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Structural Analysis of Electrolyte Solutions Comprising Magnesium−Aluminate Chloro−Organic Complexes by Raman Spectroscopy

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We report herein on a rigorous analysis of unique electrolyte solutions for novel rechargeable magnesium batteries and nonaqueous magnesium electrochemistry, which contain organometallic complex electrolyte species, by Raman spectroscopy. These solutions comprise ethereal solvents and products of reactions between R_2Mg Lewis base species and $AlCl_2R$ Lewis acid species that exist in solution in dynamic multiple equilibria. The reactions involve the exchange of ligands between the magnesium and the aluminum to form ions such as $MgCl^+$, $Mg_2Cl_3^+$, and $AlCl_{4-n}R^-_n$ ($n \leq 4$), stabilized by the ether molecules. The Raman peak assignments were based on a rigorous study of solutions containing reference compounds and some quantum-mechanical calculations. Raman spectroscopy enabled a quantitative analysis of the various species in solution.

Introduction

In 1999 a new class of nonaqueous electrolytic solutions was developed, from which metallic magnesium could be reversibly electrochemically deposited and magnesium ions could be intercalated into appropriate compounds.[1,2] These materials are the reaction products of organomagnesium with organo−halo aluminum compounds. In general, a whole range of such compounds can be synthesized by the reaction of R_xMgCl_{2-x} with R'_yAlCl_{3-y} (R and R′ are organic ligands, $x = 0-2$, $y = 0-3$) at various proportions. The nature of R and R′, the number of the organic and inorganic ligands, as expressed by x and y, and the stoichiometric ratio of aluminum to magnesium are all variables that determine the chemical and the electrochemical properties of the system.

The equilibrium species in the solutions are the result of transmetalation reactions in which the organic and inorganic ligands are exchanged between the magnesium and the aluminum cores and reactions in which the aluminum species act as Lewis acids and the magnesium species as bases.[3] The solvent also plays an important role in these reactions, both as an efficient donor and as a polar medium that enables the dissociation of the complex salts to yield solutions with high ionic conductivity.

Despite the fact that the synthesis is simple, determination of the species that exist in solution is not trivial. An attempt to isolate species from the solutions for identification by single-crystal XRD met with limited success, since it was revealed that the isolated compounds in the solid state are not identical with those in the solution phase.[2] A thorough analysis of the solutions using ^{25}Mg, ^{27}Al, ^{13}C, and ^{1}H NMR, in conjunction with electrochemical studies, provided a breakthrough in the understanding of these solution structures.[3] Nevertheless, several important questions were left unanswered, as the NMR analysis could not shed light on the identity of the magnesium species due to inherent resolution limitations.

We report here on rigorous solution Raman spectroscopy studies that enabled the identification of all the main species formed in these systems. The peak assignment in the Raman spectra of some of the relevant compounds was assisted by quantum-mechanical calculations. The results prove that the solutions contain various magnesium and aluminum species in equilibrium.

Results and Discussion

Reference Spectra of Expected Important Compounds. Among the wide spectra of different compounds that can be synthesized from the reaction of R_xMgCl_{2-x} with R'_yAlCl_{3-y} (R and R′ are organic ligands, $x = 0-2$, $y = 0-3$), one was selected as the optimal composition from an electrochemical point of view. The reaction product of 1 equiv of dibutylmagnesium (DBM) with 2 equiv of ethyl aluminum dichloride possesses reasonable ionic conductivity, has a wide electrochemical window, and magnesium is deposited from its solution with 100% Coulumbic reversibility.[2] These solutions are denoted as DCC (dichloro complex) solutions. In order to obtain the best electrochemical results with these solutions in terms of low overvoltage for Mg deposition and 100% reversibility of this process, we had to add to them 2−10% v/v of 1 M DBM in hexane. Thus, from a practical point of view, the constituents of DCC/THF solutions are of special interest.

