Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Elucidating the Structure of the Magnesium Aluminum Chloride Complex electrolyte for Magnesium-ion batteries

— Supplementary Information —

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I. EXPLANATION OF THE TERNARY PHASE-DIAGRAM

In the manuscript, Figure 8 is a projection of the four dimensions Mg-Al-Cl-charge phase diagram, where the fourth axis (out-of-plane axis) represents a charge neutralizing species. Therefore in Figure 8 some of the tie-lines connecting charged specie, such as Mg^{2+}(5THF) – $AlCl^{2+}$(2T), belong to a tie-surface shared with a negatively charged species in the full phase diagram. In the MACC electrolyte the condition of charge-neutrality must be respected solely by Mg-Al-Cl species, which are enclosed only in the orange part of Fig. 8. Thus only $MgCl_2$ and $AlCl_3$ or $MgCl^+$ and $AlCl_4^-$ can coexist in MACC.

II. IONIC CONDUCTIVITY

The ionic conductivity σ (in mS cm^{-1}) for an unconditioned MACC electrolyte is derived from ΔE of Eq. 1 using Kohlrausch's law for weak electrolytes of Eq. 2.

$$MgCl_2(2THF) + AlCl_3(1THF) \overset{\Delta E, K_d}{\longleftrightarrow} MgCl^+(3THF) + AlCl_4^- \tag{1}$$

$$\sigma = \alpha \cdot C \cdot \Lambda_\infty \tag{2}$$

where C is the concentration of the electrolyte, α is the degree of dissociation of $MgCl_2$(2THF) and $AlCl_3$(1THF) according to the equilibrium constant K_d regulating Eq. 1. Note that the maximum concentration of $MgCl_2$ in solution is dictated by the solubility of $MgCl_2$ in THF, and correspond approximately to 0.78 mM. Given that the solubility of $MgCl_2$(s) also depends on the THF concentration (see reaction (a) in the manuscript) we set this to ~ 12.33 M. Thus, α depends on $K_d = \frac{\alpha^2}{(1-\alpha)^2}$, and $K_d \approx \exp(-\Delta E/RT)$. Λ_∞ (in S cm^2 mol^{-1}) is the limiting molar conductivity and depends on the cation and anion species in the solvent as indicated by Eq. 3.

$$\Lambda_\infty = \lambda_\infty^{MgCl^+} + \lambda_\infty^{AlCl_4^-} \tag{3}$$

Using the ΔE of reaction 1 (~ -0.085 eV) for a concentration of 0.5 M $AlCl_3$ and 0.78 mM $MgCl_2$, respectively, we can re-write as $K_d = \frac{\alpha^2}{(0.5-\alpha)(7.8\times10^{-4})} \approx 27.00$ –by solving the quadratic equation we computed $\alpha \sim 0.092$. 0.092 is also the maximum concentration of $MgCl^+$ in solution as dictated by the low $MgCl_2$ solubility in THF (see reaction (a) in the manuscript).

TABLE I. Concentration for each species at equilibrium set by reactions (a), (b) and (c) in the manuscript. Brackets indicate the reactions settings the concentration values (see manuscript).

Species	THF[a]	$AlCl_3$(1THF)	$MgCl_2$(2THF)	$AlCl_4^+$	$MgCl^+$(3THF)
Concentration	12.33 (a)	0.5 (b)	7.8×10^{-4} (a)	0.092 (c)	0.092 (c)

[a]The concentration of THF is calculated from its density $\sim$ 889.2 g L^{-1} and its molar mass $\sim$ 72.11 g mol^{-1}.

For a 0.5 M solution of unconditioned MACC electrolyte in THF the σ is approximatively 1.96 mS cm^{-1} which is in very good agreement with the experimental conductivity for a MACC electrolyte ($\sim$ 2 mS cm^{-1}) measured experimentally by Doe *et al.*[3] Λ_∞ ($\sim$ 21.25 S cm^2 mol^{-1}) is obtained from $\lambda_\infty^{MgCl^+}$ that is approximated by the experimental value for $ZnBr^+$ in THF ($\sim$ 18.34 S cm^2 mol^{-1}),[1] while $\lambda_\infty^{AlCl_4^-}$ by the experimental value for $AlCl_4^-$ in diglyme ($\sim$ 2.91 S cm^2 mol^{-1}), respectively.[2] Note that we could only find these λ_∞^+, λ_∞^- values in the literature.[1,2]

III. CONVERGENCE NMR ISOTROPIC SHIFT

In Fig. 1 the convergence of the ^{35}Cl NMR isotropic shift as function of basis-set accuracy.

