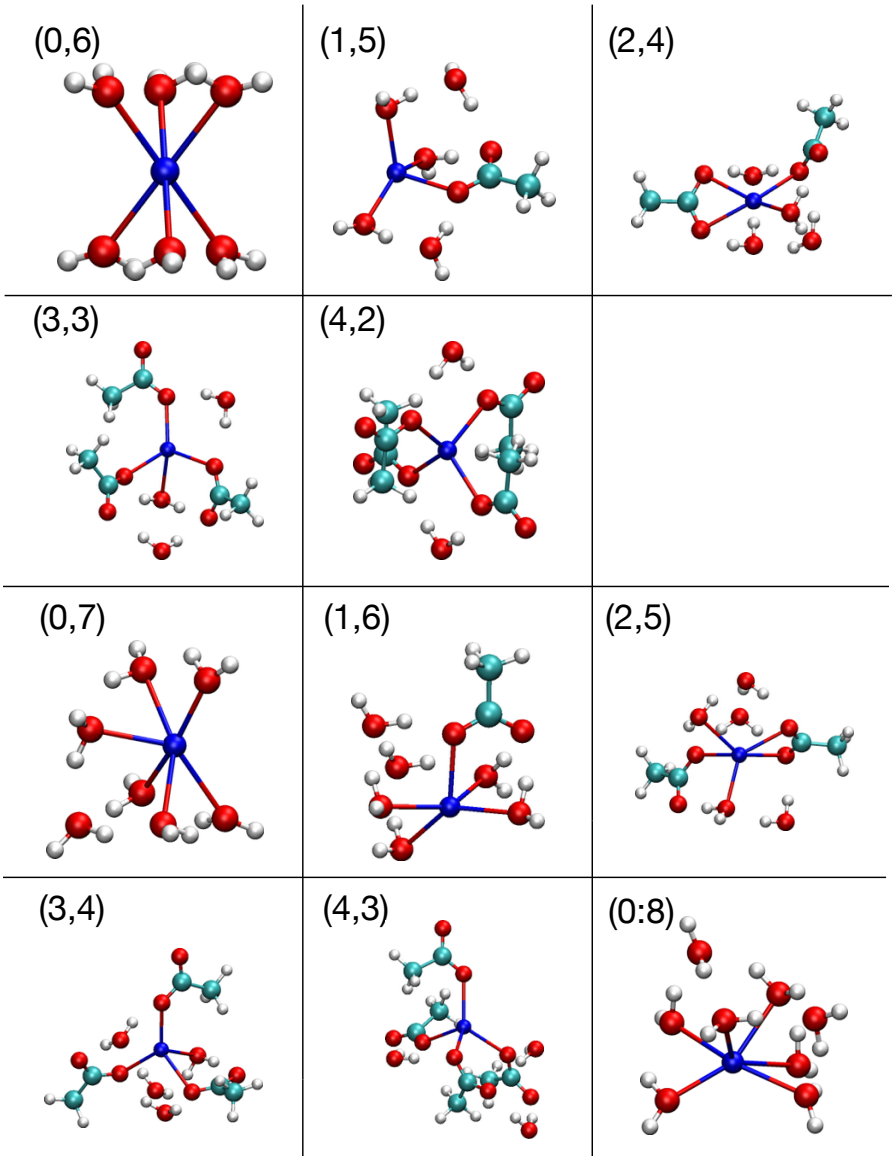


Figure S6: Optimal configurations for $Na^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). This figure shows cases for $n_A + n_W = 6$ to 8.

