Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2017

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

Seiji Tsuzuki,[*a] Toshihiko Mandai,[b] Soma Suzuki,[c] Wataru Shinoda,[d] Takenobu Nakamura,[a] Tetsuya Morishita[a] Kazuhide Ueno,[c] Shiro Seki[e] Yasuhiro Umebayashi,[f] Kaoru Dokko,[*c,g] and Masayoshi Watanabe[c]

[a] Research Center for Computational Design of Advanced Functional Materials (CD-FMat), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan,

[b] Faculty of Science and Engineering, Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

[c] Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

[d] Department of Applied Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

[e] Department of Environmental Chemistry and Chemical Engineering, School of Advanced Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji, Tokyo 192-0015, Japan

[f] Graduate School of Science and Technology Niigata University 8050, Ikarashi, 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

[g] Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyoto 615-8510, Japan

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_{form}) were calculated for the local energy minimum structures obtained by the geometry optimizations. The calculated E_{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 *trans*- or *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 $[Mg(G3)][TFSA]_2$ complex in the crystal was optimized using DMOL^3 in Materials Studio (version 4.3) of BIOVIA Dassault Systemes. In the DMOL^3 method,[S1-S3] 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.[S4] 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 $(Li(G3))^+$, $[Na(G3)]^+$, $[K(G3)]^+$, $Mg(G3)]^{2+}$, and $[Ca(G3)]^{2+}$) 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_{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 $0.4 \times 0.35 \times 0.1$ mm^3 and $0.35 \times 0.3 \times 0.1$ mm^3, respectively, soaked in Parabar 10312 (Hampton Research) to avoid absorbing moisture were mounted on a glass pin, and cooled to −50 ºC by the steady flow of a nitrogen gas stream. Crystal evaluations and data collections were performed on the abstract diffractometer using graphite monochromatic Mo Kα radiation (λ = 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[S5] and refined full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms using SHELXL-2015.[S6] 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

S1) B. Delley, *J. Chem. Phys.* **1990**, *92,* 508-517.

S2) B. Delley, *J. Phys. Chem.* **1996**, *100,* 6107-6110.

S3) B. Delley, *J. Chem. Phys.* **2000**, *113,* 7756-7764.

S4) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, *77* 3865-3868.

S5) G. M. Sheldrick, *SHELXT* – integrated space-group and crystal-structure determination. *Acta Cryst*., 2015, **A71**, 3–8.

S6) G. M. Sheldrick, Crystal structure refinement with *SHELXL*. *Acta Cryst*., 2015, **C71**, 3–8.

Table S1. Thermal decomposition temperatures of neat glymes and cation-glyme-TFSA complexes.[a]

	T_d[b]	ΔT_d[c]
Pure G3	104	
[Li(G3)][TFSA]	190	86
[Na(G3)][TFSA]	127	23
[Mg(G3)][TFSA]$_2$	241	137
Pure G4	134	
[Li(G4)][TFSA]	205	71
[Na(G4)][TFSA]	212	78
[K(G4)][TFSA]	198	64
[Mg(G4)][TFSA]$_2$	292	158
Pure G5	176	
[Li(G5)][TFSA]	220	44
[Na(G5)][TFSA]	233	57
[K(G5)][TFSA]	220	44
[Mg(G5)][TFSA]$_2$	318	142

[a] Thermal decomposition temperatures of Li, Na, and K complexes were taken from reference 6b.

[b] Thermal decomposition temperature in °C.

[c] The difference of T_d between cation-glyme-TFSA complexes and neat glyme.

Table S2. Crystallographic data of $[Mg(G3)][TFSA]_2$ and $[Mg(G5)][TFSA]_2$

	$[Mg(G3)][TFSA]_2$	$[Mg(G5)][TFSA]_2$
Chemical formula	$C_{12}H_{18}F_{12}MgN_2O_{12}S_4$	$C_{16}H_{26}F_{12}MgN_2O_{12}S_4$
Formula weight	762.83	850.94
Crystal system	Triclinic	Triclinic
Space group	$P1$ (no. 1)	$P-1$ (no. 2)
a / Å	8.7021(4)	8.9282(8)
b / Å	9.1183(6)	9.2046(8)
c / Å	9.2356(5)	19.4176(17)
α / °	97.006(5)	94.343(7)
β / °	95.727(4)	93.987(7)
γ / °	100.012(5)	91.344(7)
V / Å^3	710.77(7)	1586.7(2)
Z	1	2
D_{calc} / g cm^{-3}	1.782	1.783
μ / mm^{-1}	0.491	0.454
Temp. / °C	−50	−50
Reflections collected	8422	8367
Independent reflection, R_{int}	3649, 0.0376	3931, 0.0441
R_1 [$I > 2\sigma(I)$]	0.0473	0.2130
wR_2 (all data)	0.1294	0.5004
GooF	0.891	2.294
Largest residual density / e Å^{-3}	0.409, −0.410	1.873, −1.046

Table S3. Stabilization enthalpies and stabilization free energies of cation-glyme complexes[a]

	E_{form}[b]	H_{form}[c]	G_{form}[d]	H_{form} - E_{form}[e]	G_{form} - H_{form}[f]
$[\mathrm{Li(G3)}]^{+}$	-98.2	-93.3	-81.3	4.8	12.0
$[\mathrm{Na(G3)}]^{+}$	-72.6	-69.1	-57.9	3.5	11.2
$[\mathrm{K(G3)}]^{+}$	-52.2	-50.5	-40.6	1.7	10.0
$[\mathrm{Mg(G3)}]^{2+}$	-266.8	-260.3	-246.9	6.6	13.3
$[\mathrm{Ca(G3)}]^{2+}$	-194.1	-190.4	-178.1	3.7	12.3

[a] Energy in kcal/mol.

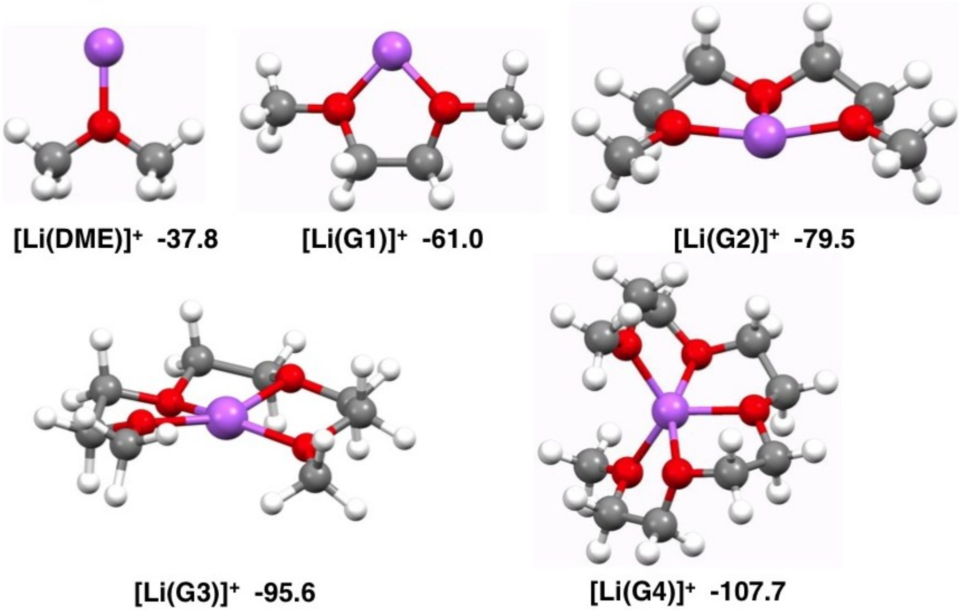
[b] Stabilization energy by the formation of complex, which is the sum of E_{int} and E_{def}. The E_{int} and E_{def} were calculated at the B3LYP/6-311+G** level. The E_{int} was calculated with the BSSE correction.