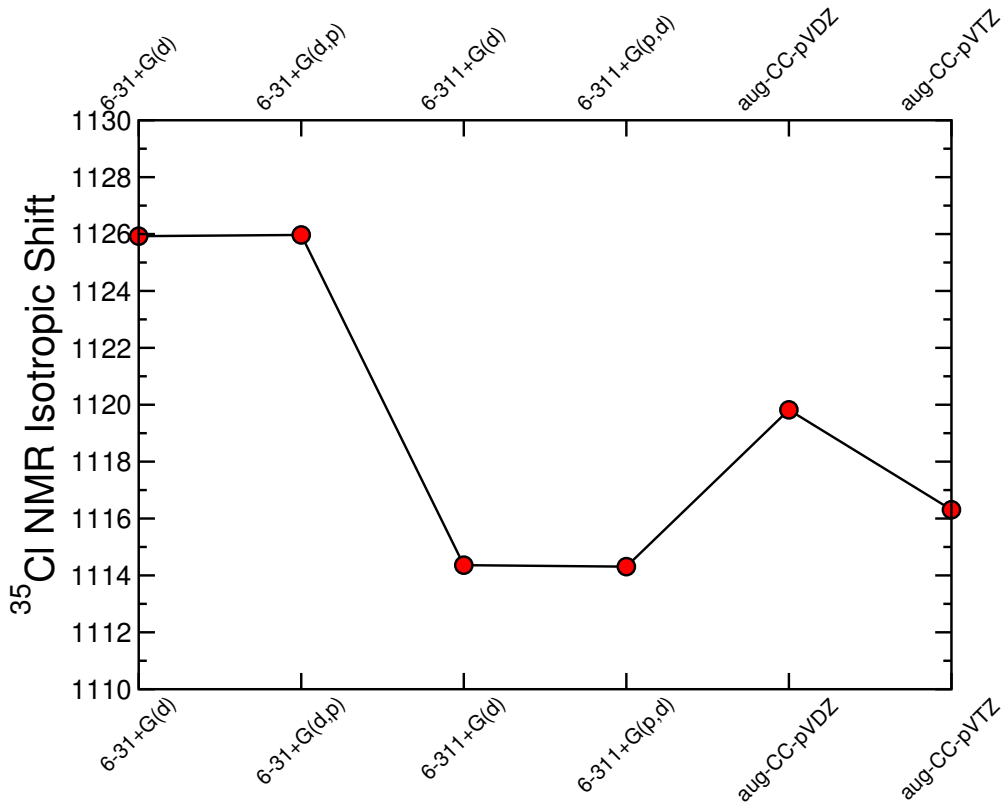

FIG. 1. Convergence of the ^{35}Cl NMR isotropic shift as function of basis-set accuracy. Augmented Dunning's correlation consistent aug-CC-pVTZ basis-set as a reference for benchmark.

IV. GEOMETRIES OF RELEVANT MACC SPECIES

x, y, and z coordinates for relevant MACC species obtained from structural relaxation using DFT with B3LYP and 6-31+G(d) basis-set.

A. $MgCl_2(2THF)$

Cl	+0.000620	+2.183750	+1.635110
Cl	+0.000440	-2.036830	+1.787160
Mg	+0.000040	+0.045280	+0.834770
C	+2.492880	+1.181670	-0.675460
O	+1.650170	+0.006110	-0.423880
C	+2.346540	-1.211680	-0.833450
C	+3.815590	-0.810610	-0.892050
C	+3.734020	+0.642600	-1.390070
H	+1.908920	+1.890410	-1.267180
H	+2.718460	+1.634650	+0.293070
H	+2.104010	-1.983440	-0.101260

```
H     +1.963980 -1.504700 -1.819520
H     +4.261900 -0.854550 +0.108290
H     +4.395240 -1.460150 -1.555300
H     +4.625830 +1.229840 -1.150880
H     +3.596350 +0.665070 -2.477950
C     -2.493480 +1.181740 -0.674850
O     -1.650830 +0.006350 -0.422930
C     -2.346970 -1.211640 -0.832640
C     -3.815990 -0.810610 -0.891970
C     -3.734280 +0.642640 -1.389980
H     -2.719640 +1.634730 +0.293560
H     -1.909380 +1.890620 -1.266290
H     -1.963940 -1.504700 -1.818500
H     -2.104540 -1.983210 -0.100220
H     -4.395330 -1.460160 -1.555480
H     -4.262750 -0.854540 +0.108170
H     -3.596080 +0.665120 -2.477780
H     -4.626240 +1.229820 -1.151220
```

