Rechargeable magnesium batteries have attracted much interest due their high volumetric capacity, potential for safe operation, and the natural abundance of magnesium. However, the development of magnesium batteries for practical applications has been obstructed by the lack of understanding of the liquid structure of electrolytes. Herein, we use quantum density functional theory coupled with a continuum solvent model to investigate the structure of Mg(BH₄)₂ in two ethereal solvents: tetrahydrofuran (THF), and monoglyme (G1). The most energetically favorable clusters of Mg(BH₄)₂, MgBH₄⁻, and Mg₂⁺, with associated solvent molecule ligands, are determined. The free energy required to generate monovalent ions in the electrolyte is positive and the formation of divalent complexes is prohibitive. Singly and doubly charged complexes are more stable in G1 than THF, which is consistent with experimental findings. From the standpoint of free energy, clusters containing multiple magnesium atoms are not favored. Theoretical ²⁵Mg-NMR, ¹³B-NMR spectra, and infrared vibrational modes of borohydride were calculated for each cluster. The relationships between cluster charge and the signals of each spectrum are determined. These analytical descriptors could be useful to characterize the degree of ion dissociation in the electrolyte.

For rechargeable batteries to become widespread in electric vehicle and grid energy storage applications, it is imperative that they are safe and low cost.¹² These challenges have motivated researchers in recent years to consider alternatives to lithium-ion batteries, such as sodium,⁴ and multivalent⁶,battery chemistries. Ever since the first prototypes were developed,⁷,⁸ magnesium batteries have attracted much interest from the research community. Compared with lithium-ion batteries, magnesium batteries have several advantages, such as their high volumetric capacity (3832 mAh/cm³), which is a result of the divalency of magnesium. Additionally, the cycling of plating/stripping of Mg²⁺ onto the magnesium metal anode does not produce dendrites, which alleviates one of safety concerns of lithium batteries.⁹,¹⁰

However, magnesium batteries face crucial challenges before they can succeed in practical applications.¹¹ In particular, the choice of the electrolyte is critical to their performance.¹²,¹³ There are only a handful of electrolytes known to be stable¹² during battery cycling, due to the reactivity of the Mg anode.⁸,¹³ Lu et al. considered different classes of organic solvents;⁴ those containing carbonate or nitrile groups led to the formation of surface films on the anode, but ethereal solvents remained inactive. Additionally, salt anions such as ClO₄⁻ and BF₄⁻ led to the formation of passivation layers with high impedance. Magnesium organohalolaulminates,¹⁶ seventeen popularized by Aurbach et al.,⁸ and the magnesium aluminum chloride complex¹⁸ are examples of electrolytes which have successfully demonstrated high anodic stability and the capability to reversibly plate magnesium, but they contain halides which are corrosive to some battery parts.

In 2012, Mohdadi et al. reported¹⁹ that an electrolyte consisting of magnesium borohydride in an ethereal solvent, such as tetrahydrofuran or monoglyme, could reversibly plate/strip Mg²⁺ onto a magnesium metal anode. X-ray photoelectron spectroscopy¹⁹ has shown that a Mg anode using this electrolyte did not yield signals for boron or carbon, implying that the electrolyte is electrochemically stable during charge and discharge cycles. This marked the discovery of the first stable, halide-free electrolyte for magnesium batteries. Since then, there have been a number of experimental¹¹,¹²,¹³,¹⁴,²³ and theoretical¹¹,¹²,¹³,²⁰ studies aimed at improving battery performance.

Presently, there are some problems with this electrolyte, including low ionic conductivity and solubility.²₀,²³ These properties can be improved with the addition LiBH₄, but at the expense of using costly lithium. Previous studies have not focused on elucidating the electroactive species in the electrolyte or the liquid structure of the ions. Some previous studies have performed classical molecular dynamics simulations²,²³ using the OPLS-AA²⁷ and Generalized AMBER²⁸ force fields to study magnesium borohydride in ethereal solvents, but these studies have not focused in detail on the coordination of solvated magnesium borohydride complexes, or the energetics of ionic dissociation. Moreover, the force field parameters used in these studies have not been validated for accuracy in this application.

It has been hypothesized that important properties of the electrolyte, such as conductivity and solubility, depend on the interaction of solvent and solute in the electrolyte.¹⁵,²⁰ In particular, it has been asserted¹⁹,¹⁰ that the “denticity” of the solvent molecule, the number of ligand oxygens per solvent molecule, plays an important factor in the coulombic efficiency and level of dissociation of BH₄⁻ in the electrolyte.

In the present study, we use quantum density functional theory to investigate the structures and energetics of neutral and charged ion-solvent clusters in electrolytes containing magnesium borohydride in tetrahydrofuran (THF), and monoglyme (G1). The solvent environment beyond the first shell is approximated by using a continuum solvation model. The description of the interactions among magnesium borohydride in both neutral and cationic states and solvent molecules provides valuable information about the liquid structure, which is difficult to obtain by experimental measurement. This work also prepares a baseline for developing force fields which can be used with classical molecular dynamics to simulate electrolyte using explicit solvent molecules.