[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_{form} and E_{form}.

[f] Difference between G_{form} and H_{form}. The contribution of entropy to stabilization free energy ($T\Delta S$).



$[Li(DME)]^+$ -37.8

$[Li(G1)]^+$ -61.0

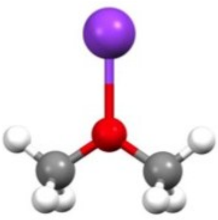
$[Li(G2)]^+$ -79.5

$[Li(G3)]^+$ -95.6

$[Li(G4)]^+$ -107.7

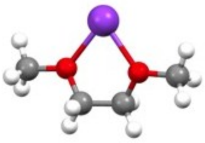
Figure S1. HF/6-311G** level optimized geometries and MP2/6-311G** level stabilization energies in kcal/mol calculated for the most stable $[Li(DME)]^+$ and $[Li(glyme)]^+$ complexes.

[Na(DME)]$^+$ complex

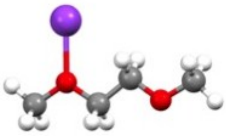


1a -24.9

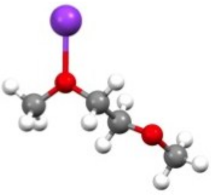
[Na(G1)]$^+$ complex



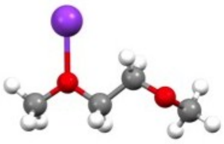
2a -40.6



2b -23.9

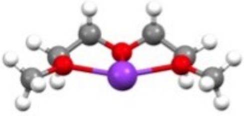


2c -23.8



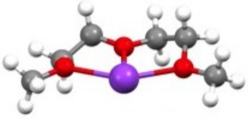
2d -22.3

[Na(G2)]$^+$ complex

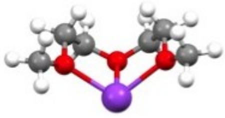


3a -54.3

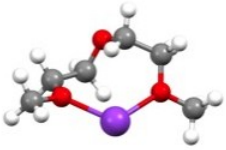
3b -53.0



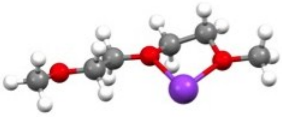
3c -51.2



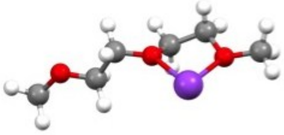
3d -50.4



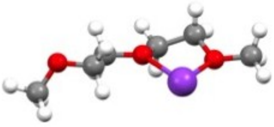
3e -40.3



3f -39.8

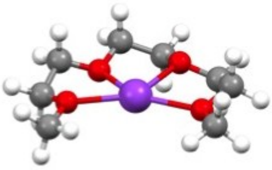


3g -39.8

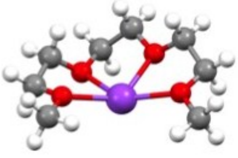


3h -37.8

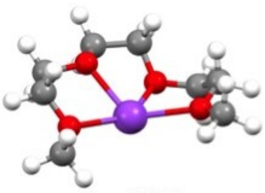
[Na(G3)]$^+$ complex



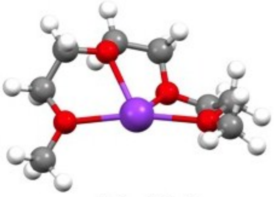
4a -66.4



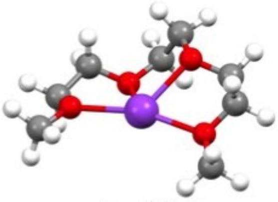
4b -64.9



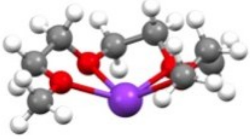
4c -64.9



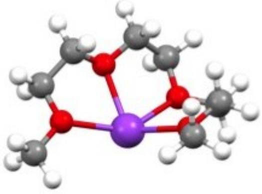
4d -63.5



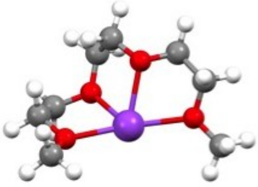
4e -63.5



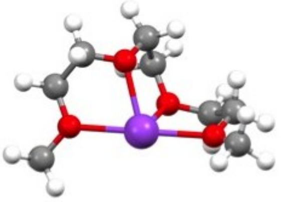
4f -63.2



4g -62.5



4h -61.2



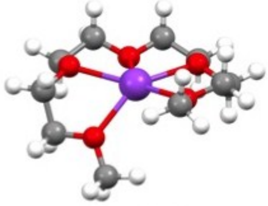
4i -58.6

4j -54.3

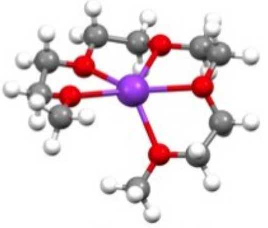
4k -53.2

[Na(G4)]$^+$ complex

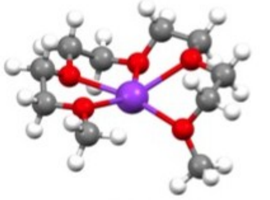
5a -77.1



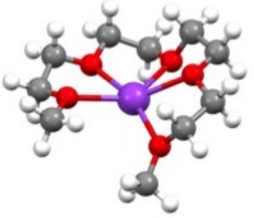
5b -76.3



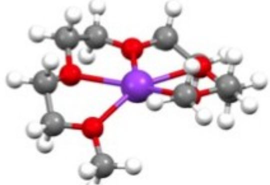
5c -75.4



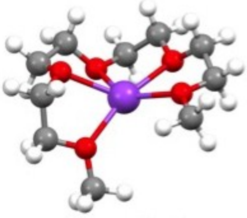
5d -75.3



5e -75.1

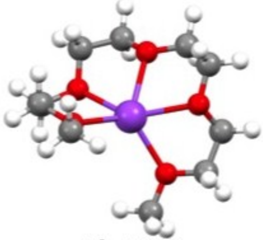


5f -74.9

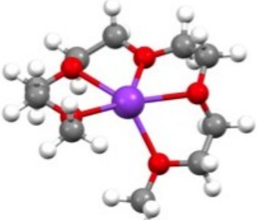


5g -74.3

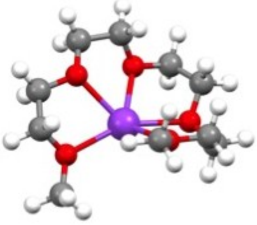
5h -74.2



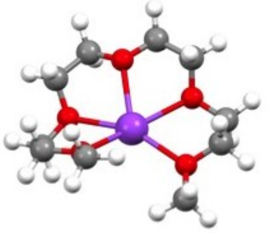
5i -73.8



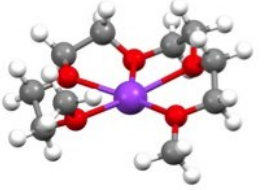
5j -73.7



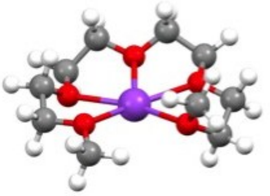
5k -73.7



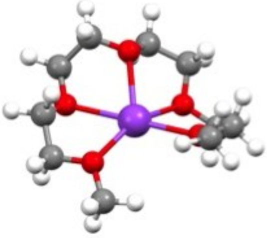
5l -73.6



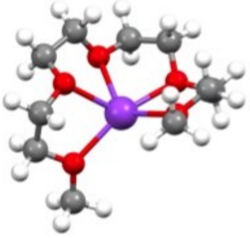
5m -73.6



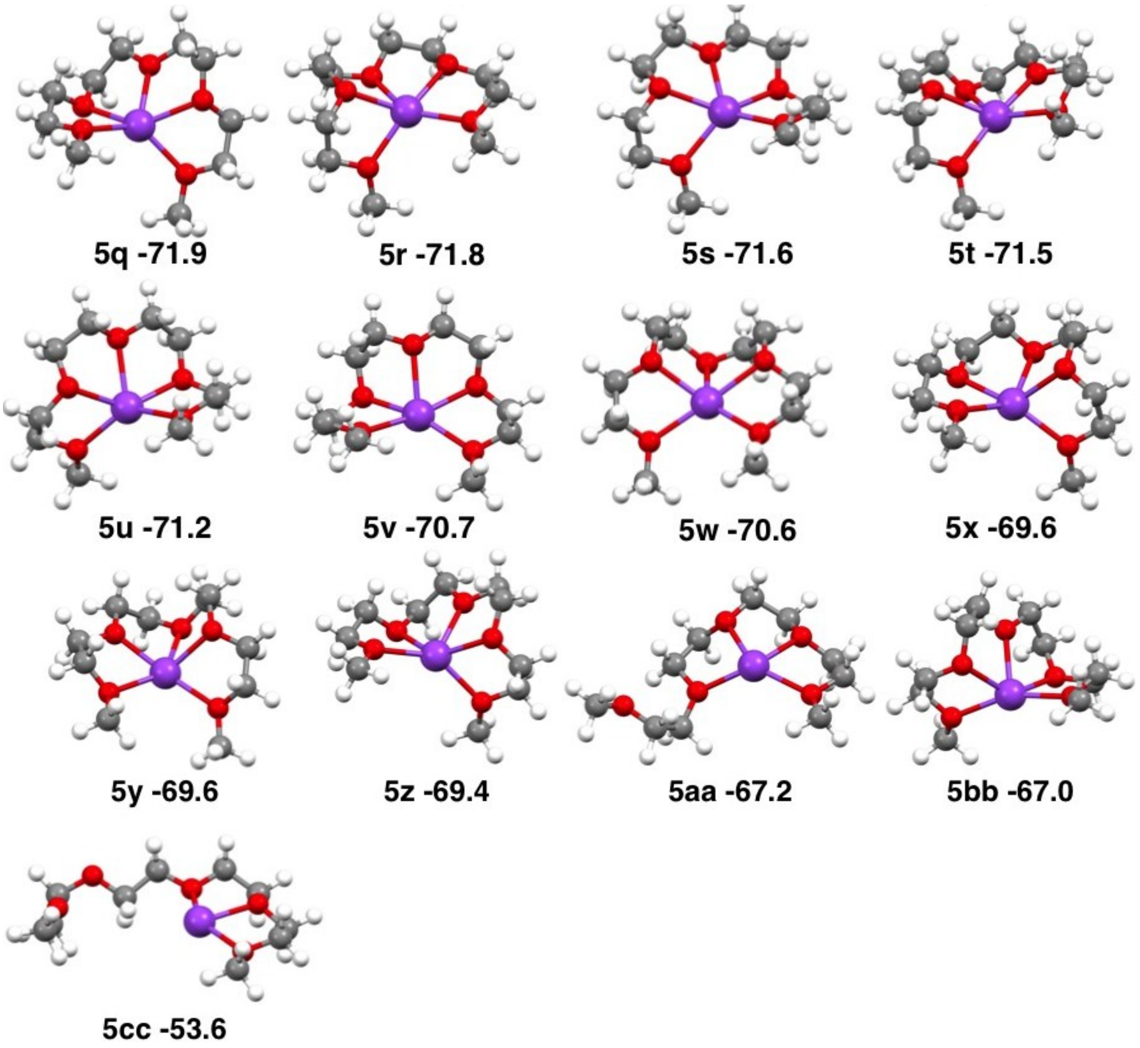
5n -73.3



5o -73.1



5p -72.3



5q -71.9 5r -71.8 5s -71.6 5t -71.5

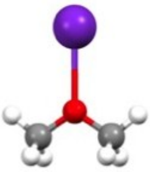
5u -71.2 5v -70.7 5w -70.6 5x -69.6

5y -69.6 5z -69.4 5aa -67.2 5bb -67.0

5cc -53.6

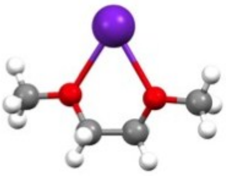
Figure S2. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the $[Na(DME)]^+$, $[Na(G1)]^+$, $[Na(G2)]^+$, $[Na(G3)]^+$, and $[Na(G4)]^+$ complexes and their MP2/6-311G** level stabilization energies in kcal/mol.