B. $MgCl^{+}$(3THF)

```
Cl    +0.001741 -0.003388 +2.815101
Mg    +0.000523 -0.004595 +0.573417
C     -2.407650 -0.668396 -1.343990
O     -1.547549 -1.051952 -0.213475
C     -2.197569 -2.127208 +0.572063
C     -3.647673 -2.114817 +0.107405
C     -3.522672 -1.710626 -1.371641
H     -2.785849 +0.339219 -1.143980
H     -1.788025 -0.656164 -2.244768
H     -1.690172 -3.064630 +0.321855
H     -2.045715 -1.890519 +1.626811
H     -4.125571 -3.089376 +0.240763
H     -4.226258 -1.372697 +0.668948
H     -3.230476 -2.571216 -1.983974
H     -4.449193 -1.301312 -1.783766
C     +1.795492 -1.718244 -1.364365
O     +1.685976 -0.812095 -0.210169
C     +2.935279 -0.856864 +0.585724
C     +3.648322 -2.111425 +0.101678
C     +3.254251 -2.169278 -1.383564
H     +1.103852 -2.550373 -1.197276
H     +1.491730 -1.160719 -2.254439
H     +3.496106 +0.056204 +0.360247
H     +2.646591 -0.865800 +1.638447
```

H	+4.729760	-2.046819	+0.250881
H	+3.281481	-2.992876	+0.639260
H	+3.865222	-1.475620	-1.972343
H	+3.363199	-3.167427	-1.816412
C	+0.589290	+2.411876	-1.361482
O	-0.140148	+1.863463	-0.207860
C	-0.716051	+2.966633	+0.597323
C	+0.013845	+4.211043	+0.111234
C	+0.252668	+3.901388	-1.376138
H	+1.655757	+2.228656	-1.195746
H	+0.258480	+1.871737	-2.252528
H	-1.788851	+2.999715	+0.380687
H	-0.556133	+2.714134	+1.647269
H	-0.580645	+5.115800	+0.265822
H	+0.963462	+4.332097	+0.644418
H	-0.656793	+4.085833	-1.958902
H	+1.060750	+4.495069	-1.812449

C. $Mg_2Cl_3^+$(4THF)

Cl	-0.006065	+1.654445	-1.355459
Cl	+0.005731	-1.656068	-1.354273
Cl	+0.000498	+0.000308	+1.706822
Mg	+1.486467	+0.005566	-0.244301
Mg	-1.486254	-0.006412	-0.243838
C	+3.718155	+1.513574	+1.250516
O	+3.022603	+1.371835	-0.037495
C	+3.376290	+2.490074	-0.925390
C	+4.038877	+3.517570	-0.015136
C	+4.731176	+2.635677	+1.036804
H	+2.966377	+1.769695	+2.004483
H	+4.161450	+0.545092	+1.491912
H	+4.067524	+2.101381	-1.681852
H	+2.458200	+2.831543	-1.403603
H	+4.736803	+4.157812	-0.562247
H	+3.282778	+4.157787	+0.453445
H	+5.674702	+2.236937	+0.646188
H	+4.948448	+3.168225	+1.967115
C	+3.874756	-1.848996	-0.883510
O	+2.881039	-1.484187	+0.131237
C	+2.584088	-2.648415	+0.983197
C	+3.250859	-3.831582	+0.288475
C	+4.454086	-3.179608	-0.412427
H	+3.357171	-1.948343	-1.845105
H	+4.600648	-1.033815	-0.937152

```
H     +3.014929 -2.441482 +1.968241
H     +1.499419 -2.730035 +1.065303
H     +3.542403 -4.609833 +0.999692
H     +2.570892 -4.274967 -0.447197
H     +5.274707 -3.014989 +0.295475
H     +4.837956 -3.774286 -1.246217
C     -3.719439 -1.512888 +1.250647
O     -3.023000 -1.371839 -0.036977
C     -3.377241 -2.489792 -0.925034
C     -4.041058 -3.516703 -0.015036
C     -4.733271 -2.634166 +1.036404
H     -2.968298 -1.769615 +2.005042
H     -4.162044 -0.544021 +1.491741
H     -4.067846 -2.100538 -1.681784
H     -2.459225 -2.831993 -1.402865
H     -4.739148 -4.156514 -0.562442
H     -3.285666 -4.157399 +0.454037
H     -5.676220 -2.234669 +0.645164
H     -4.951574 -3.166444 +1.966630
C     -2.583087 +2.648451 +0.983275
O     -2.880286 +1.484126 +0.131600
C     -3.873488 +1.849100 -0.883602
C     -4.452485 +3.180024 -0.413013
C     -3.249216 +3.831712 +0.288082
H     -3.014233 +2.441988 +1.968289
H     -1.498407 +2.729681 +1.065630
H     -3.355498 +1.948058 -1.845019
H     -4.599665 +1.034180 -0.937344
H     -4.835890 +3.774642 -1.247061
H     -5.273377 +3.015873 +0.294685
H     -2.568876 +4.274652 -0.447514
H     -3.540659 +4.610249 +0.999027
```