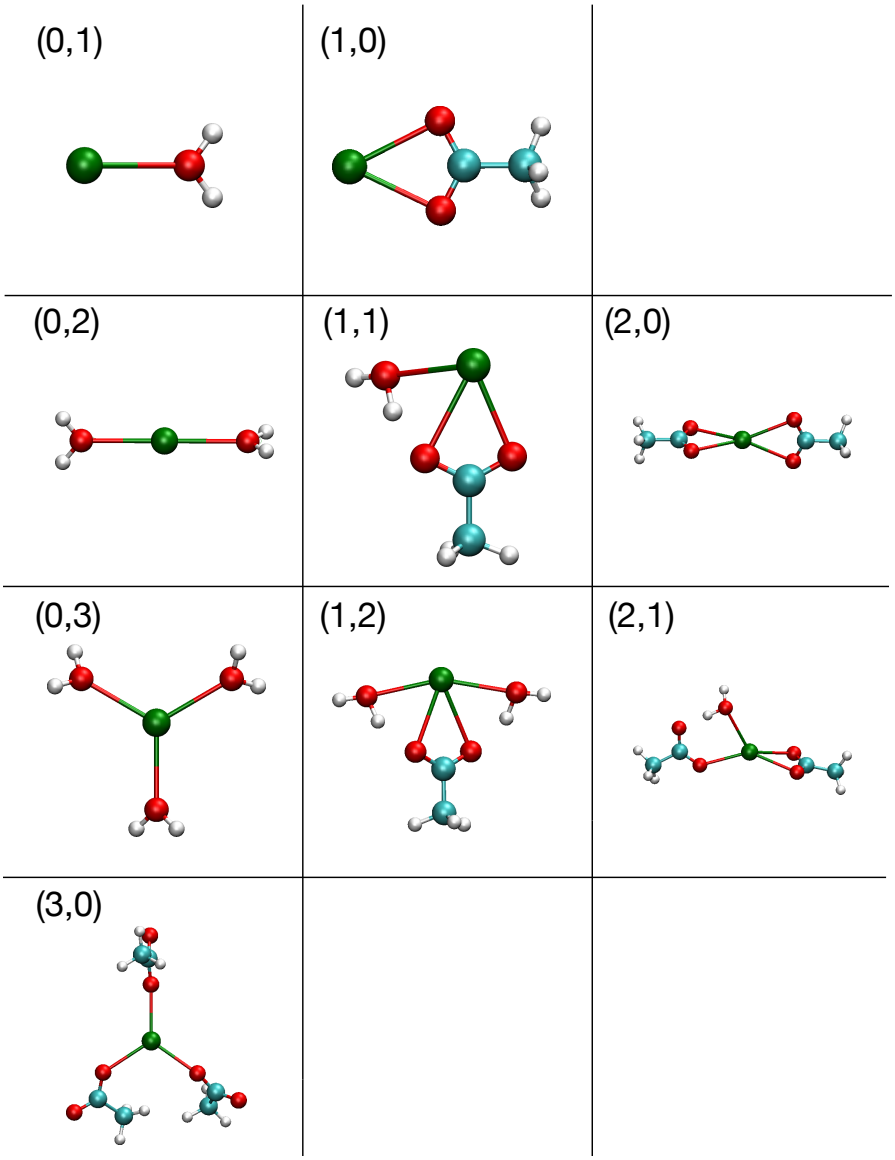


Figure S7: Optimal configurations for $K^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). Potassium is green. This figure shows cases for $n_A + n_W = 1$ to 3.

