Effect of the cation on the stability of cation-glyme complexes and their interactions with the [TFSA]- anion

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Electronic Supplementary Information
Procedures of geometry optimizations, calculations of stabilization enthalpies and free energies, measurements of thermal properties, and X-ray crystallography. Thermal decomposition temperatures. Crystallographic data. Optimized geometries and stabilization energies of the complexes. Crystal structures of [Mg(G3)][TFSA]$_2$ and [Mg(G5)][TFSA]$_2$ complexes. DSC analysis and TG curves.
Geometry optimizations of the cation-glyme and cation-glyme-TFSA complexes

Initial geometries for the geometry optimizations of the cation-glyme complexes were prepared from various rotamers of glymes and metal cations. Geometry optimizations of cation-G1, cation-G2, cation-G3, and cation-G4 complexes were performed from 9, 14, 40, and 295 initial geometries, respectively. The stabilization energies for the formation of the complexes ($E_{\text{form}}$) were calculated for the local energy minimum structures obtained by the geometry optimizations. The calculated $E_{\text{form}}$s were compared to find the most stable geometries of the complexes.

Initial geometries for the geometry optimizations of the cation-glyme-TFSA complexes were prepared by combining the local energy minimum structures of the cation-glyme complexes and $\text{trans-}$ or $\text{cis-}$TFSA anion. Geometry optimizations of cation-G1-TFSA, cation-G2-TFSA, cation-G3-TFSA, and cation-G4-TFSA complexes were performed from 4-8, 4-16, 56-128, and 88-320 initial geometries, respectively.

The structure of the $\text{[Mg(G3)][TFSA]}_2$ complex in the crystal was optimized using DMOL³ in Materials Studio (version 4.3) of BIOVIA Dassault Systemes. In the DMOL³ method, the physical wave functions are expanded in terms of accurate numerical basis sets. We used the double-numerical quality basis set with polarization functions (DNP) for the geometry optimizations. The PBE functionals were used for the DFT calculations. The positions of the atoms in the crystal were optimized by the periodic DFT calculations. The experimental lattice parameters were fixed during the optimization.

Stabilization enthalpies and stabilization free energies of cation-glyme complexes

The stabilization enthalpies and stabilization free energies of the cation-glyme complexes ($\text{Li(G3)}^+$, $\text{Na(G3)}^+$, $\text{K(G3)}^+$, $\text{Mg(G3)}^{2+}$, and $\text{Ca(G3)}^{2+}$) from isolated species were calculated using vibrational analysis. The thermal properties were calculated from the vibrational frequencies of cation-glyme complexes and isolated
species at 298.15 K. The vibrational frequencies were calculated at the B3LYP/6-311+G** level. The calculated stabilization enthalpies and stabilization free energies were compared with the $E_{\text{form}}$ calculated at the same level as summarized in Table S3 to elucidate the effects of vibration and entropy on the stabilization energies.

**Thermal properties of [Mg(G3)][TFSA]$_2$, [Mg(G4)][TFSA]$_2$, and [Mg(G5)][TFSA]$_2$**

Mg[TFSA]$_2$ salt was synthesized by neutralization of bis(trifluoromethanesulfonyl)amide (H[TFSA], Kanto Chemical) with Mg(OH)$_2$ (Wako Pure Chemical Industries). Triglyme (G3) tetraglyme (G4), and pentaglyme (G5) were kindly supplied by Nippon Nyukazai. [Mg(glyme)][TFSA]$_2$ was prepared by mixing Mg[TFSA]$_2$ and glyme (G3, G4, or G5) in a 1 : 1 molar ratio in an Ar-filled glove box. To obtain uniform samples, the mixtures were stirred at elevated temperatures (120, 160, and 160 °C for G3, G4, and G5 samples, respectively) for 12 h and cooled to room temperature. The thermal properties of [Mg(G3)][TFSA]$_2$ and [Mg(G5)][TFSA]$_2$ were determined using differential scanning calorimetry (DSC; DSC6220, Seiko) and thermogravimetry (TG/DTA 6200, Seiko). For the DSC measurements, the samples were hermetically sealed in aluminum pans in a glove box. The sample pans were first annealed at certain temperatures to avoid hysteresis followed by cooling to −150 °C at 10 °C min$^{-1}$ and then heated to specific temperatures at a heating rate of 10 °C min$^{-1}$. The thermal stability of [Mg(glyme)][TFSA]$_2$ was evaluated by TG measurements. The samples were heated from room temperature to 500 °C at a heating rate of 10 °C min$^{-1}$ under a nitrogen atmosphere. The thermal decomposition temperature ($T_d$) was defined as the temperature with 5% weight loss.