In a previous study that combined the use of multinuclear NMR and electrochemistry, it was revealed that for spectroscopic measurements a model complex salt system made up of molecules with higher symmetry is desirable.[3] We found that, in terms of electrochemical properties, the use of diethylmagnesium as a reactant instead of DBM yields solutions with very similar electrochemical properties, which can thus be used for spectroscopic investigations. The reason that DBM has been used so far in practical electrochemical systems is due to its

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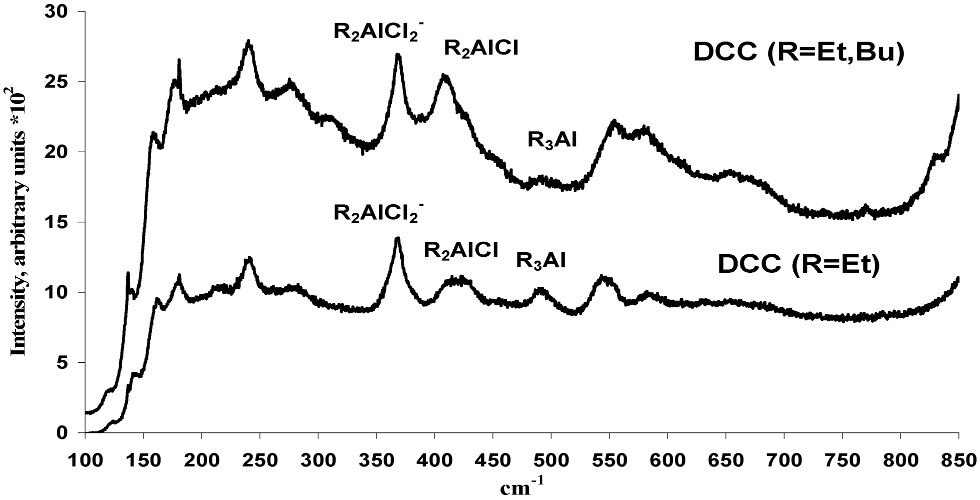

Figure 1. Raman spectra of ethyl−butyl DCC and all-ethyl DCC solutions in THF.

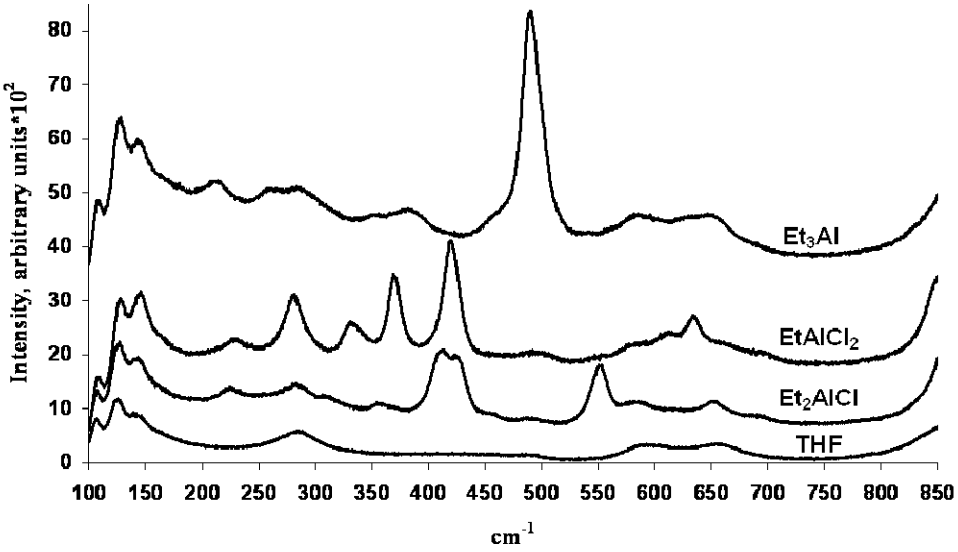

Figure 2. Raman spectra of organo−halo aluminum compounds in THF.

availability and low cost. Figure 1 presents a comparison between Raman spectra measured from DCC solutions based on DBM and from all ethyl DCC solutions in which diethylmagnesium was used as a precursor.