Methods

Geometry optimization and calculation of free energy.—In crystals formed by precipitation from solutions of magnesium borohydride dissolved in THF²⁰ or diglyme,³⁰ each magnesium atom is chelated directly by BH₄⁻ and solvent oxygens. In this study, clusters of magnesium cations, borohydride anions, and solvent molecules (G1 and THF depicted in Fig. 1A) are modeled in the liquid phase using quantum density functional theory. Solvent molecules in the first solvation shell are represented explicitly, whereas the outer solvation shells are represented implicitly using a solvent reaction field,¹⁷ the SMD solvation model.¹⁷ An illustration of this method applied to Mg(BH₄)₂ at G1 is shown in Fig. 1B. The SMD model considers the electrostatic and short range dispersion interactions of solvent in the outer shells, together with the atoms modeled explicitly inside of the first shell. The Gibbs free energy of clusters of magnesium, borohydride, and solvent molecules.

Footnote:

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18 The magnesium aluminum chloride complex is an example of an electrolyte that is corrosive to some battery parts.

19 The capability to reversibly plate magnesium, but they contain electrolytes which have successfully demonstrated high anodic stability and the capability to reversibly plate magnesium, but they contain halides which are corrosive to some battery parts.

20 These properties can be improved with the addition LiBH₄, but at the expense of using costly lithium. Previous studies have not focused on elucidating the electroactive species in the electrolyte or the liquid structure of the ions.
Density functionals have been successfully applied in the study of coordination chemistry. For the purposes of coordination to magnesium, each BH₄⁻ anion and solvent oxygen occupy a single coordination site. For example, the initial geometry of four-coordinate Mg(BH₄)₂(THF)₂ was forming assumed tetrahedral coordination. In more complex coordination environments, there may be more than one possible arrangement of the anions and solvent molecules. In this case, all possible geometries were considered and generated as initial structures.

The optimal geometry of each cluster is obtained using the GEDiIs⁴⁰ energy minimization algorithm without implicit solvation. The Gibbs free energy of each cluster is then computed using Eq. 1. To compute the first term of Eq. 1, the total energy of the cluster in the implicit solvent is computed without further optimization of the atomic coordinates. The final three terms of Eq. 1 are computed by calculating the vibrational frequencies of each cluster, followed by thermochemical analysis in the absence of the solvation model. This procedure is similar to what has been used to study magnesium aluminum chloride complexes.⁴¹

The cluster free energy is calculated using Eq. 2 below.

\[ \Delta G_C = G(M_g(BH_4)_yS_z) - xG(Mg^{2+}) - yG(BH_4^-) - zG(S) \]

where \( \Delta G_C \) is the cluster free energy, and \( M_g(BH_4)_yS_z \) is a cluster with \( x \) magnesium atoms, \( y \) borohydride anions, and \( z \) solvent molecules (S).

Validation of methods.—We examined the M06 functional using different basis sets by optimizing the geometry of clusters consisting of dimethyl ether (DME), magnesium, and borohydride. The geometries of DME, BH₄⁻, Mg(BH₄)₂(DME)₂, and MgBH₄⁺(DME)₃ were obtained by energy minimization at different levels of theory, from M06/6-31+G(d) to M06/6-311++G(d,p), and at MP2/6-311++G(d,p) for comparison. Dissociation energies of Mg(BH₄)₂(DME)₂, and MgBH₄⁺(DME)₃ are calculated by subtracting the energies of these clusters to their constituent Mg²⁺, DME, and BH₄⁻ groups in vacuum.

A comparison of the dissociation energies of these clusters, calculated using different basis sets, is shown in Table I. The results from M06 using different basis sets are shown alongside MP2/6-311+G(d,p). For comparison, we also show results for the M06-2X⁴⁰ and M06-L⁴² functionals in Table I. The “reaction energy” shown in Table I is calculated for the dissociation of one borohydride anion in the following transformation:

Reaction 1 : Mg(BH₄)₂(DME)₃+DME → MgBH₄⁺(DME)₃+BH₄⁻

For convenience, the percent deviation from MP2/6-311+G(d,p) is shown in parentheses in Table I. In general, the M06 functional performs better than either M06-2X or M06-L in predicting dissociation energies. For prediction of the reaction energy, the M06-2X functional has performance rivaling M06, but it falls short in predicting dissociation energies. The size of the basis set used with M06 does not seem to make much difference in predicting dissociation or reaction energies. Thus, unless otherwise stated the M06/6-31+G(d) method was used for all calculations in this study.

Calculation of FTIR and NMR spectra.—Vibration frequencies were computed by normal mode analysis in the absence of the SMD solvation model. Based on the recommendation of the Computational Chemistry Comparison and Benchmark Database for the M06-2X density functional,⁵⁶ we use a scaling factor of 0.95 applied to our computed vibrational frequencies.

