A Cold Spectroscopic Study on Metal Ion–Benzo-Crown Ether Complexes in the Gas Phase

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PACIFICHEM 2015, “Dissociation of Biomolecules in the Gas Phase for Structural Characterization” (#352)
20/12/2015
DB18C6 captures $K^+$ selectively in water.

$$M^+ + DB18C6 \rightleftharpoons M^+\cdot DB18C6$$

in water, 298 K

Our final goal is to reveal the origin of ion selectivity spectroscopically.
ΔH for Complex Formation

Bare complexes cannot explain the ion selectivity in solution.

\[ M^+ + \text{DB18C6} \xleftrightarrow{\Delta H} M^+ \cdot \text{DB18C6} \]

Solvent effects play important roles for the ion selectivity.

Properties of complexes reflect selectivity?

Energy

$\Delta G$

Structure?

Isomers?

guest  host

+
Our Studies on Host-Guest Complexes

“Solvated” Host-Guest Complexes

“Cold” Spectroscopy in the Gas Phase

IR Spectroscopy on Gold Surface
Cold Spectroscopy in the Gas Phase

This Study

- $M^+\cdot DB18C6\cdot (H_2O)_n$
- $M^{2+}\cdot B15C5\cdot L$, $M^{2+}\cdot B18C6\cdot L$ \hspace{1cm} (L = H$_2$O, CH$_3$OH)

- UV and IR spectroscopy in a cold, 22-pole ion trap
- Relation between ion selectivity and properties of ion complexes.
UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.

- Produce ion complexes with electrospray
- Select one species with 4-pole mass
- Cool down and irradiate UV laser to them in 22-pole ion trap
- Detect fragment ions with 4-pole mass
All the complexes show sharp UV bands. Conformer-specific IR spectra can be measured.

Conformer-specific IR spectra can be measured by IR-UV double-resonance.

UV spectra

![Diagram of UV spectra with peaks labeled A, B, C, and D.]

![Energy level diagram with S0, S1, IR, and UV transitions.]
IR Spectra of $\text{M}^+ \cdot \text{DB18C6}$

Different IR features originate from different conformers.

Inokuchi et al., *JACS*, 2011, **133**, 12256.
Structure of $M^+\cdot DB18C6$ ($M^+ = Li^+, Na^+$)

UV Wavenumber (cm$^{-1}$)

M$^+ = Li^+$

Na$^+$

K$^+$

Rb$^+$

Cs$^+$

Ether rings distorted for Li$^+$ and Na$^+$

M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.
Structure of $M^+\cdot$DB18C6  ($M^+ = K^+, Rb^+, Cs^+$)

Oscillator Strength

UV Wavenumber (cm$^{-1}$)

M05-2X/6-31+G(d) with Stuttgart RLC ECP
A scaling factor of 0.8340 is used.

Ether rings largely open

K$^+$  in the ring

Rb$^+$, Cs$^+$  on the ring
Structure of $M^+\cdot$DB18C6 ($M^+ = K^+, Rb^+, Cs^+$)

*Distance between $M^+$ and DB18C6 becomes longer with increasing ion size.*

<table>
<thead>
<tr>
<th>Ion radii/Å</th>
<th>$K^+$</th>
<th>1.52</th>
<th>0.51</th>
<th>K-a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Rb^+$</td>
<td>1.66</td>
<td>1.00</td>
<td>1.00</td>
<td>Rb-a</td>
</tr>
<tr>
<td>$Cs^+$</td>
<td>1.81</td>
<td>1.36</td>
<td>1.36</td>
<td>Cs-b</td>
</tr>
</tbody>
</table>
UV Spectra of $\text{K}^+ \cdot \text{DB18C6} \cdot (\text{H}_2\text{O})_n$

UV spectra also show sharp bands. Conformer-specific IR spectra can be measured.
Conformers of $\text{K}^+\cdot\text{DB18C6}\cdot(\text{H}_2\text{O})_3$

Two conformers for $\text{K}^+$. 

Inokuchi et al., *JACS*, 2014, 136, 1815.
Conformers of $\text{M}^+\cdot\text{DB18C6}\cdot(\text{H}_2\text{O})_3$

One conformer for $\text{Rb}^+$ and $\text{Cs}^+$.

- Rb3a
- Cs3a

Two conformers for $\text{K}^+$.

- K3a
- K3g

Inokuchi et al., *JACS*, 2014, 136, 1815.
The Number of Conformers

If the metal ion is completely surrounded by CE, multiple conformers can exist for solvated complexes.
UV Spectra of $\text{Ca}^{2+} \cdot \text{CE} \cdot \text{L}$

$\text{Ca}^{2+} \cdot \text{B15C5} \cdot \text{H}_2\text{O}$

$\text{Ca}^{2+} \cdot \text{B15C5} \cdot \text{CH}_3\text{OH}$

$\text{Ca}^{2+} \cdot \text{B18C6} \cdot \text{H}_2\text{O}$

$\text{Ca}^{2+} \cdot \text{B18C6} \cdot \text{CH}_3\text{OH}$

The Number of Conformers for $\text{M}^{2+}\cdot\text{CE}\cdot\text{L}$

<table>
<thead>
<tr>
<th>L</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{CH}_3\text{OH}$</th>
<th>Ion radii (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B15C5</td>
<td>B18C6</td>
<td>B15C5</td>
</tr>
<tr>
<td>CE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

$n_{\text{B15C5}} < n_{\text{B18C6}}$, but $n_{\text{B15C5}} \approx n_{\text{B18C6}}$ for Ba$^{2+}$
The Number of Conformers of $\text{M}^{2+}\cdot\text{CE}\cdot\text{L}$

If the metal ion is completely surrounded by CE, multiple conformers can exist for solvated complexes.
Summary

We are still on a way to revealing the whole picture of the ion selectivity at a molecular level, but...

- $\text{M}^+\cdot\text{DB18C6}$
- $\text{M}^+\cdot\text{DB18C6}\cdot(\text{H}_2\text{O})_n$
- $\text{M}^{2+}\cdot\text{B15C5}\cdot\text{L}$ and $\text{M}^{2+}\cdot\text{B18C6}\cdot\text{L}$
- UV and IR spectroscopy in a cold, 22-pole ion trap

- The structure and number of conformers are determined.

- Host-guest complexes with an optimum matching in size tend to give multiple conformers with solvent molecules, resulting in entropic advantages.
Acknowledgment

École Polytechnique Fédérale de Lausanne (EPFL)

Prof. Thomas R. Rizzo       Dr. Oleg V. Boyarkin       LCPM members

Hiroshima University

Prof. Takayuki Ebata       Dr. Ryoji Kusaka
Acknowledgment

The Japan Society for the Promotion of Science (JSPS)
The Mitsubishi Chemical Foundation
The Sumitomo Foundation
The Kurata Memorial Hitachi Science and Technology Foundation