The spectra in Figure 1 are indeed similar and allow a conclusive study to be carried out with the all-ethyl DCC solutions. (The peak assignments marked in the figure are based on the spectral studies described later in this paper.) In our NMR study we identified the aluminum complex structures to be Et_4Al^-, $Et_3Al{\cdot}THF$, and $Et_4Al_2Cl_3^-$ as the reaction products of 1 equiv of diethylmagnesium with 0.5, 1, and 2 equiv of ethylaluminum dichloride, respectively.[3] Interestingly, we noticed that for ^{27}Al NMR spectra, in general, the influence of chloride ligands on the chemical shift was similar to that of THF. This made discrimination between $Et_2AlCl_2^-$ and $Et_2AlCl{\cdot}THF$ (or their dimer), the hypothesized species in DCC solutions, to be impossible. In that study, parallel ^{25}Mg NMR studies were not conclusive.

The scientific literature demonstrates some studies on the vibrational spectroscopy of organo−halo aluminum compounds[4] and fewer studies on organo and organo−halo magnesium compounds.[5] However, these data contain only a few spectra of structures that we presume to be present in our solutions. Moreover, the data are not consistent, and various authors report on different spectral bands for the same molecules. In addition, since the solvent, namely THF, has an important role in the stabilization of the systems and influences the equilibria and the molecular structures, it is very important to compare only spectroscopic data that were acquired in THF solutions. Thus, as a first step, Raman spectra for a collection of compounds to be used as a database were systematically measured. For this purpose we analyzed the spectra of solutions of pure, known compounds, as well as a set of solutions of reaction products whose structures had been previously identified by NMR. In addition, we acquired spectra of THF solutions of reaction products of simple model compounds, relevant to the studied systems.

Figure 2 presents the Raman spectra of THF solutions of Et_3Al, Et_2AlCl, and $EtAlCl_2$, as well as that of pure THF for comparison. The data are also given in Table 1 (together with results from the quantum-mechanical calculations). Note that these three compounds are all tetracoordinated in THF, with one THF ligand attached (proven by NMR studies). The spectrum of $AlCl_3$ in THF was seriously disturbed by fluorescence and thus is not presented. In many respects, these spectra

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Table 1. Summary of Peak Positions in Raman Spectra of a Variety of Organo−Halo Aluminum and Magnesium Species[a]

compd or species	peak position, cm^{-1}			
	M−R bond		M−Cl bond	
Et_3Al	490 s	(510 sym)		
Et_2AlCl	553	(611 sym, 616 asym)	413 424	(408)
$EtAlCl_2$	634	(642)	282 333 369 420 s	(292 sym) (329 asym) (420 sym)
Et_4Al^-	460	(483 sym, 532 asym, w, 622 asym, w)		
Et_3AlCl^-	490	(500 sym, 580 asym, w)	367 s	(342)
$Et_2AlCl_2^-$	539	(594 sym, 606 asym, w)	367 s	(350 sym, 401 asym, w)
$EtAlCl_3^-$	611	(621)	181 346 w 367 s	(179 bend) (367 sym, 442 asym, w, 459 asym, w)
$AlCl_4^-$			346 s	(344 sym, 483 asym, w)

[a] Calculated frequencies and assignments are given in parentheses. Legend: sym, symmetric stretching; asym, asymmetric stretching; w, low intensity.