[K(DME)]$^+$ complex

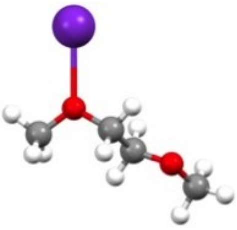


1a -18.5

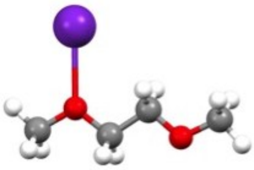
[K(G1)]$^+$ complex



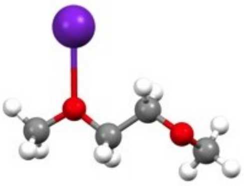
2a -30.7



2b -17.5



2c -17.4

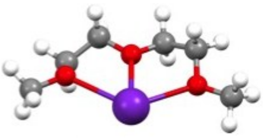


2d -15.9

[K(G2)]$^+$ complex

3a -42.3

3b -41.2

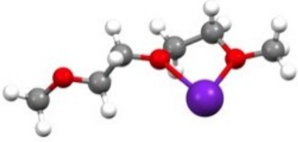


3c -39.5

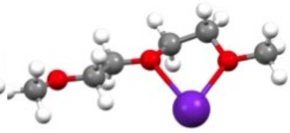
3d -39.1

3e -38.8

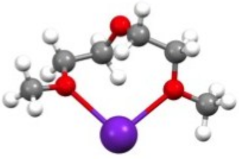
3f -38.4



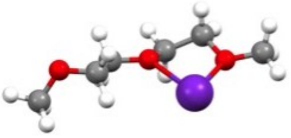
3g -30.0



3h -29.9

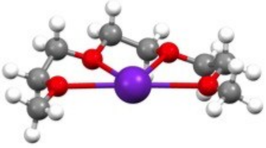


3i -29.7

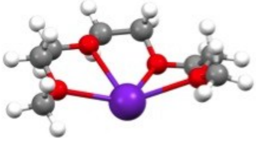


3j -28.1

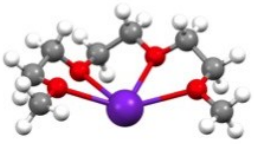
[K(G3)]$^+$ complex



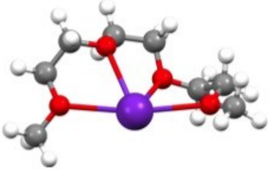
4a -52.5



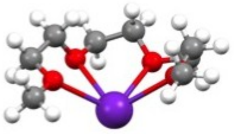
4b -51.4



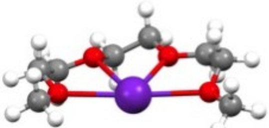
4c -51.3



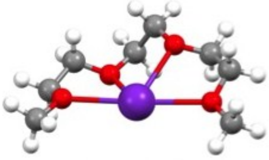
4d -50.2



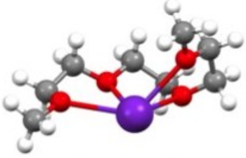
4e -50.1



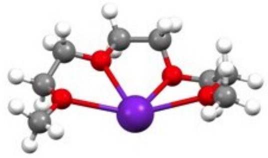
4f -50.0



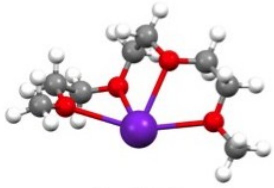
4g -49.6



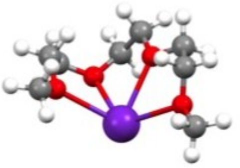
4h -49.5



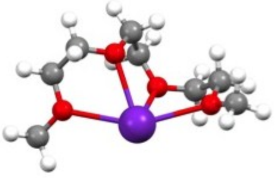
4i -49.1



4j -48.3

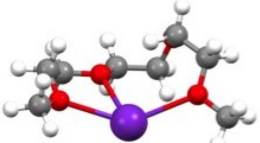


4k -47.3

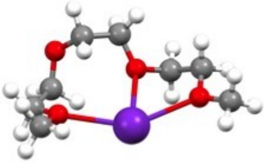


4l -45.7

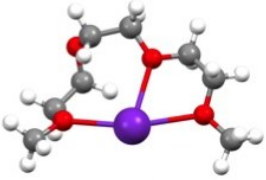
4m -44.4



4n -41.1

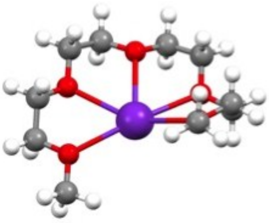


4o -40.0



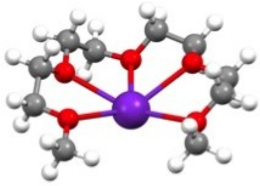
4p -39.5

[K(G4)]$^+$ complex

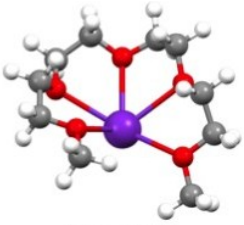


5a -60.9

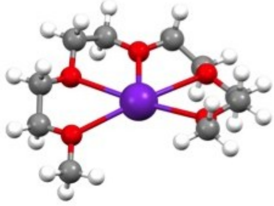
5b -60.8