D. $Mg_3Cl_5^+$(6THF)

```
Cl    +1.436253 +2.494330 -0.042694
Cl    -0.001108 -0.021274 -1.737591
Cl    +1.433620 -2.495938 +0.042901
Cl    -0.001539 +0.021167 +1.737501
Cl    -2.878714 +0.001496 -0.000616
Mg    -0.965093 +1.676866 -0.019050
Mg    +1.927467 -0.001108 +0.000216
Mg    -0.966927 -1.675892 +0.018687
C     -3.086719 -3.274606 -1.645339
O     -1.666325 -2.987371 -1.441759
```

```
C     -0.883619 -3.463211 -2.587388
C     -1.849497 -4.327299 -3.394278
C     -3.206779 -3.660602 -3.116764
H     -3.358011 -4.102946 -0.980199
H     -3.647854 -2.381681 -1.364658
H     -0.543989 -2.583064 -3.141705
H     -0.016981 -3.996472 -2.192945
H     -1.590059 -4.345797 -4.456992
H     -1.845728 -5.360382 -3.026749
H     -3.331648 -2.766312 -3.738316
H     -4.057626 -4.323814 -3.298878
C     -2.512444 -2.450996 +2.662482
O     -1.752412 -2.912719 +1.496862
C     -1.333870 -4.303393 +1.684961
C     -1.647783 -4.622279 +3.144909
C     -2.861707 -3.722888 +3.429030
H     -1.865220 -1.781495 +3.238013
H     -3.370017 -1.889634 +2.288380
H     -1.918552 -4.920702 +0.993292
H     -0.275047 -4.370806 +1.427778
H     -1.854422 -5.685916 +3.296248
H     -0.804486 -4.344442 +3.787769
H     -3.778626 -4.174799 +3.032251
H     -3.012419 -3.529812 +4.495333
C     -1.329190 +4.305104 -1.684623
O     -1.748930 +2.914698 -1.497180
C     -2.508952 +2.454023 -2.663231
C     -2.857023 +3.726490 -3.429351
C     -1.642508 +4.624856 -3.144513
H     -1.913493 +4.922614 -0.992819
H     -0.270362 +4.371534 -1.427196
H     -1.862062 +1.784263 -3.238835
H     -3.367058 +1.893150 -2.289617
H     -3.007560 +3.533966 -4.495779
H     -3.773724 +4.178927 -3.032668
H     -0.799252 +4.346688 -3.787283
H     -1.848322 +5.688712 -3.295439
C     -0.880953 +3.463625 +2.587355
O     -1.663709 +2.988935 +1.441268
C     -3.083911 +3.277418 +1.644507
C     -3.204097 +3.662784 +3.116078
C     -1.846336 +4.328211 +3.394302
H     -0.542269 +2.582955 +3.141414
H     -0.013733 +3.996305 +2.193402
H     -3.354166 +4.106386 +0.979724
H     -3.645801 +2.385189 +1.363141
H     -4.054444 +4.326618 +3.298262
```

```
H     -3.329886 +2.768298 +3.737163
H     -1.841588 +5.361436 +3.027184
H     -1.587205 +4.346065 +4.457102
C     +3.400331 -0.832453 +2.668624
O     +3.407768 +0.001331 +1.463730
C     +4.403703 +1.067589 +1.593579
C     +4.881721 +0.997818 +3.042999
C     +4.702710 -0.490734 +3.384355
H     +2.518858 -0.561026 +3.258344
H     +3.311191 -1.870225 +2.343236
H     +5.209641 +0.853198 +0.882612
H     +3.922022 +2.009369 +1.323891
H     +5.914011 +1.343716 +3.150701
H     +4.246498 +1.617675 +3.686312
H     +5.533182 -1.083139 +2.982094
H     +4.640760 -0.679337 +4.460274
C     +4.402701 -1.072302 -1.593104
O     +3.407973 -0.004925 -1.463187
C     +3.401734 +0.829159 -2.667853
C     +4.704222 +0.486636 -3.382995
C     +4.881701 -1.002224 -3.042208
H     +5.208435 -0.859330 -0.881484
H     +3.919746 -2.013692 -1.324328
H     +2.520361 +0.558548 -3.258108
H     +3.313196 +1.866904 -2.342227
H     +4.643048 +0.675766 -4.458866
H     +5.534974 +1.078148 -2.979995
H     +4.246344 -1.621213 -3.686225
H     +5.913748 -1.348996 -3.149424
```