**X-ray crystallography**

The crystal structure of [Mg(G4)][TFSA]$_2$ was reported elsewhere.$^{6d}$ Single crystals of [Mg(G3)][TFSA]$_2$ were prepared as follows. The [Mg(G3)][TFSA]$_2$ complex and a fluorinated ether (1,1,2,2-tetrafluoroethyl(2,2,3,3-tetrafluoropropyl)ether, Daikin Industries) were mixed in a 1 : 4 molar ratio in a vial at room temperature to obtain a homogeneous solution. Then, the fluorinated ether was evaporated slowly at 30 °C, and single crystals of [Mg(G3)][TFSA]$_2$ precipitated at the bottom of the vial.
Single crystals of [Mg(G5)][TFSA]$_2$ were grown from mixtures of Mg[TFSA]$_2$ and G5 (1 : 9 molar ratio). The mixture was heated to 120 °C and stirred for 12 h and cooled to room temperature. The mixture was stored at ambient temperature for 7 days, and the single crystals of [Mg(G5)][TFSA]$_2$ precipitated in the solution.

Single crystals of [Mg(G3)][TFSA]$_2$ and [Mg(G5)][TFSA]$_2$ with dimensions of 0.4 × 0.35 × 0.1 mm$^3$ and 0.35 × 0.3 × 0.1 mm$^3$, respectively, soaked in Parabar 10312 (Hampton Research) to avoid absorbing moisture were mounted on a glass pin, and cooled to −50 °C by the steady flow of a nitrogen gas stream. Crystal evaluations and data collections were performed on the abstract diffractometer using graphite monochromatic Mo Ka radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using spherical harmonics was implemented in the SCALE3 ABSPACK scaling algorithm (Oxford Diffraction, 2006). The structures were solved by the direct method using SHELXT$^{55}$ and refined full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms using SHELXL-2015.$^{56}$ All the hydrogen atoms were introduced at geometrically ideal positions and refined using the riding model. All data collections and calculations, expect for the refinement, were performed using the CrysAlisPro 1.171.38.43 software package (Rigaku). Although refinements on [Mg(G5)][TFSA]$_2$ could not be accomplished well (namely poor $R_1$ and $wR_2$ values) due to its low crystallinity, the structural information is very helpful for discussing the coordination environment of Mg$^{2+}$ in this complex. Thus, the solvation and packing structures are provided in Figures S6-S9, and the crystallographic data is summarized in Table S2.

References for Electronic Supplementary Information


Table S1. Thermal decomposition temperatures of neat glymes and cation-glyme-TFSA complexes.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$T_\text{db}$</th>
<th>$\Delta T_\text{dc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure G3</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>[Li(G3)][TFSA]</td>
<td>190</td>
<td>86</td>
</tr>
<tr>
<td>[Na(G3)][TFSA]</td>
<td>127</td>
<td>23</td>
</tr>
<tr>
<td>[Mg(G3)][TFSA]</td>
<td>241</td>
<td>137</td>
</tr>
<tr>
<td>Pure G4</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>[Li(G4)][TFSA]</td>
<td>205</td>
<td>71</td>
</tr>
<tr>
<td>[Na(G4)][TFSA]</td>
<td>212</td>
<td>78</td>
</tr>
<tr>
<td>[K(G4)][TFSA]</td>
<td>198</td>
<td>64</td>
</tr>
<tr>
<td>[Mg(G4)][TFSA]</td>
<td>292</td>
<td>158</td>
</tr>
<tr>
<td>Pure G5</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>[Li(G5)][TFSA]</td>
<td>220</td>
<td>44</td>
</tr>
<tr>
<td>[Na(G5)][TFSA]</td>
<td>233</td>
<td>57</td>
</tr>
<tr>
<td>[K(G5)][TFSA]</td>
<td>220</td>
<td>44</td>
</tr>
<tr>
<td>[Mg(G5)][TFSA]</td>
<td>318</td>
<td>142</td>
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</table>

\textsuperscript{a} Thermal decomposition temperatures of Li, Na, and K complexes were taken from reference 6b.

\textsuperscript{b} Thermal decomposition temperature in °C.