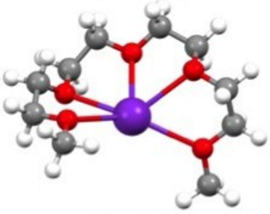
5c -60.7



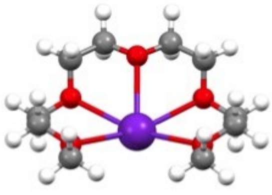
5d -59.9



5e -59.8

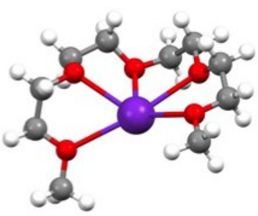


5f -59.7

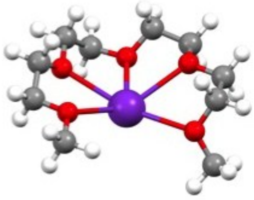


5g -59.6

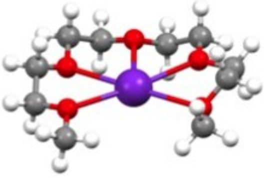
5h -59.6



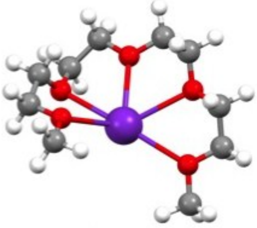
5i -59.6



5j -59.5



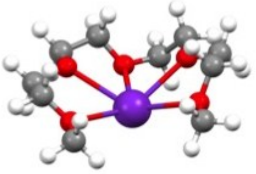
5k -59.4



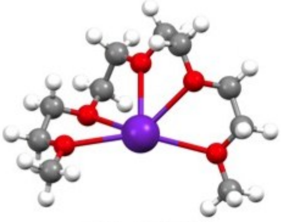
5l -59.3

5m -59.1

5n -59.0



5o -58.9

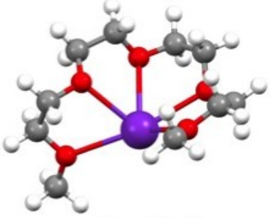


5p -58.8

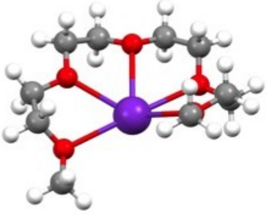
5q -58.8

5r -58.5

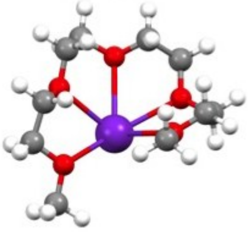
5s -58.4



5t -58.3

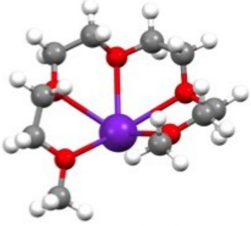


5u -58.3

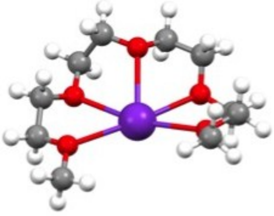


5v -58.1

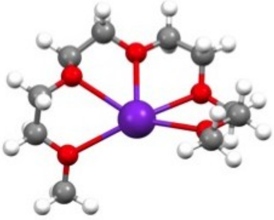
5w -58.1



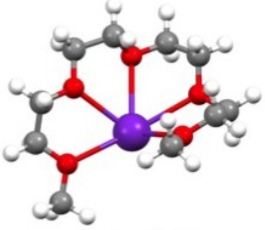
5x -58.0



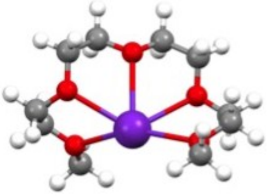
5y -58.0



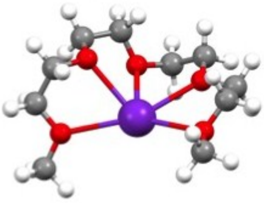
5z -57.9



5aa -57.8



5bb -57.7



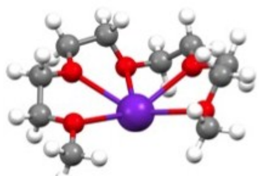
5cc -57.7

5dd -57.7

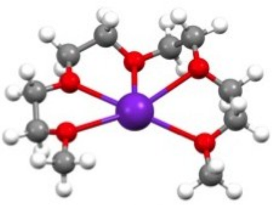
5ee -57.3

5ff -57.1

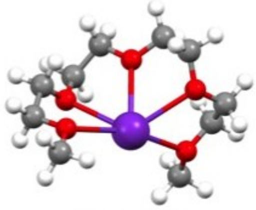
5gg -57.0



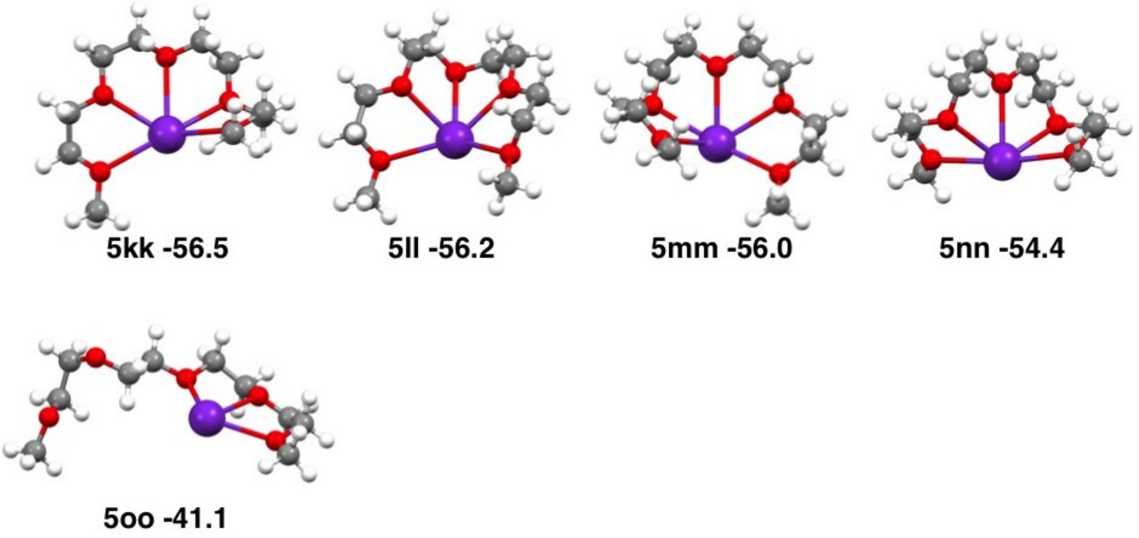
5hh -56.8



5ii -56.7



5jj -56.6

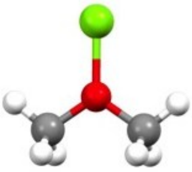


5kk -56.5 **5ll -56.2** **5mm -56.0** **5nn -54.4**

5oo -41.1

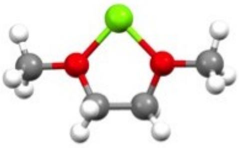
Figure S3. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the $[K(DME)]^+$, $[K(G1)]^+$, $[K(G2)]^+$, $[K(G3)]^+$, and $[K(G4)]^+$ complexes and their MP2/6-311G** level stabilization energies in kcal/mol.