For the most stable neutral, singly, and doubly charged clusters, the ¹¹B and ²⁵Mg NMR isotropic shielding tensors are calculated using Gaussian 09.⁵³ All chemical shifts were computed using the gauge-independent atomic orbital method.⁵⁴ A larger 6–31+G(d) basis set was used for these computations, which was found to yield better agreement with MP2/6-311++G(d,p). Reference signals for ¹¹B- and ²⁵Mg-NMR were obtained using BF₃-Diethylether (103.6 ppm) and Mg²⁺(H₂O)₅ (565 ppm), respectively.
Table I. Validation of basis set and density functionals against energies of Mg(BH4)2(DME)2 and MgBH4+(DME)3 dissociation and of Reaction 1. The percent difference of each method to MP2/6-311++G(d,p) is in parentheses.

| Method/Basis Set  | Mg(BH4)2(DME)2 Dissociation Energy (kcal/mol) | MgBH4+(DME)3 Dissociation Energy (kcal/mol) | Reaction Energy (kcal/mol) |
|------------------|---------------------------------------------|---------------------------------------------|---------------------------|
| MP2/6-311++G(d,p) | 476.38                                      | 580.50                                      | 104.12                    |
| M06/6-31+G(d)     | 470.41 (1.25)                               | 577.17 (0.57)                               | 106.76 (–2.53)            |
| M06/6-31++G(d,p)  | 470.82 (1.17)                               | 577.39 (0.54)                               | 106.57 (–2.36)            |
| M06-L/6-31       | 470.10 (1.32)                               | 576.70 (0.65)                               | 106.60 (–2.38)            |
| M06-2X/6-31+G(d) | 470.25 (1.29)                               | 577.14 (0.58)                               | 106.88 (–2.65)            |
| M06-2X/6-31++G(d,p) | 489.21 (–2.69)                           | 595.98 (–2.67)                              | 106.78 (–2.55)            |
| M06-L/6-31+G(d)  | 490.53 (–2.97)                               | 596.87 (–2.82)                              | 106.34 (–2.13)            |
| M06-L/6-31++G(d,p) | 466.40 (2.09)                              | 576.31 (0.72)                               | 109.91 (–5.56)            |
| M06-L/6-31++G(d,p) | 466.94 (1.98)                              | 577.46 (0.52)                               | 110.52 (–6.15)            |

Results

**THF solvent.**—The optimized geometries of clusters containing magnesium, borohydride anions and different numbers of THF ligands are shown in Figure 2. The first, second, and third rows of Fig. 2 depict neutral, singly, and doubly charged clusters. The free energies for association of THF molecules between clusters are shown in red, in which a negative value corresponds to exothermicity. In Fig. 2a, the geometries correspond to different numbers of THF molecules associated to Mg(BH4)2, and coordination numbers of three to six. The coordination geometries of these clusters are roughly trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral arrangements of chelating groups surrounding the magnesium atom. This is also true of the singly and doubly charged clusters depicted in Figs. 2b–2c, depicting coordination numbers of three to six. In Mg2+(THF)6, O-Mg-O angles match closely (89–91°) with octahedral (90°) coordination. In Mg(BH4)2(THF)3, which approximates a trigonal bipyramidal coordination, the B-Mg-B angle along the equator is 138°, which is greater than the ideal value of 120°, implying that the borohydride ligands are bulkier in the coordination sphere of magnesium than THF molecules.

![Figure 2](image-url)
Beginning with Mg(BH$_4$)$_2$(THF) the free energy decreases by 6.7 kcal/mol with an additional chelating THF molecule in Mg(BH$_4$)$_2$(THF)$_2$ and a further 1.8 kcal/mol to Mg(BH$_4$)$_2$(THF)$_3$. With the addition of another THF molecule to Mg(BH$_4$)$_2$(THF)$_3$ the free energy increases by 11.5 kcal/mol. As the coordination of the magnesium atom becomes more crowded, additional THF ligands increase the free energy due to steric repulsion. Among neutral clusters, the five-coordinate Mg(BH$_4$)$_2$(THF)$_3$ has the lowest free energy. It was discovered using X-ray diffraction that precipitates from a Mg(BH$_4$)$_2$ solution in THF contain Mg(BH$_4$)$_2$(THF)$_3$ crystals. It is interesting that the lowest free energy cluster corresponds to this experimental observation, although the chemical environment in the crystal is different than in solvent.

For singly charged clusters in THF, it is again found that a coordination number of five is the most favorable with MgBH$_4$ (THF)$_5$. Among the doubly charged clusters, a coordination number of six is most favorable. The cluster Mg$^{2+}$ (THF)$_6$ has been observed as part of some crystal structures involving weak anions. There are two factors contributing to the stability of six-coordinate Mg$^{2+}$ (THF)$_6$; despite the preference for five ligands in neutral and singly charged clusters. The first factor is that THF solvent occupies less area in the coordination sphere of magnesium than BH$_4^-$. Each borohydride ligand coordinates magnesium by two or three bridging hydrogens and contain more negative charge. The second factor is an increased cationic charge on magnesium that strengthens association of THF. As the coordination number changes from three to four, the association free energy changes from -6.7 kcal/mol for charge neutral clusters to -17.4 kcal/mol for doubly charged clusters, indicating that magnesium is becoming more electrophilic as cluster charge increases.

For clusters which have the same coordination number, but different charges, the Mg-O and Mg-B distances decrease with increasing cluster charge. This implies that when borohydride anions are removed from a cluster, the electronegativity of magnesium increases, which allows the ligands to be drawn closer. In lowly coordinated clusters, the borohydride anion rotates so that an edge of its tetrahedron contacts the magnesium atom. This behavior can be seen in Mg(BH$_4$)$_2$(THF) and Mg(BH$_4$)$_2$(THF)$_2$, where the Mg-B distance is 2.10–2.16 Å. However, as the coordination number in the cluster increases, the borohydride anion rotates so that an edge of its tetrahedron contacts the magnesium atom, resulting in two bridging hydrogens. This behavior has been discussed in greater detail in literature.