\textsuperscript{c} The difference of $T_\text{db}$ between cation-glyme-TFSA complexes and neat glyme.
<table>
<thead>
<tr>
<th></th>
<th>[Mg(G3)][TFSA]$_2$</th>
<th>[Mg(G5)][TFSA]$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical formula</strong></td>
<td>C$<em>{12}$H$</em>{18}$F$_{12}$MgN$<em>2$O$</em>{12}$S$_4$</td>
<td>C$<em>{16}$H$</em>{26}$F$_{12}$MgN$<em>2$O$</em>{12}$S$_4$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>762.83</td>
<td>850.94</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P1 (no. 1)</td>
<td>P$-1$ (no. 2)</td>
</tr>
<tr>
<td><strong>a / Å</strong></td>
<td>8.7021(4)</td>
<td>8.9282(8)</td>
</tr>
<tr>
<td><strong>b / Å</strong></td>
<td>9.1183(6)</td>
<td>9.2046(8)</td>
</tr>
<tr>
<td><strong>c / Å</strong></td>
<td>9.2356(5)</td>
<td>19.4176(17)</td>
</tr>
<tr>
<td><strong>α / °</strong></td>
<td>97.006(5)</td>
<td>94.343(7)</td>
</tr>
<tr>
<td><strong>β / °</strong></td>
<td>95.727(4)</td>
<td>93.987(7)</td>
</tr>
<tr>
<td><strong>γ / °</strong></td>
<td>100.012(5)</td>
<td>91.344(7)</td>
</tr>
<tr>
<td><strong>V / Å$^3$</strong></td>
<td>710.77(7)</td>
<td>1586.7(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>D$_{calc}$ / g cm$^{-3}$</strong></td>
<td>1.782</td>
<td>1.783</td>
</tr>
<tr>
<td><strong>μ / mm$^{-1}$</strong></td>
<td>0.491</td>
<td>0.454</td>
</tr>
<tr>
<td><strong>Temp. / °C</strong></td>
<td>−50</td>
<td>−50</td>
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<tr>
<td><strong>Reflections collected</strong></td>
<td>8422</td>
<td>8367</td>
</tr>
<tr>
<td><strong>Independent reflection, R$_{int}$</strong></td>
<td>3649, 0.0376</td>
<td>3931, 0.0441</td>
</tr>
<tr>
<td><strong>R$_1$ [I &gt; 2σ(I)]</strong></td>
<td>0.0473</td>
<td>0.2130</td>
</tr>
<tr>
<td><strong>wR$_2$ (all data)</strong></td>
<td>0.1294</td>
<td>0.5004</td>
</tr>
<tr>
<td><strong>GooF</strong></td>
<td>0.891</td>
<td>2.294</td>
</tr>
<tr>
<td><strong>Largest residual density / e Å$^{-3}$</strong></td>
<td>0.409, −0.410</td>
<td>1.873, −1.046</td>
</tr>
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</table>
Table S3. Stabilization enthalpies and stabilization free energies of cation-glyme complexes.

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{form}})</th>
<th>(H_{\text{form}})</th>
<th>(G_{\text{form}})</th>
<th>(H_{\text{form}} - E_{\text{form}})</th>
<th>(G_{\text{form}} - H_{\text{form}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Li(G3)}]^+)</td>
<td>-98.2</td>
<td>-93.3</td>
<td>-81.3</td>
<td>4.8</td>
<td>12.0</td>
</tr>
<tr>
<td>([\text{Na(G3)}]^+)</td>
<td>-72.6</td>
<td>-69.1</td>
<td>-57.9</td>
<td>3.5</td>
<td>11.2</td>
</tr>
<tr>
<td>([\text{K(G3)}]^+)</td>
<td>-52.2</td>
<td>-50.5</td>
<td>-40.6</td>
<td>1.7</td>
<td>10.0</td>
</tr>
<tr>
<td>([\text{Mg(G3)}]^2+)</td>
<td>-266.8</td>
<td>-260.3</td>
<td>-246.9</td>
<td>6.6</td>
<td>13.3</td>
</tr>
<tr>
<td>([\text{Ca(G3)}]^{2+})</td>
<td>-194.1</td>
<td>-190.4</td>
<td>-178.1</td>
<td>3.7</td>
<td>12.3</td>
</tr>
</tbody>
</table>

\(a\) Energy in kcal/mol.
\(b\) Stabilization energy by the formation of complex, which is the sum of \(E_{\text{int}}\) and \(E_{\text{def}}\). The \(E_{\text{int}}\) and \(E_{\text{def}}\) were calculated at the B3LYP/6-311+G** level. The \(E_{\text{int}}\) was calculated with the BSSE correction.
\(c\) Stabilization enthalpy by the formation of complex at 298.15 K.
\(d\) Stabilization free energy by the formation of complex at 298.15 K.
\(e\) Difference between \(H_{\text{form}}\) and \(E_{\text{form}}\).
\(f\) Difference between \(G_{\text{form}}\) and \(H_{\text{form}}\). The contribution of entropy to stabilization free energy \((T\Delta S)\).
Figure S1. HF/6-311G** level optimized geometries and MP2/6-311G** level stabilization energies in kcal/mol calculated for the most stable [Li(DME)]\(^+\) and [Li(glyme)]\(^+\) complexes.
[Na(DME)]^+ complex