E. $AlCl_3$(1THF)

```
Al    -0.988134 +0.000527 +0.012487
Cl    -1.569992 -1.647758 -1.205421
Cl    -1.150984 -0.335600 +2.116261
Cl    -1.593797 +1.934491 -0.645198
C     +1.731213 -1.190900 -0.236994
O     +0.909587 +0.042212 -0.247512
C     +1.749088 +1.231230 +0.003612
C     +3.158207 +0.743709 -0.301258
C     +3.122277 -0.717711 +0.177141
H     +1.267773 -1.889579 +0.461294
H     +1.688823 -1.594647 -1.250626
H     +1.374251 +2.020588 -0.647093
H     +1.614594 +1.512824 +1.052617
```

```
H     +3.357014 +0.797449 -1.377715
H     +3.912841 +1.342098 +0.217512
H     +3.905366 -1.333274 -0.275029
H     +3.234809 -0.767253 +1.265869
```

F. $AlCl_4^-$

```
Al    +0.009756 +0.007267 +0.000887
Cl    +0.326400 -1.978600 +0.838088
Cl    -1.731933 +0.905586 +0.953060
Cl    -0.361819 -0.178015 -2.136324
Cl    +1.759927 +1.245498 +0.344501
```

V. BASIS-SET AND FUNCTIONAL CONVERGENCE

Table II shows the convergence of the reaction energy (ΔE) for the reaction in Eq. 4 with different basis-set and functionals.

$$MgCl^+(3THF) + MgCl_2(2THF) \rightarrow Mg_2Cl_3^+(4THF) + THF \tag{4}$$

TABLE II. Computed ΔE (in eV) for reaction in Eq. 4.

Basis-set (B3LYP)	ΔE
6-31+G(d)	–0.2456
6-31+G(d,p)	–0.3776
6-311+G(d,p)	–0.3954
aug-CC-pVDZ	–0.4282

The ΔEs of Eq. 4 vary as function of the basis-set quality form 6-31+G(d) to aug-CC-pVDZ, not showing substantial convergence within chemical accuracy. For this reason the minimal basis-set 6-31+G(d) is chosen easing the large computational effort of this study.

VI. RADIAL DISTRIBUTION FUNCTIONS

Radial distribution function as obtained with the Classical molecular dynamics setup explained in the methodology section of the manuscript.