[Mg(DME)]$^{2+}$ complex

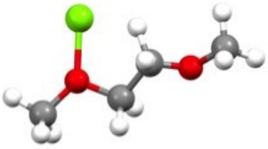


1a -95.3

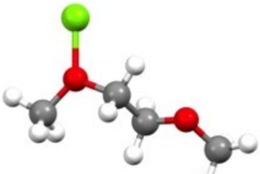
[Mg(G1)]$^{2+}$ complex



2a -157.6

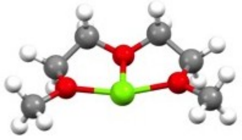


2b -112.5

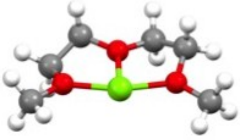


2c -99.5

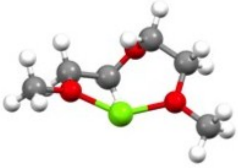
[Mg(G2)]$^{2+}$ complex



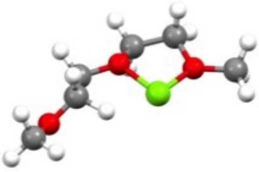
3a -209.6



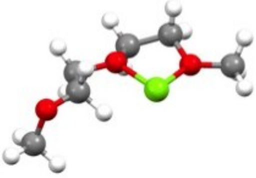
3b -207.2



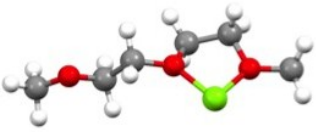
3c -170.8



3d -166.4

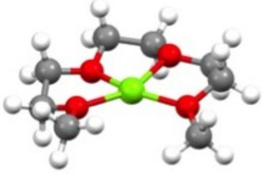


3e -162.2

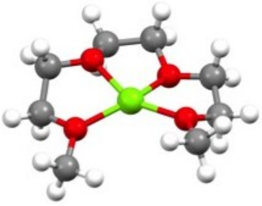


3f -160.1

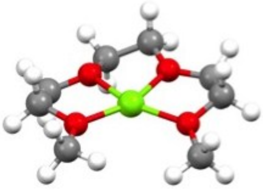
[Mg(G3)]$^{2+}$ complex



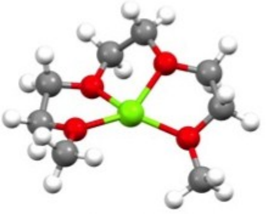
4a -255.0



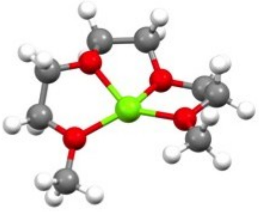
4b -252.9



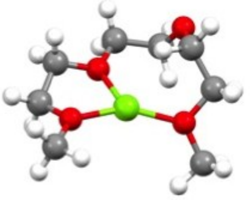
4c -252.7



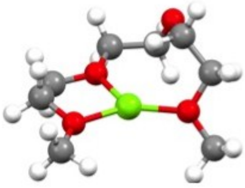
4d -251.5



4e -251.2

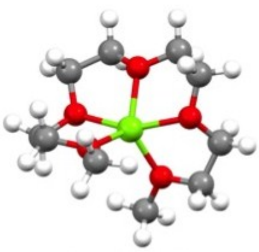


4f -221.2

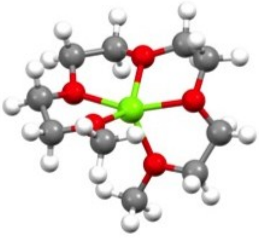


4g -221.1

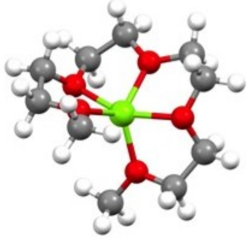
[Mg(G4)]$^{2+}$ complex



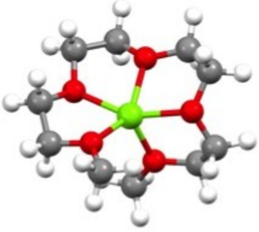
5a -288.3



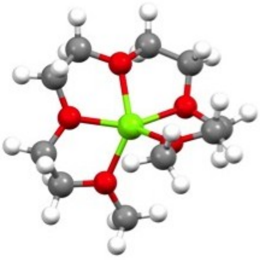
5b -287.9



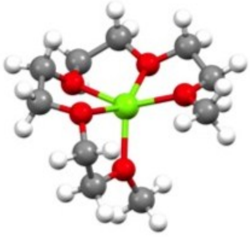
5c -287.6



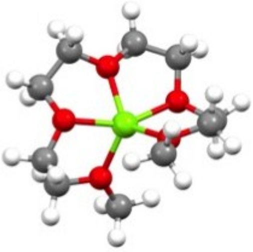
5d -286.9



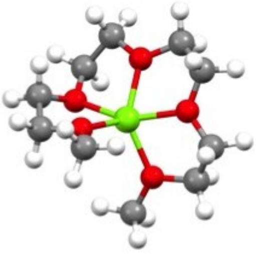
5e -286.6



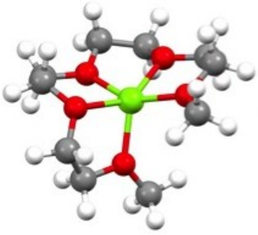
5f -286.2



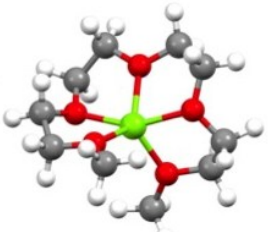
5g -285.8



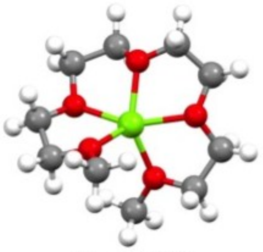