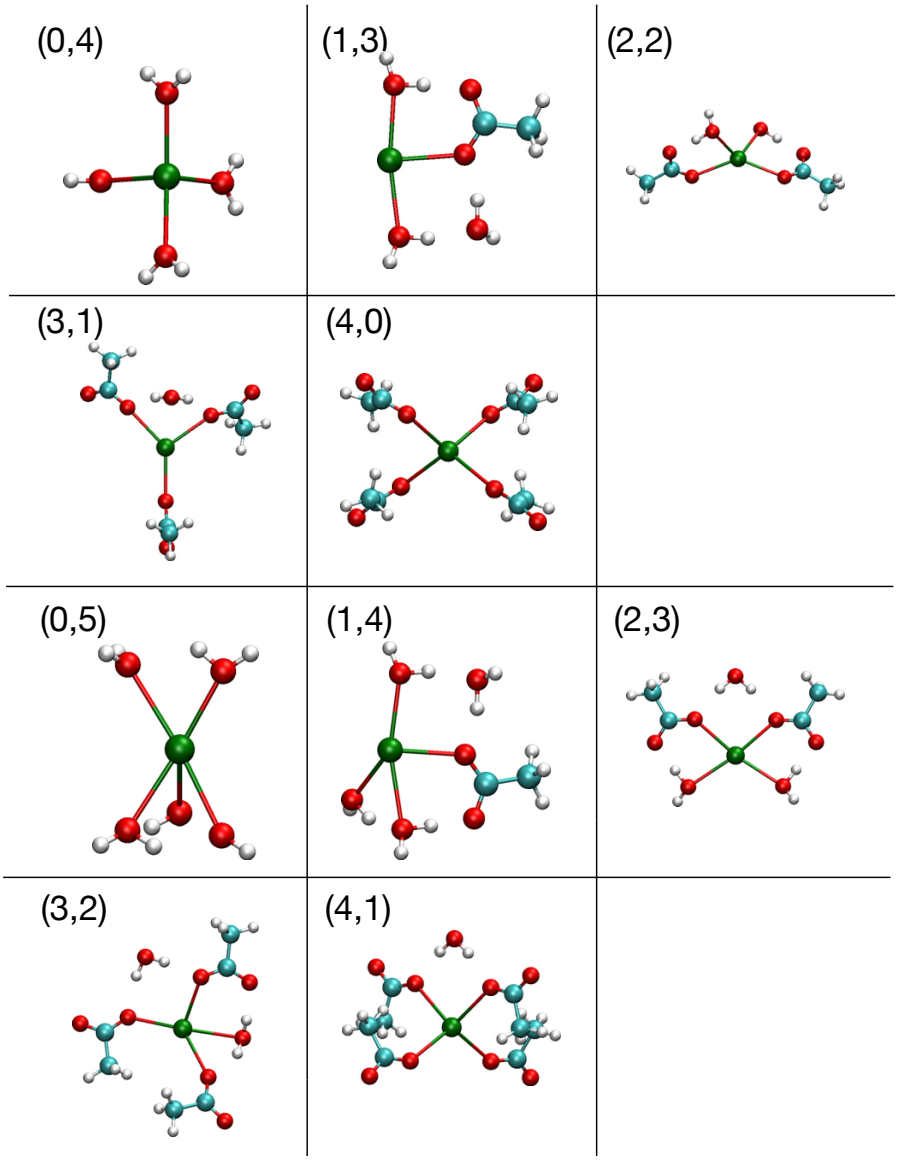


Figure S8: Optimal configurations for $K^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). This figure shows cases for $n_A + n_W = 4$ to 5.