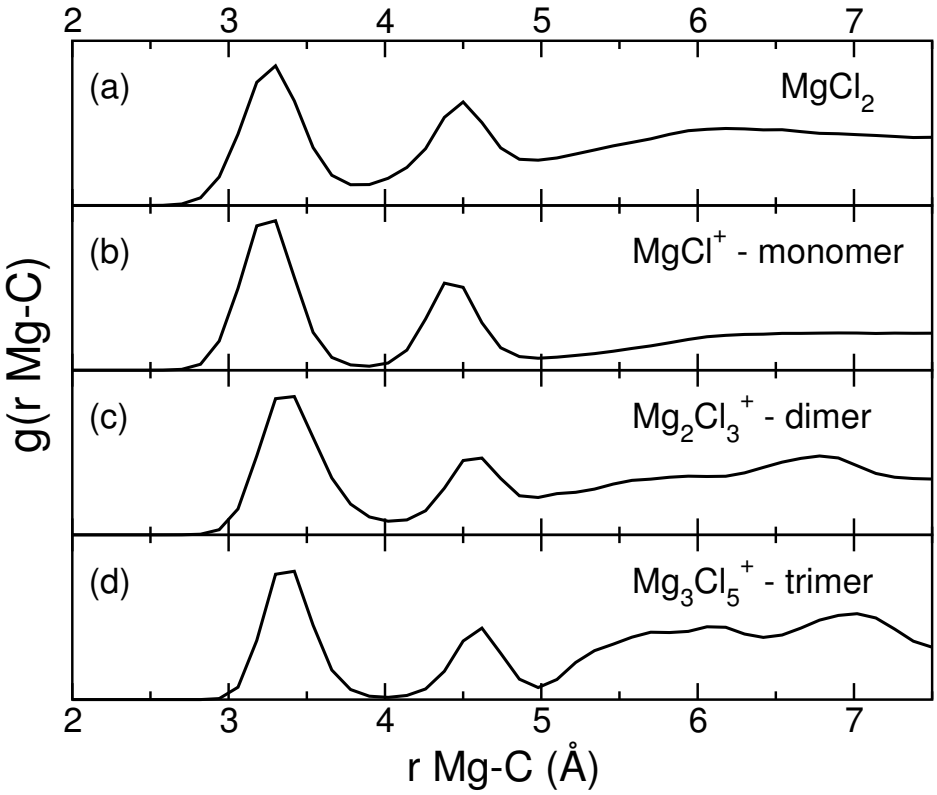

FIG. 2. Mg-C(THF) radial distribution functions (in Å) for a) $MgCl_2$, b) $MgCl^+$ (monomer), c) $Mg_2Cl_3^+$ (dimer) and d) $Mg_3Cl_5^+$ (trimer).

[1] A. A. Al-Najar and H. S. Abbo, Bull. Chem. Soc. Jpn. **63**, 2447 (1990).

[2] A. Kidata, K. Nakamura, K. Fukami, and K. Murase, Electochemistry **82**, 946 (2014).

[3] R. E. Doe, R. Han, J. Hwang, A. J. Gmitter, I. Shterenberg, H. D. Yoo, N. Pour, and D. Aurbach, Chem. Commun. **50**, 243 (2014).

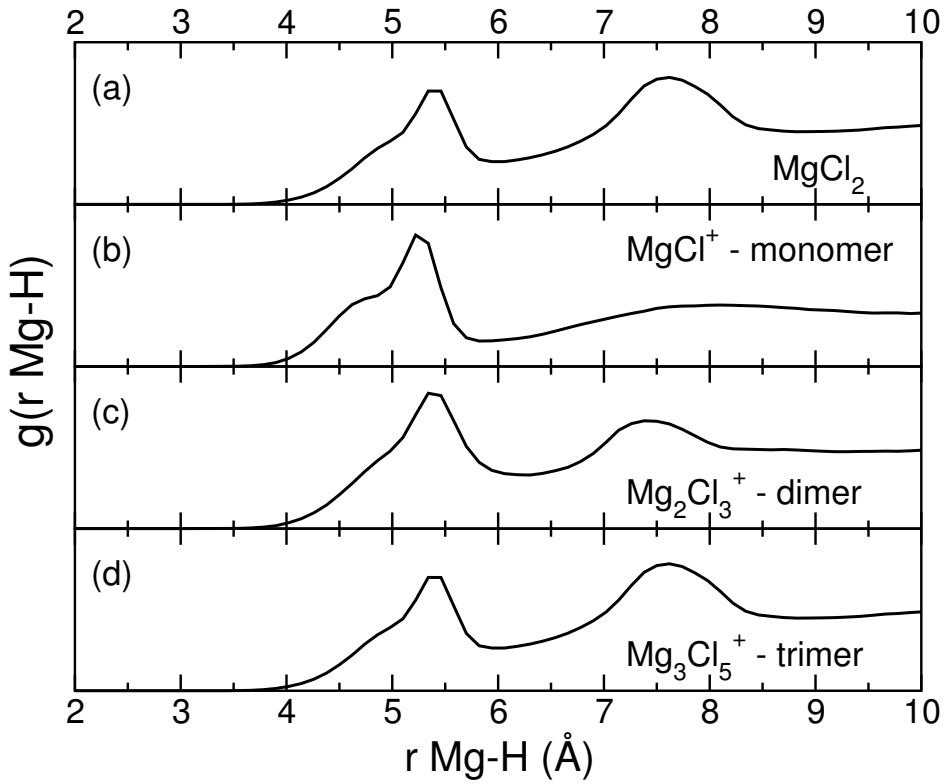

FIG. 3. Mg-H(THF) radial distribution functions (in Å) for a) $MgCl_2$, b) $MgCl^+$ (monomer), c) $Mg_2Cl_3^+$ (dimer) and d) $Mg_3Cl_5^+$ (trimer).