5h -285.5



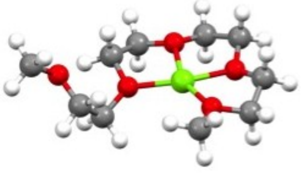
5i -285.1



5j -285.0



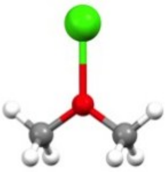
5k -283.0



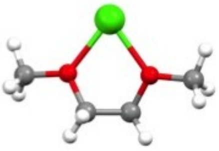
5l -262.4

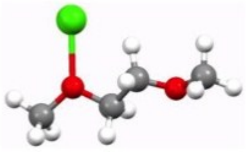
Figure S4. Local energy minimum structures obtained by HF/6-311G** level geometry optimizations of the [Mg(DME)]$^{2+}$, [Mg(G1)]$^{2+}$, [Mg(G2)]$^{2+}$, [Mg(G3)]$^{2+}$, and [Mg(G4)]$^{2+}$ complexes and their MP2/6-311G** level stabilization energies in kcal/mol.

$[Ca(DME)]^{2+}$ complex


1a -66.1

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

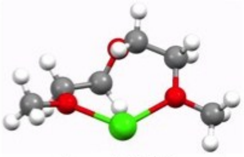

2a -111.9

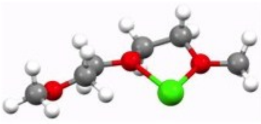

2b -73.0

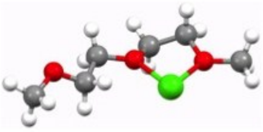
$[Ca(G2)]^{2+}$ complex

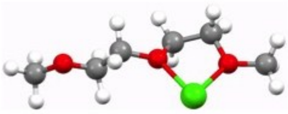

3a -150.5


3b -148.7

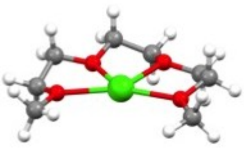

3c -116.2

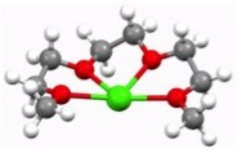

3d -115.7

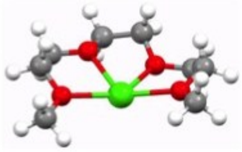

3e -114.9

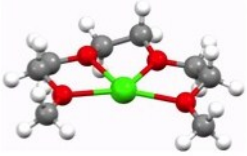

3f -113.9

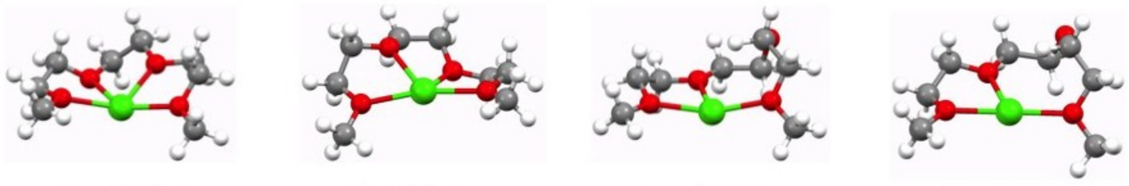
$[Ca(G3)]^{2+}$ complex


4a -185.0


4b -183.3

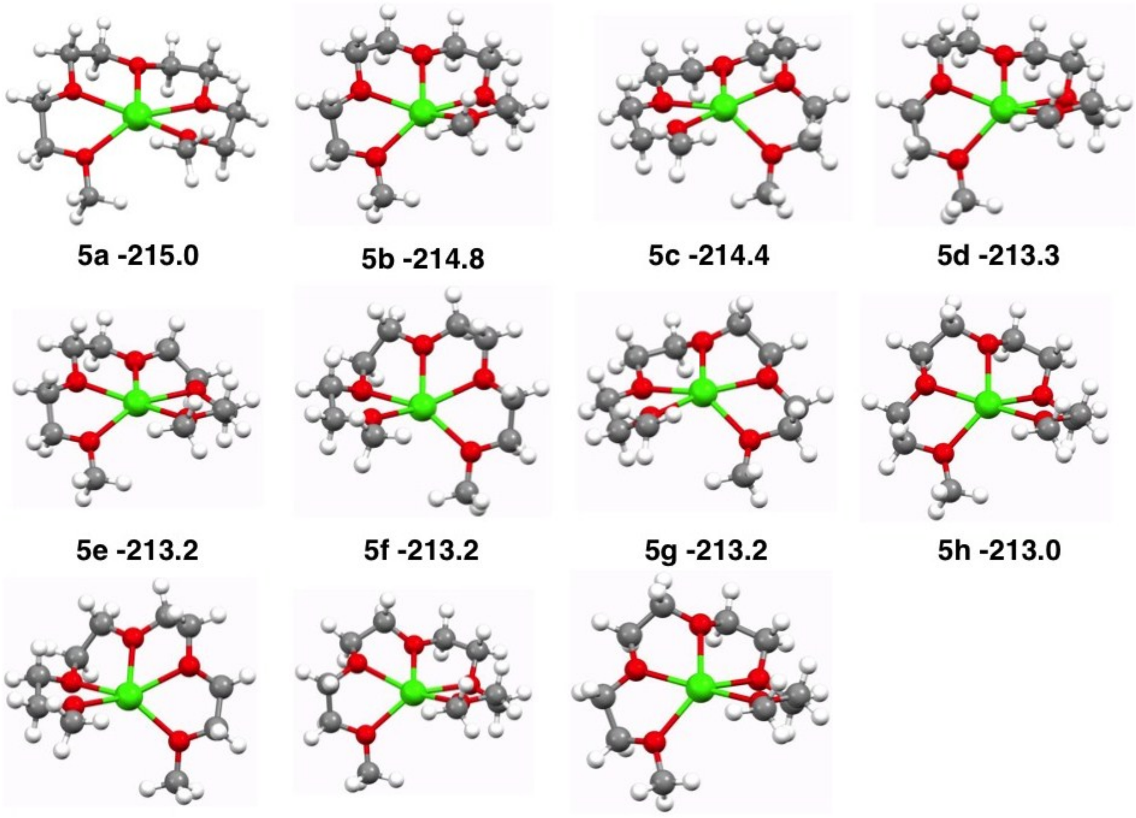

4c -183.3


4d -183.2



4e -181.8 **4f -181.4** **4g -154.1** **4h -153.6**

[Ca(G4)]$^{2+}$ complex



5a -215.0 **5b -214.8** **5c -214.4** **5d -213.3**

5e -213.2 **5f -213.2** **5g -213.2** **5h -213.0**

5i -212.1 **5j -211.5** **5k -211.2**

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.