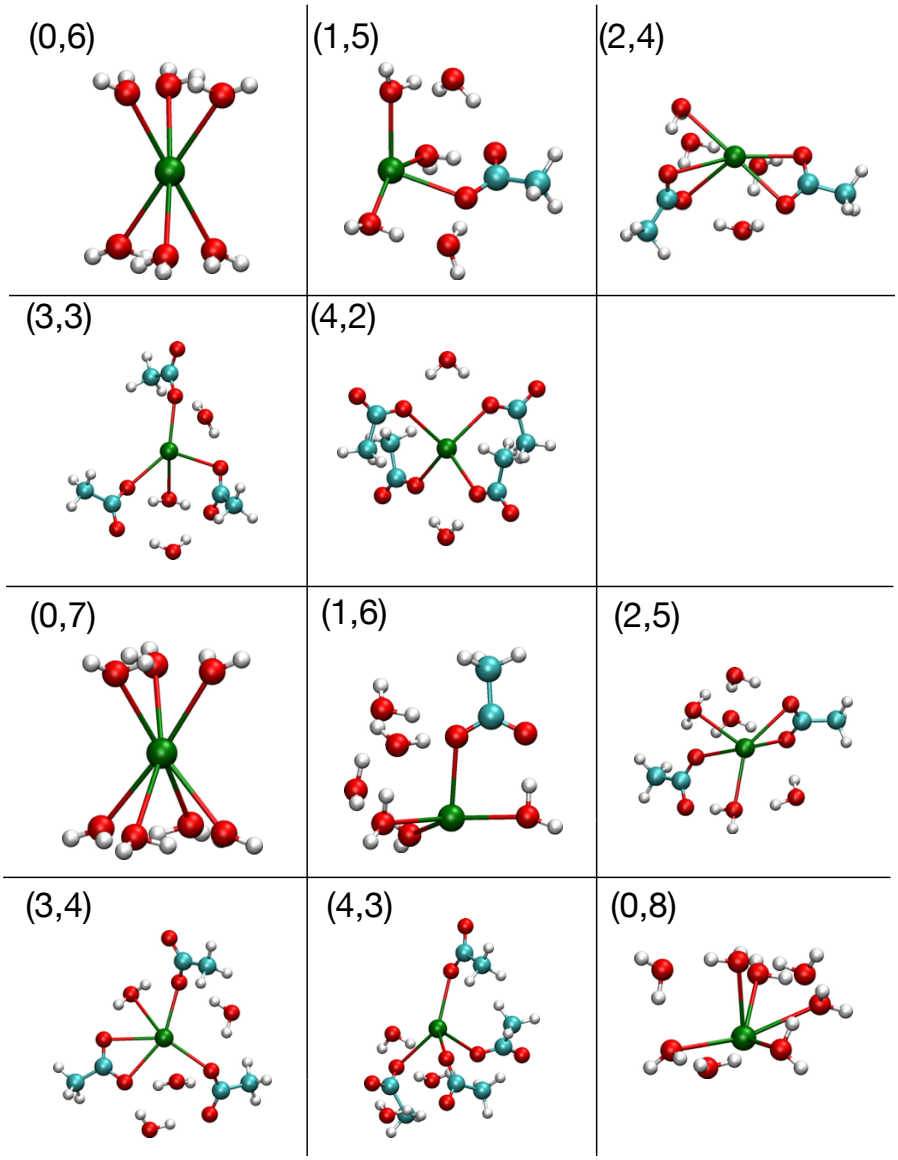


Figure S9: Optimal configurations for $K^+$ complexes with acetate and water. The number of acetates $n_A$ and number of waters $n_W$ are represented at ($n_A$,$n_W$). This figure shows cases for $n_A + n_W = 6$ to 8.

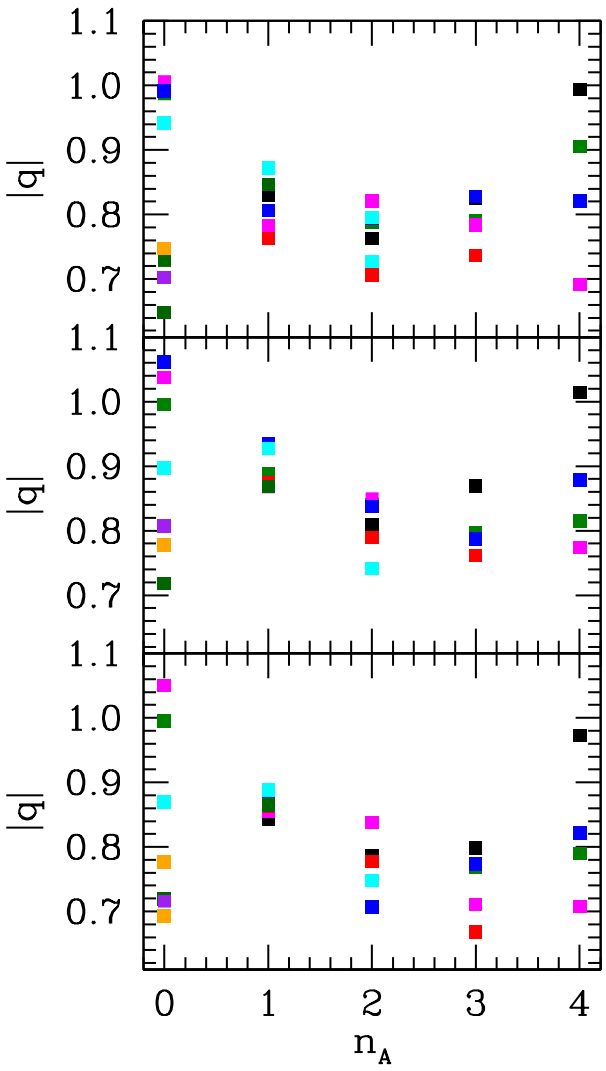


Figure S10: ChelpG charges for cations as a function of $n_{\mathrm{A}}$. From top to bottom the cation is Li, Na, and K. The number of waters is indicated by the color: 0:black, 1:green, 2:magenta, 3:blue, 4:red, 5:cyan, 6:darkgreen, 7:purple, 8:orange.