Additionally, Table II lists the average contact distance between magnesium and borohydride hydrogens. In this study, we differentiate between hydrogens in direct contact with magnesium, which are denoted Hb, as in “bridging” hydrogens, from terminal hydrogens, Ht. At first glance, the Mg-Hb column in Table II appears to adopt no

### Table II. Formation free energies and Mg-O/Mg-B/Mg-H contact distances for Mg(BH$_4$)$_y$(THF)$_z$ clusters. Also depicted are B-H distances for bridging (Hb) and terminal (Ht) hydrogens. Relevant experimental data are shown in parentheses.

| Cluster | $\Delta G_f$, kcal/mol | Mg-O Distance, Å | Mg-B Distance, Å | # Mg-Hb Contacts | Mg-Hb Distance, Å | Mg-Ht Distance, Å | B-Hb/B-Ht Distances, Å |
|---------|------------------------|------------------|------------------|------------------|------------------|------------------|-----------------------|
| Mg(BH$_4$)$_2$(THF) | -86.20 | 2.00 | 2.16 | 6 | 2.05 | 1.244/1.196 |
| Mg(BH$_4$)$_2$(THF)$_2$ | -92.86 | 2.11 | 2.22 | 6 | 2.11 | 1.239/1.200 |
| Mg(BH$_4$)$_2$(THF)$_3$ | -94.62 | 2.15 (2.09) | 2.45 (2.45) | 4 | 2.00 | 1.245/1.216 |
| Mg(BH$_4$)$_2$(THF)$_4$ | -83.10 | 1.99 | 2.10 | 3 | 2.00 | 1.238/1.219 |
| Mg(BH$_4$)$_2$(THF)$_5$ | -68.91 | 1.99 | 2.10 | 3 | 2.00 | 1.251/1.188 |
| Mg(BH$_4$)$_2$(THF)$_6$ | -80.10 | 2.12 | 2.37 | 2 | 1.94 | 1.258/1.208 |
| Mg(BH$_4$)$_2$(THF)$_7$ | -83.11 | 2.12 | 2.37 | 2 | 1.94 | 1.258/1.208 |
| Mg$^{2+}$(THF)$_8$ | -78.15 | 2.22 | 2.49 | 2 | 2.03 | 1.238/1.214 |
| Mg$^{2+}$(THF)$_9$ | -35.87 | 2.19 | 2.37 | 2 | 1.94 | - | - |
| Mg$^{2+}$(THF)$_{10}$ | 53.30 | 2.12 | 2.37 | 2 | 1.94 | - | - |
| Mg$^{2+}$(THF)$_{11}$ | 62.30 | 2.12 | 2.37 | 2 | 1.94 | - | - |
| Mg$^{2+}$(THF)$_{12}$ | 72.52 | 2.12 (2.10) | - | - | - | - | - |
Figure 4. Illustration of the geometry and free energy changes (depicted in red in kcal/mol) for oligomers in THF. The most stable monomer cluster is shown with a blue label. The color scheme of the atoms is the same as Figure 2.

particular trend. However, keeping in mind the number of Hb contacts to Mg, the orientation of the borohydride anions can be understood. In Mg(BH₄)₂(THF) and Mg(BH₄)₂(THF)₂, each borohydride is oriented such that a face of its tetrahedron is facing the magnesium, which results in six Hb contacts. When an additional THF ligand is added from Mg(BH₄)₂(THF) to Mg(BH₄)₂(THF)₂, the Mg-Hb distance increases from 2.05 to 2.11 Å. With the addition of another THF to form Mg(BH₄)₂(THF)₃, there is no longer space for facial coordination of borohydride. Instead, each anion rotates so that an edge of the tetrahedron is contacting the magnesium. With this, the Mg-Hb distance decreases, yet the Mg-B distance increases. This might imply repulsive forces between magnesium and boron. This trend is repeated for singly charged clusters in THF, although with smaller Mg-Hb distances, which points to the enhanced electrophile character of magnesium with increased cluster charge.

The difference between bridging and terminal borohydride bond lengths (B-Hb and B-Ht bonds) provides some interesting observations. A general trend is observed in Table II that when B-Hb bonds are lengthened, due to bonding with magnesium, B-Ht bonds shorten. This provides some evidence that bonding between borohydride and magnesium do not follow an ideal ionic character, but that there are some covalent interactions. As magnesium draws the electrons of Hb closer to it, the boron atom becomes under-coordinated, and subsequently pulls Ht atoms closer.

It has been reported that multimeric species⁴¹⁻⁴⁶ (clusters containing two or three magnesium atoms) may form in the MACC electrolyte. Recognizing the potential importance of this, we have optimized the structures of some oligomers, which are depicted in Figure 4. However, the oligomeric species we have considered, in comparison to monomers of the same charge, are not energetically favorable to form.

The most stable neutral dimer is Mg₂(BH₄)₄(THF)₂, which only has two THF ligands. In this cluster, each magnesium is coordinated by one THF and three borohydrides. This dimer can be formed with 7.2 kcal/mol from two Mg(BH₄)₂(THF)₃ clusters. As discussed before, a coordination number of five is preferred by neutral monomers. However, this dimer has a coordination number of four. Experimental data⁴⁸⁻⁵⁰ indicates that magnesium can be coordinated by a maximum of four borohydride groups, in contrast to the hexa-coordinate Mg²⁺(THF)₆ when only THF is a ligand. It is reasonable to assume that borohydride ligands are bulkier than THF. This rationalizes the stability of four-coordinate magnesium in Mg₂(BH₄)₄(THF)₂. Although the formation free energy is high (7.2 kcal/mol), when placed in context of the energy difference (11.5 kcal/mol) between Mg(BH₄)₂(THF)₃ and Mg(BH₄)⁺(THF)₂, the formation of dimeric Mg₂(BH₄)₄(THF)₂ is more likely in solution.