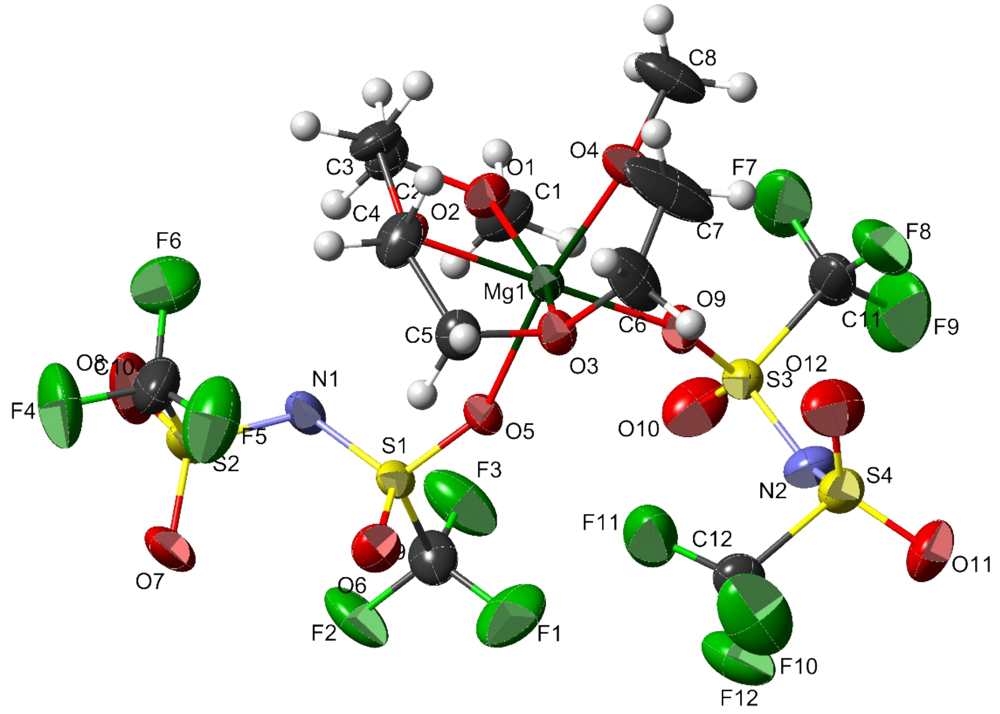


Figure S6. Thermal ellipsoid model of the crystal of [Mg(G3)][TFSA]$_2$. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels on the hydrogen atoms are omitted for clarity. CCDC: 1541951.

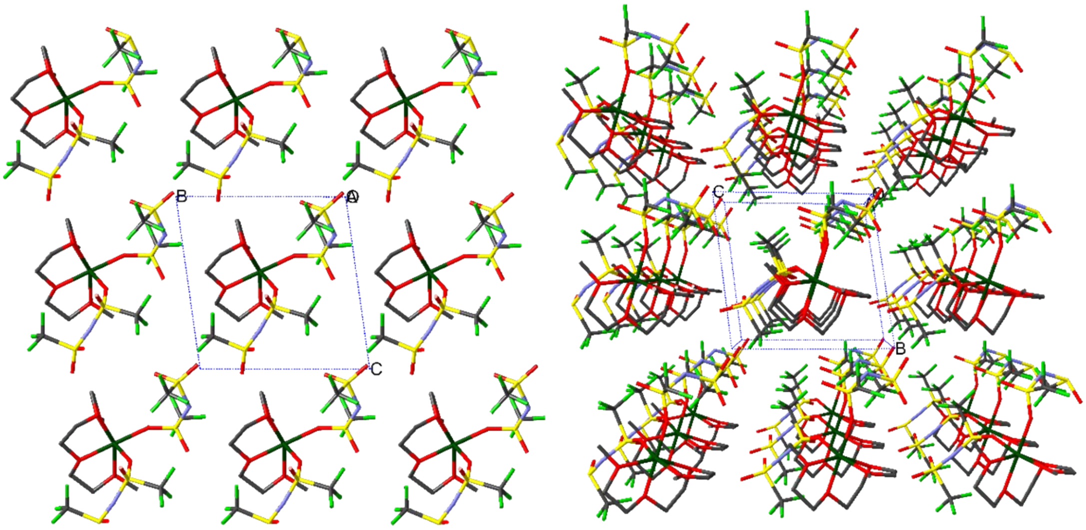


Figure S7. Packing diagrams of the crystal of [Mg(G3)][TFSA]$_2$ drawn along the *a*-axis (left) and its perspective view (right). Hydrogen atoms are omitted for clarity. Green, Mg; red, O; gray, C; blue, N; yellow, S; light green, F.

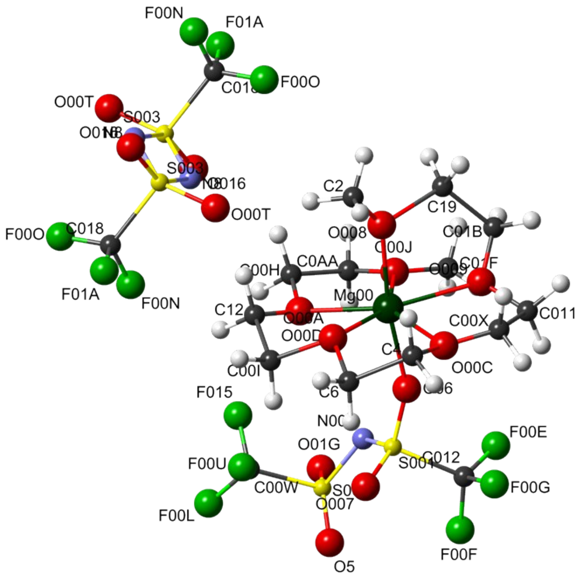


Figure S8. Ball and stick model of the crystal of [Mg(G5)][TFSA]$_2$. The *R* value of this crystal is higher than 20%, indicating poor refinement. An expanded structure with disordered atoms on the isolated TFSA anion is shown here. The labels on the hydrogen atoms are omitted for clarity.

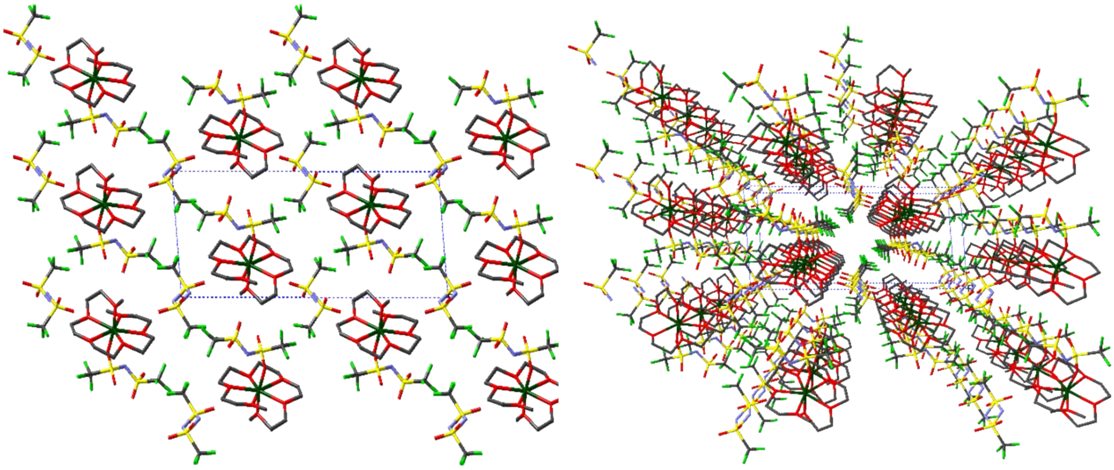


Figure S9. Packing diagrams of the crystal of $[Mg(G5)][TFSA]_2$ drawn along the *a*-axis (left) and its perspective view (right). Hydrogen atoms are omitted for clarity. Green, Mg; red, O; gray, C; blue, N; yellow, S; light green, F.