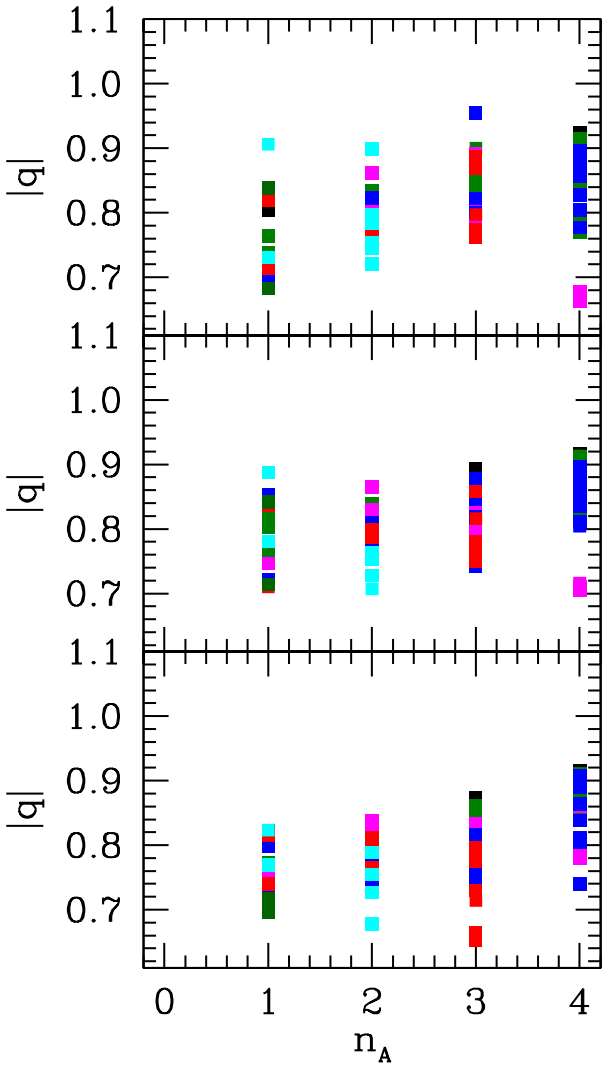


Figure S11: ChelpG charges for carboxylate oxygen atoms as a function of $n_{\mathrm{A}}$ and $n_{\mathrm{W}}$. From top to bottom the cation is Li, Na, and K. Same colors as Fig. S10.

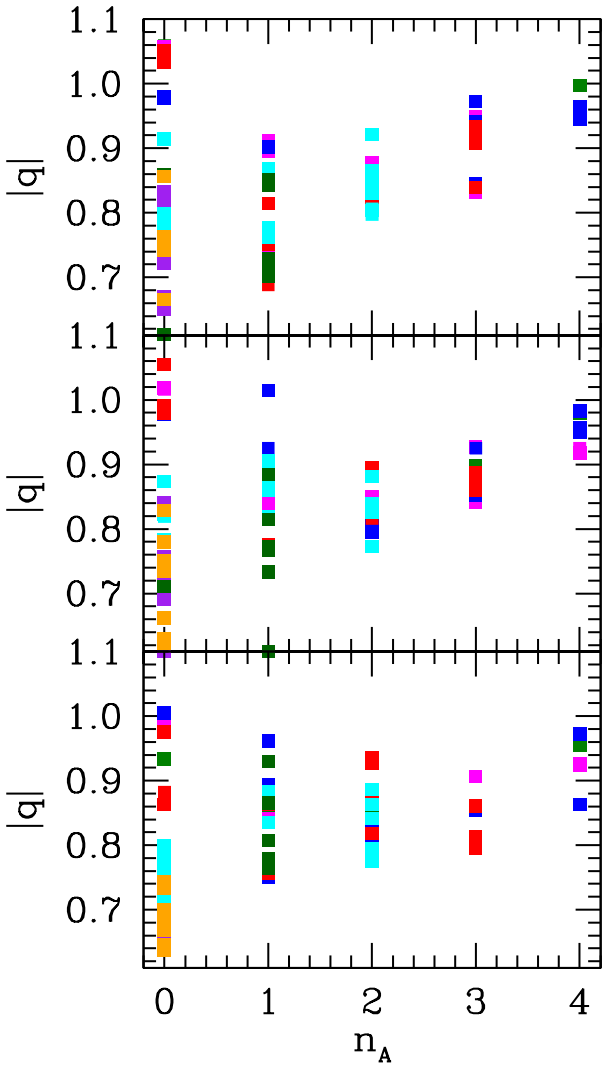


Figure S12: ChelpG charges for water oxygen atoms as a function of $n_{\mathrm{A}}$ and $n_{\mathrm{W}}$. From top to bottom the cation is Li, Na, and K. Same colors as Fig. S10.