The most stable singly charged dimer is Mg₂(BH₄)₃⁺(THF)₆, which has a structure similar to Mg(BH₄)₂(THF)₃, only that each magnesium shares one borohydride anion. The formation of this dimeric species from two Mg(BH₄)₂(THF)₃ costs 12.8 kcal/mol, which is only slightly greater than the energy required to form monomeric Mg(BH₄)⁺(THF)₂ (11.5 kcal/mol).

The oligomeric clusters we have optimized are energetically unfavorable. Their instability in THF can be rationalized based on the
Figure 5. Illustration of the geometry and free energy changes (depicted in red in kcal/mol) for Mg(BH₄)ₒ(G₁): a) Mg(BH₄)₂ clusters, b) MgBH₄⁺ clusters, c) Mg²⁺ clusters. The color scheme of the atoms is the same as Figure 2.

following. Magnesium atoms repel each other in oligomeric species, in which borohydride bridges place them close together. Entropy may favor monomers, with higher disorder, over dimeric clusters. Admittedly, due to the vast number of potential structures for oligomeric species, there may be other, more stable clusters which we have not considered here. However, each oligomer is energetically unfavorable in comparison to the most stable monomeric counterparts bearing the same charge.

**G₁ solvent.**—Stable configurations of clusters containing magnesium, borohydride, and G₁ solvent molecules are shown in Figure 5. Each row of clusters in the figure depicts neutral, singly, and doubly charged clusters and transformation free energies between clusters are depicted in red, with negative values corresponding to favorable changes. The coordination number of the magnesium atom is indicated by a suffix in the chemical formula. For example, in Mg(BH₄)₂(G₁)-4C the magnesium atom is coordinated by two borohydride anions and two oxygen atoms. Unlike THF, G₁ contains two oxygens and is a much stronger ligand as both oxygen atoms can act as electron donors. To compute free energy differences between clusters involving the association of G₁ molecules, the trans conformation of G₁ is used.

Four charge neutral clusters are shown in Fig. 5a: Mg(BH₄)₂(G₁)-4C, Mg(BH₄)₂(G₁)-5C, Mg(BH₄)₂(G₁)-6C-A, and Mg(BH₄)₂(G₁)-6C-B. Starting with Mg(BH₄)₂G₁-4C, the addition of a trans G₁ molecule leads to Mg(BH₄)₂(G₁)-5C, with an increase of 4.7 kcal/mol in the free energy. With the addition of a gauche G₁ molecule instead, either Mg(BH₄)₂(G₁)-6C-A or Mg(BH₄)₂(G₁)-6C-B is formed at costs of 2.5 or 7.5 kcal/mol, respectively. In the most stable six coordinate neutral cluster, Mg(BH₄)₂(G₁)-6C-A, the two borohydrides occupy opposite corners of the octahedral coordination. The alternative structure (Mg(BH₄)₂(G₁)-6C-B), in which the two anions sit in neighboring corners, is about 5 kcal/mol higher in energy.

For the addition of a gauche G₁ to Mg(BH₄)₂G₁-4C to form Mg(BH₄)₂(G₁)-6C-A, although the coordination number increases from 4 to 6, the transformation energy is minimal, only 2.5 kcal/mol, indicating the strong steric effect of using G₁ as a ligand. The lowest free energy state of G₁ is the trans conformer, however the gauche conformer was calculated to be only 0.8 kcal/mol greater in free energy, indicating that the direct association of gauche G₁ to Mg(BH₄)₂G₁-4C may be preferred.

The geometry of Mg(BH₄)₂G₁-4C and Mg(BH₄)₂(G₁)-6C-A roughly coincide with tetrahedral and octahedral coordination, respectively. In both clusters, each pair of coordinated oxygen atoms are constrained as they belong to the same G₁ molecule. The O-Mg-O bond angle is about 77° in the 4-coordinate cluster and 67–70° in the 6-coordinate cluster, which differs significantly from standard tetrahedral (109.8°) and octahedral (90°) angles. This is a common theme among G₁ clusters, in which chelation only approximates ideal coordination.

For singly and doubly charged clusters in G₁, it is found that coordination numbers of five and six are preferred. The hexacoordinate cluster of Mg²⁺(G₁)₆C has been observed as part of the crystal structure of Mg(BH₄)₂ in G₁. Interestingly, whenever the magnesium atom is coordinated by an odd number of oxygens, implying a dangling uncoordinated oxygen as G₁ has two oxygens, the free energy associate this oxygen is always exothermic. This demonstrates that clusters in which all solvent oxygens are chelated to magnesium are more stable. Put another way, if there is an entropic cost to the association of a G₁ solvent molecule, as opposed to remaining in the bulk, it is more favorable to associate all solvent oxygen, rather than only some of them.
The most stable neutral (Mg(BH₄)₂(G1)-4C), singly (MgBH₄⁺(G1)₂-5C), and doubly (Mg²⁺(G1)₂-6C) charged clusters are shown in Fig. 6. In comparison to THF, the free energy required to form singly (5.0 kcal/mol) and doubly charged (12.1 kcal/mol) are drastically reduced. This may indicate that cations form more freely in G1 than THF. Mohtadi et al. indicated that in comparing THF and G1 for use in a Mg(BH₄)₂-based battery, an electrolyte containing G1 resulted in higher current density. This suggests that the electroactive species in G1 is either more mobile or present at a higher concentration than in THF. Despite their formation in G1 being more likely than in THF, the existence of doubly charged clusters in G1 is still unlikely, due to the high free energy required.