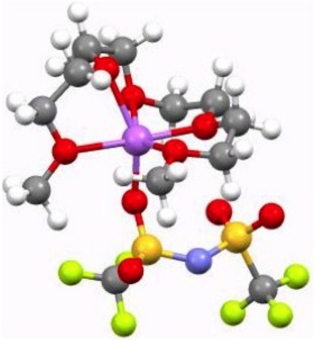


Figure S10. HF/6-311G** level optimized geometry of the second most stable conformational isomer of the [Li(G4)][TFSA] complex.

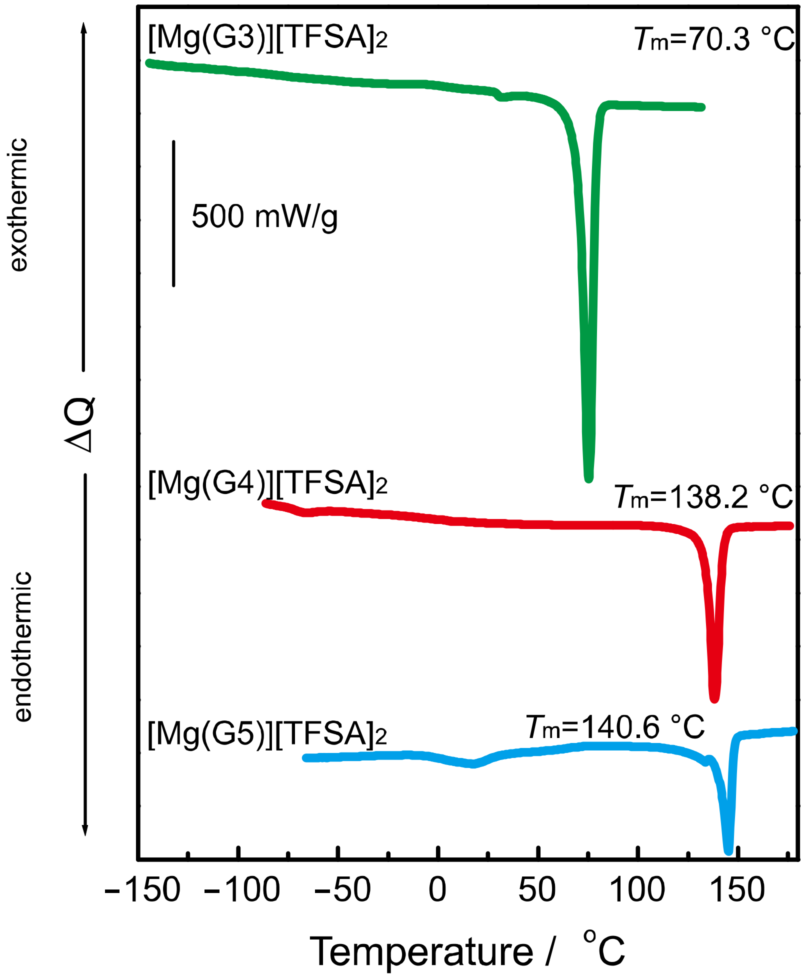


Figure S11. DSC thermograms of $[Mg(glyme)][TFSA]_2$. The DSC thermogram of $[Mg(G4)][TFSA]_2$ was taken from reference 6d.

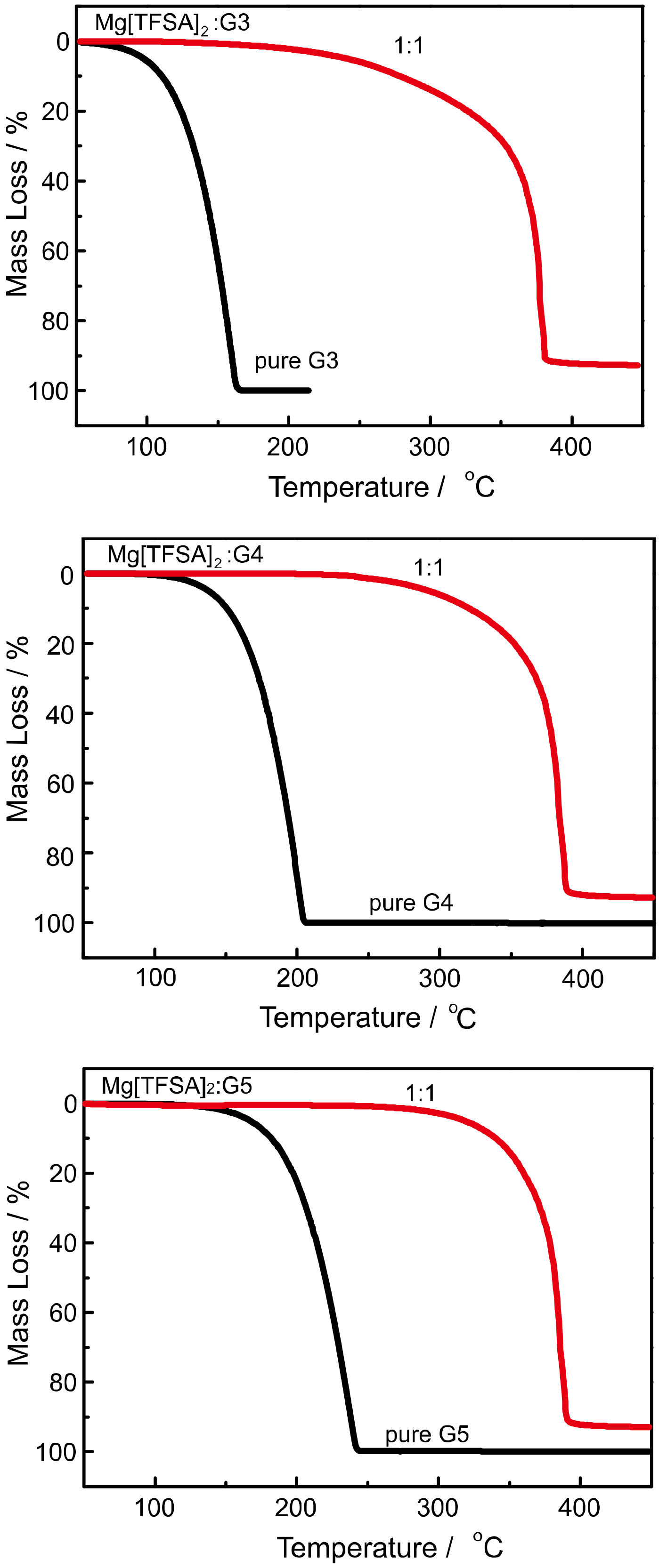


Figure S12. TG curves of [Mg(glyme)][TFSA]$_2$ complexes. The curves of pure glymes are also included as references.