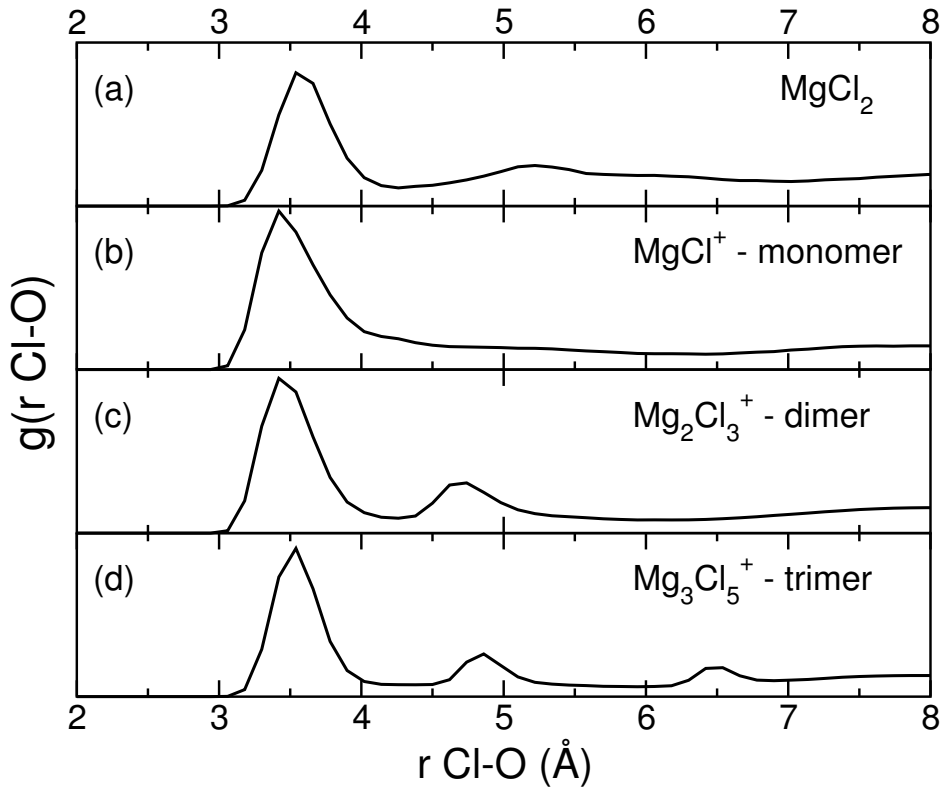

FIG. 4. Cl-O(THF) radial distribution functions (in Å) for a) $MgCl_2$, b) $MgCl^+$ (monomer), c) $Mg_2Cl_3^+$ (dimer) and d) $Mg_3Cl_5^+$ (trimer).