The cluster free energies (ΔGₖ), and Mg-O, Mg-B interatomic distances for all G1 clusters are tabulated in Table III. For the only cluster in which there is a direct comparison with experimental crystal structure data, Mg²⁺(G1)₂-6C, good agreement is obtained. In similar fashion to THF, as the number of coordinated oxygen atoms increases, the environment surrounding the magnesium becomes more crowded, and the Mg-B and Mg-O distances increase. As the cluster charge increases from neutral to single and double charged, these distances decrease, which may be due to an increasingly electronegative magnesium, or due to fewer bulky BH₄⁻ ligands, which enables G1 to approach more closely to magnesium.

Previously, it was suggested based off of integrals of proton resonances in ¹H-NMR that the structure of Mg(BH₄)₂ in G1 has a ratio of 1.5 G1 molecules for every two BH₄⁻ clusters in G1 which consist of two kinds of clusters, having charges of +2 and -2. A simple cubic repeating array of hexacoordinate Mg²⁺(G1)₃ and tetrahedral Mg(BH₄)₆⁻ is formed in this crystal, which matches the description of 1.5 G1 for every two BH₄⁻. Using the crystal structure provided by this study, a single solvated Mg²⁺(G1)₃ and Mg(BH₄)₆⁻ pair was formed by removing other atoms in the crystal. After geometry optimization, the structure decomposes to a pair of MgBH₄⁺(G1)₃ and Mg(BH₄)₆⁻ (shown at the bottom-center of Fig. 7). The free energy required to form this complex from two Mg(BH₄)₂G1-4C and a G1 is ca. 23 kcal/mol, which is much less stable than Mg(BH₄)₂(G1)-4C. It is more energetically favorable for MgBH₄⁺(G1)₃ and Mg(BH₄)₆⁻ to be separated in the solvent and not exist as a pair (as shown at the bottom of Fig. 7). In both of these scenarios, the formation of Mg(BH₄)₆⁻, which was observed in crystals, is not favorable in solution. It might be that, in the crystalline environment, the repeating array of +2 and -2 charges stabilizes the clusters.

Similar to THF, the possibility of forming oligomeric clusters containing multiple magnesium atoms was investigated for G1. Some possible dimeric clusters are depicted in Fig. 7. As mentioned, Mg₂(BH₄)₆(G1)₁ is slightly unfavorable, requiring 7.6 kcal/mol to form. The removal of one BH₄⁻ from this cluster, to form the most stable singly charged dimer, requires an additional 3.5 kcal/mol. The structure of Mg₂(BH₄)₆(G1)₁⁺ is similar to that of the most stable singly charged dimer in THF, Mg₂(BH₄)₆(THF)₆⁺. Each magnesium has a coordination number of five and they share a borohydride anion. The oligomeric species we have considered in Fig. 7 are energetically unfavorable in comparison to monomeric clusters of similar charge.

### NMR shifts and FTIR vibrations
We have calculated the isotropic ¹¹B- and ²³Mg-NMR chemical shifts for the most stable neutral, singly, and doubly charged clusters of Mg(BH₄)₂ in THF, Mg(BH₄)₂(G1)-4C, Mg²⁺(G1)₂-5C, and Mg³⁺(G1)₂-6C. Each magnesium has a coordination number of five and they share a borohydride anion. The oligomeric species we have considered in Fig. 7 are energetically unfavorable in comparison to monomeric clusters of similar charge.