[Na(G1)]^+ complex

[Na(G2)]^+ complex

[Na(G3)]^+ complex
[Na(G4)]$^+$ complex
Figure S2. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the [Na(DME)]^+, [Na(G1)]^+, [Na(G2)]^+, [Na(G3)]^+, and [Na(G4)]^+ complexes and their MP2/6-311G** level stabilization energies in kcal/mol.
[K(DME)]⁺ complex

1a -18.5

[K(G1)]⁺ complex

2a -30.7  
2b -17.5  
2c -17.4  
2d -15.9

[K(G2)]⁺ complex

3a -42.3  
3b -41.2  
3c -39.5  
3d -39.1

3e -38.8  
3f -38.4  
3g -30.0  
3h -29.9

3i -29.7  
3j -28.1
[K(G3)]^+ complex

4a -52.5  
4b -51.4  
4c -51.3  
4d -50.2  
4e -50.1  
4f -50.0  
4a -49.6  
4h -49.5  
4i -49.1  
4j -48.3  
4k -47.3  
4l -45.7  
4m -44.4  
4n -41.1  
4o -40.0  
4p -39.5  

[K(G4)]^+ complex

5a -60.9  
5b -60.8  
5c -60.7  
5d -59.9  
5e -59.8  
5f -59.7  
5g -59.6  
5h -59.6
Figure S3. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the [K(DME)]⁺, [K(G1)]⁺, [K(G2)]⁺, [K(G3)]⁺, and [K(G4)]⁺ complexes and their MP2/6-311G** level stabilization energies in kcal/mol.
$[\text{Mg(DME)}]^2^+ \text{ complex}$

$[\text{Mg(G1)}]^2^+ \text{ complex}$

$[\text{Mg(G2)}]^2^+ \text{ complex}$

$[\text{Mg(G3)}]^2^+ \text{ complex}$
Figure S4. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the [Mg(DME)]$^{2+}$, [Mg(G1)]$^{2+}$, [Mg(G2)]$^{2+}$, [Mg(G3)]$^{2+}$, and [Mg(G4)]$^{2+}$ complexes and their MP2/6-311G** level stabilization energies in kcal/mol.
[Ca(DME)]^{2+} complex

[Ca(G1)]^{2+} complex

[Ca(G2)]^{2+} complex

[Ca(G3)]^{2+} complex
Figure S5. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the [Ca(DME)]^{2+}, [Ca(G1)]^{2+}, [Ca(G2)]^{2+}, [Ca(G3)]^{2+}, and [Ca(G4)]^{2+} complexes and their MP2/6-311G** level stabilization energies in kcal/mol.
Figure S6. Thermal ellipsoid model of the crystal of [Mg(G3)][TFSA]$_2$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels on the hydrogen atoms are omitted for clarity. CCDC: 1541951.
Figure S7. Packing diagrams of the crystal of [Mg(G3)][TFSA]₂ drawn along the a-axis (left) and its perspective view (right). Hydrogen atoms are omitted for clarity. Green, Mg; red, O; gray, C; blue, N; yellow, S; light green, F.
Figure S8. Ball and stick model of the crystal of [Mg(G5)][TFSA]$_2$. The $R$ value of this crystal is higher than 20%, indicating poor refinement. An expanded structure with disordered atoms on the isolated TFSA anion is shown here. The labels on the hydrogen atoms are omitted for clarity.
Figure S9. Packing diagrams of the crystal of [Mg(G5)][TFSA]₂ drawn along the a-axis (left) and its perspective view (right). Hydrogen atoms are omitted for clarity. Green, Mg; red, O; gray, C; blue, N; yellow, S; light green, F.
Figure S10. HF/6-311G** level optimized geometry of the second most stable conformational isomer of the [Li(G4)][TFSA] complex.
Figure S11. DSC thermograms of $\text{[Mg(glyme)][TFSA]}_2$. The DSC thermogram of $\text{[Mg(G4)][TFSA]}_2$ was taken from reference 6d.
Figure S12. TG curves of [Mg(glyme)][TFSA]₂ complexes. The curves of pure glymes are also included as references.