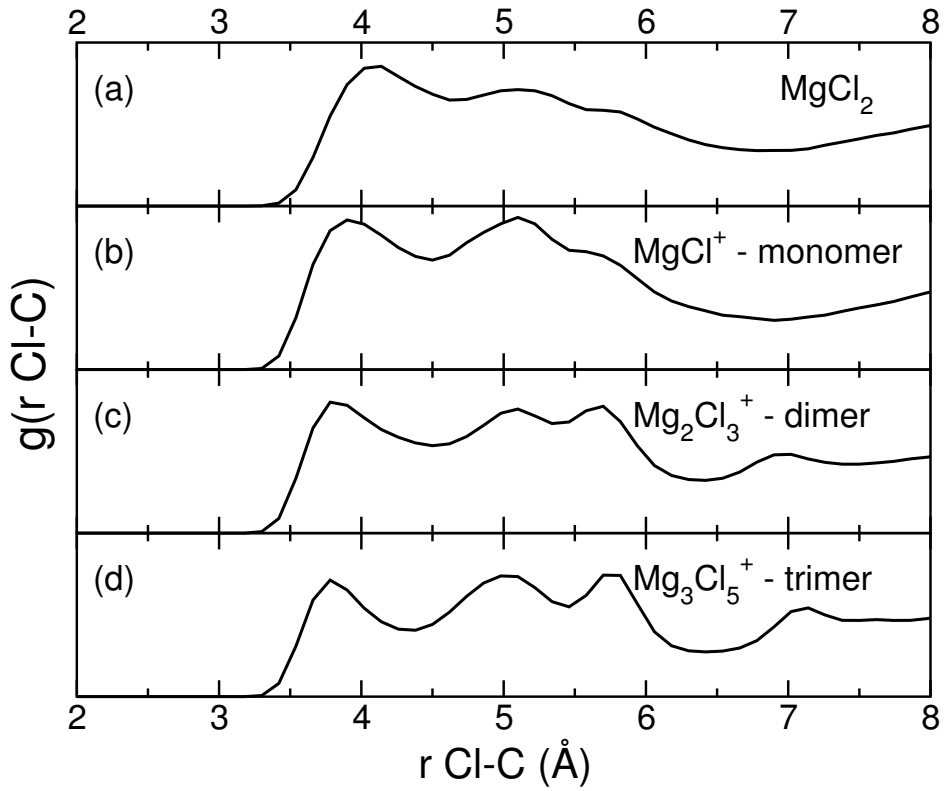

FIG. 5. Cl-C(THF) radial distribution functions (in Å) for a) $MgCl_2$, b) $MgCl^+$ (monomer), c) $Mg_2Cl_3^+$ (dimer) and d) $Mg_3Cl_5^+$ (trimer).

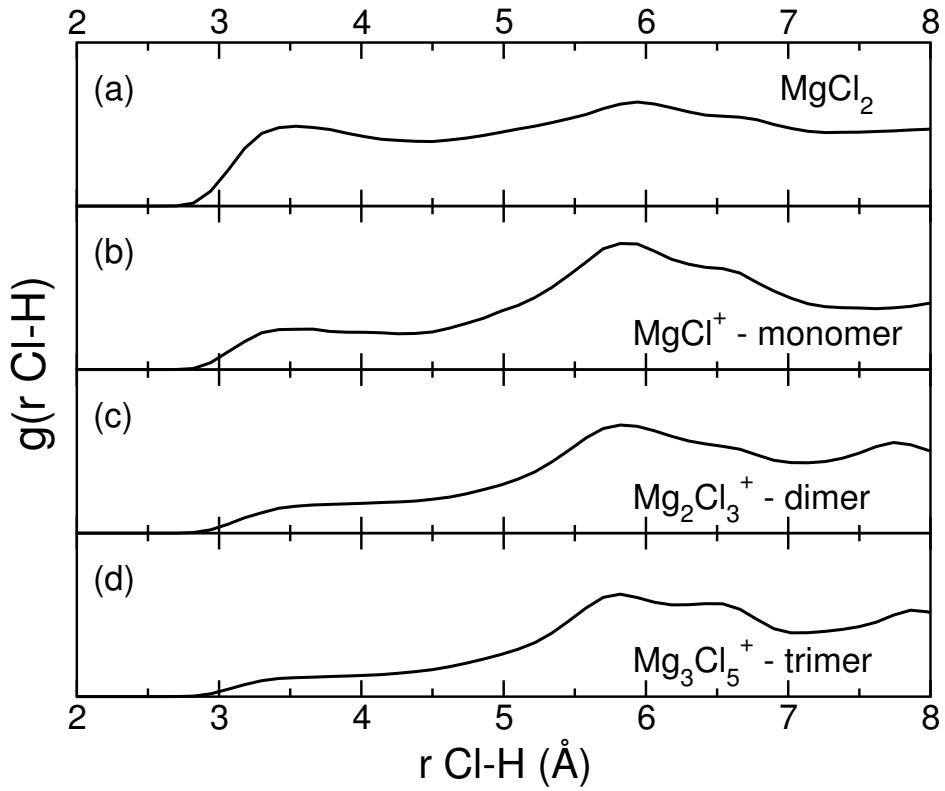

FIG. 6. Cl-H(THF) radial distribution functions (in Å) for a) $MgCl_2$, b) $MgCl^+$ (monomer), c) $Mg_2Cl_3^+$ (dimer) and d) $Mg_3Cl_5^+$ (trimer).