### Table III. Formation free energies and Mg-O/Mg-B/Mg-H contact distances for Mg(BH₄)₂(G1) clusters.

| Cluster | ΔGₖ, kcal/mol | Mg-O Distance, Å | Mg-B Distance, Å | # Mg-Hb Contacts | Mg-Hb Distance, Å | B-Hb/B-H Distance, Å |
|---------|--------------|------------------|------------------|-----------------|------------------|---------------------|
| Mg(BH₄)₂(G1)-4C | -99.33       | 2.14             | 2.20             | 6               | 2.10             | 1.241/1.199         |
| Mg(BH₄)₂(G1)₂-5C | -94.64       | 2.23             | 2.37             | 4               | 1.99             | 1.247/1.214         |
| Mg(BH₄)₂(G1)₂-6C-A | -96.88       | 2.35             | 2.38             | 5               | 2.12             | 1.236/1.213         |
| Mg(BH₄)₂(G1)₂-6C-B | -91.81       | 2.29             | 2.43             | 4               | 2.02             | 1.243/1.217         |
| MgBH₄⁺(G1)-3C     | -75.27       | 2.02             | 2.07             | 3               | 1.98             | 1.254/1.186         |
| MgBH₄⁺(G1)₂-4C    | -80.96       | 2.06             | 2.11             | 3               | 2.00             | 1.250/1.189         |
| MgBH₄⁺(G1)₂-5C    | -94.31       | 2.11             | 2.31             | 2               | 1.91             | 1.260/1.206         |
| MgBH₄⁺(G1)₂-6C    | -83.92       | 2.21             | 2.38             | 2               | 1.99             | 1.246/1.210         |
| Mg²⁺(G1)₂-3C      | -39.03       | 1.97             | -               | -               | -                | -                   |
| Mg²⁺(G1)₂-4C      | -59.76       | 2.00             | -               | -               | -                | -                   |
| Mg²⁺(G1)₂-5C      | -67.42       | 2.05             | -               | -               | -                | -                   |
| Mg³⁺(G1)₂-6C      | -87.25       | 2.11 (2.07)      | -               | -               | -                | -                   |
Figure 7. Illustration of the geometry and free energy changes (depicted in red in kcal/mol) for oligomers in G1. The most stable monomer cluster is shown with a blue label. The color scheme of the atoms is the same as Figure 2.

and G1. The calculated shift values are tabulated in Table IV. We compare the chemical shifts calculated here to other studies, which have used $^{13}$B-NMR \cite{19,20,23,53} and $^{25}$Mg-NMR \cite{23,41,54} to characterize magnesium-based electrolytes.

By inspection of the signals for $^{25}$Mg-NMR, it is seen that the chemical shift of magnesium depends on the cluster charge. In fact, the Mg signals of doubly charged clusters are shifted downwards by 25 ppm from the neutral state. This drastic difference is caused by the changes in the polarization of the magnesium, which draws the oxygen atoms in each hexagonal MgO$_6$ closer to its nucleus, and increases its shielding. Experimental spectra do not provide evidence for a secondary peak ca. –20 ppm \cite{23} in ethereal solvents, which indicates that the concentration of doubly charged clusters in G1 and THF may be extremely low. Between the neutral and singly charged states, there does not appear to be a clear trend between Mg signals that applies to both solvents. However, there is a clear difference in the signal for each cluster charge, which should aid experimental characterization of the electrolyte. In DFT calculations of $^{25}$Mg-NMR chemical shifts in the MACC electrolyte, \cite{41} the signals corresponding to neutral clusters were distinctly different than that of singly charged clusters.

$^{11}$B-NMR signals in Table IV have a clear trend between neutral and singly charged clusters. For each solvent, the singly charged state is shifted upwards by more than 2 ppm. The $^{11}$B signal for Mg(BH$_4$)$_2$G1-4C occurs at –46.4 ppm in comparison to Mg(BH$_4$)$_2$(THF)$_3$ at –41.4 ppm. The location of the $^{11}$B signal in THF in comparison to G1 corroborates experimental observations. \cite{19}

For Mg(BH$_4$)$_2$(G1)-4C, the borohydride anions contact magnesium

| Cluster                  | $^{25}$Mg (ppm) | $^{11}$B (ppm) |
|--------------------------|-----------------|----------------|
| Mg(BH$_4$)$_2$(THF)$_3$   | 5.45            | -41.43         |
| MgBH$_4$+(THF)$_4$       | 3.87            | -39.01         |
| Mg$^{2+}$(THF)$_6$       | -26.74          |                |
| Mg(BH$_4$)$_2$(G1)-4C    | -1.32           | -46.38         |
| MgBH$_4$+(G1)$_2$-5C     | 5.70            | -39.56         |
| Mg$^{2+}$(G1)$_3$-6C     | -21.09          |                |
| BH$_4^-$                 | -               | -46.66         |
with three hydrogens each, as opposed to two contacts per borohydride in Mg(BH₄)₂(THF)₃. For this reason, the close Mg-B distance reduces the shielding of boron in Mg(BH₄)₂(G₁)−4C beyond that of Mg(BH₄)₂(THF)₃. However, despite the calculated difference in the ¹¹B signals between neutral and singly charged species in Table IV, experimental spectra only contain a single quintet located from −40 to −43 ppm.

Infrared spectroscopy has confirmed that Mg(BH₄)₂ in ethereal solvents, the existence of two separate bands in the B-H stretching region. Bremer reported that solvates of Mg(BH₄)₂ in diethyl ether exhibit four B-H stretching bands. The first two bands occur at lower frequency, and correspond to the asymmetric and symmetric vibrations of borohydride hydrogens bridging to magnesium (Hb). The second set of bands occur at higher frequency and correspond to the symmetric and asymmetric vibrations of the terminal hydrogens (Ht). In Table V, frequencies of B-Hb and B-Ht vibrations are tabulated. There is a gap between the B-Hb and B-Ht bands. The slower B-Hb vibrations correspond to magnesium drawing borohydride hydrogens closer and stabilizing stretched conformations.

The most stable neutral cluster in G₁ was determined to be Mg(BH₄)₂(G₁)−4C. In this cluster each borohydride coordinates magnesium by three bridging hydrogens (Hb), with C₃v symmetry, and has six signals in the B-Hb region ranging from 2153–2282 cm⁻¹. An experimental spectrum of Mg(BH₄)₂ in G₁ indicates three peaks in the B-Hb vibrational region at approximately 2145, 2175, and 2240 cm⁻¹. The calculated frequencies for Mg(BH₄)₂(G₁)−4C beyond that of Mg(BH₄)₂(THF)₃ agree with experimental observations. The calculated chemical shifts for ²⁵Mg and ¹¹B and vibrational frequencies support the prediction of stable clusters. The shift of ¹¹B varies by 2–5 ppm between the neutral and singly charged states, which agree with experimental observations. The calculated chemical shifts in doubly charged clusters are considerably different (ca. −23 ppm). No signals are found at this shift in experimental spectra. The calculated infrared frequencies exhibit two B-H stretching regions, differentiating borohydride hydrogens which are coordinated with magnesium from those that are not, which agrees well with experimental spectra. The frequency of B-H vibrations, for hydrogens coordinated with magnesium, is slowed for singly charged clusters (2040–2100 cm⁻¹) in comparison to neutral clusters (2153–2282 cm⁻¹), owing to the electrophilic character of cationic magnesium.

There are some interesting research directions that can be taken in future studies. In addition to considering polyethylene oxide as a coelectrolyte to Mg(BH₄)₂, there is a need to explore the existence of pairs and chains of two or more borohydrides in the liquid. Regardless of the solvent, the formation of +2 charged clusters is prohibitive, which is generally agreed upon.

The high free energy of BH₄⁻ dissociation may partially explain low conductivity of Mg(BH₄)₂ in ethereal solvent. The free energies of Mg(BH₄)₂ to generate singly or doubly charged clusters are lower in G₁ (5.1 and 12.2 kcal/mol) than in THF (11.5 and 22.2 kcal/mol). This indicates that cations form more freely in G₁ than THF, which aligns with experimental observations. The calculated chemical shifts for Mg(BH₄)₂ and ¹¹B were found to be plausible but unfavorable in free energy. However, this is associated with the fact that the calculations were carried out using the implicit solvent model with a fixed dielectric constant of the solvent, which implies an infinite dilute solution. In more concentrated electrolyte, the complexes of multiple magnesium atoms might be further stabilized.

In THF, an experimental spectrum indicates two peaks in the B-Hb vibrational region (2176 and 2240 cm⁻¹) and two peaks in the B-Ht region, which may imply contact by two bridging hydrogens per borohydride. Mg(BH₄)₂(THF)₃ was determined to be the most stable cluster, which has four vibrational modes in the B-Hb region coinciding with these from 2158–2216 cm⁻¹. The frequencies of B-Ht vibrations (ca. 2348–2393 cm⁻¹) also agree with experimental data (ca. 2380 cm⁻¹). There is a consistent pattern that distinguishes borohydride vibrations in singly charged clusters from those of neutral charge. B-Hb vibrations take place at lower frequency (2041–2046 cm⁻¹ in G₁ and 2099–2104 cm⁻¹ in THF) in singly charged clusters compared to neutral clusters. This is due to the enhanced electrophilicity of magnesium in cationic clusters, which further stabilizes the extension of the B-Hb bonds. In an experimental spectrum of ¹¹B some minor peaks are observed in solutions of 0.5M Mg(BH₄)₂ in THF and 0.1M Mg(BH₄)₂ in G₁ at around 2075 cm⁻¹. The elucidation of some of vibrations in this region will allow further study of singly charged species in electrolyte.

### Conclusions

We have elucidated the liquid structure of Mg(BH₄)₂ in two ethereal solvents: tetrahydrofuran (THF), and glyme (G₁). To accomplish this, we have used density functional theory to optimize the geometries of hundreds of clusters, of neutral, single, or double charge, consisting of Mg²⁺, BH₄⁻, and coordinated solvent molecules. The free energy of these clusters was determined using the M06 exchange-correlation functional and the SMD solvation model.

The geometries of the most favorable neutral and doubly charged clusters in THF and G₁ align closely with available experimental crystal structure data. For neutral clusters with two borohydride anions, the most favored coordination ranges from two (G₁) to three (THF) oxygen ligands. Singly charged clusters prefer four oxygen ligands, whereas doubly charged favor six. The ideal number of ligands is a result of competition between attraction to positively charged magnesium, steric repulsion between coordinated groups, and the entropic cost of associating ligands from solution. When G₁ is used as a solvent, clusters containing uncoordinated dangling oxygens are found to be energetically unfavorable. However, more complex structures may be formed in solution than we have modeled here which stabilize these dangling oxygens.

The free energy to form cationic clusters has been calculated for each solvent. The free energy to generate singly charged clusters in THF is high, suggesting that a low concentration of these ions is present in the liquid. Regardless of the solvent, the formation of +2 charged clusters is prohibitive, which is generally agreed upon.

The high free energy of BH₄⁻ dissociation may partially explain low conductivity of Mg(BH₄)₂ in ethereal solvent. The free energies to generate singly or doubly charged clusters are lower in G₁ (5.1 and 12.2 kcal/mol) than in THF (11.5 and 22.2 kcal/mol). This indicates that cations form more freely in G₁ than THF, which aligns with experimental observations. The calculated chemical shifts for Mg(BH₄)₂ and ¹¹B were found to be plausible but unfavorable in free energy. However, this is associated with the fact that the calculations were carried out using the implicit solvent model with a fixed dielectric constant of the solvent, which implies an infinite dilute solution. In more concentrated electrolyte, the complexes of multiple magnesium atoms might be further stabilized.

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