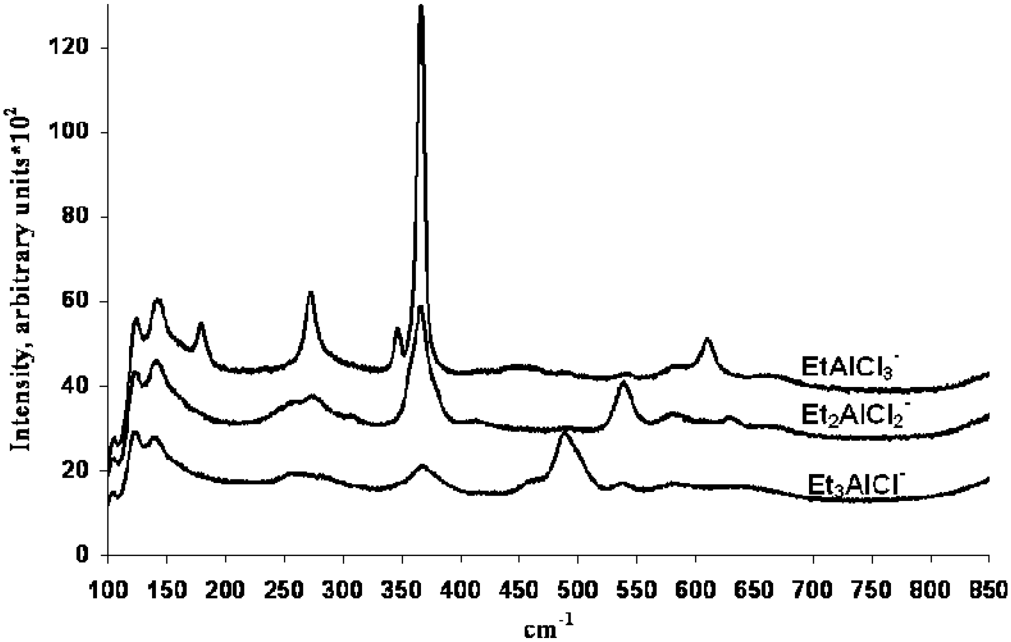

Figure 3. Raman spectra of lithium organo−halo aluminum complexes with the general structure $Li^+[Et_xAlCl_{4-x}]^-$ in THF.

correlate with the published data on the same compounds in diethyl ether.[6]

The strongest spectral bands in Figure 2 can be divided into those between 250 and 430 cm^{-1}, which relate mainly to Al−Cl bonds, and those in the 450−650 cm^{-1} region, which relate mainly to Al−R (well supported by the calculations). Interestingly, the spectral bands of the Al−R bonds of this homologous series show a trend that depends on the Cl/R ratio. The higher this ratio, the higher the scattering wavenumber of the Al−R bands. In a similar manner, the higher the R/Cl ratio, the stronger the Al−R bands relative to the Al−Cl bands.

When the above compounds are reacted with an equimolar quantity of LiCl, an acid−base reaction takes place that results in a complex salt formation. The generation of $Li^+[Et_xAlCl_{4-x}]^-$ is evident both from the dramatic increase in the ionic conductivity of the solutions (LiCl alone is only slightly soluble in THF, thus forming solutions with no practical ionic conductivity) and from ^{27}Al NMR data for these materials.[7] From the NMR study, it is clear that these three anionic complexes are also tetracoordinated.[3,7] The Raman spectra for these salt solutions are presented in Figure 3, along with the data, which are given in Table 1.

The spectra in Figure 3 show several very interesting trends. First, the principal peak that corresponds to an Al−Cl stretching vibration appears in all cases at 367 cm^{-1}. The positions of the Al−R bands (stretching vibrations) show an almost linear correlation to the Cl/R ratio, with the highest wavenumber for the $EtAlCl_3^-$ ion, at 611 cm^{-1}. In this series, the Al−R vs Al−Cl peak height ratios also correspond to the ratio between the number of the chlorine ligands vs the number of organic ligands. These results suggest that the strength of the Al−R bonds increases with the Lewis acidity of the compound, which in turn increases as the number of electron-withdrawing chlorine ligands increases. This trend in bond strength gains further proof from the electrochemical window measurements. In these

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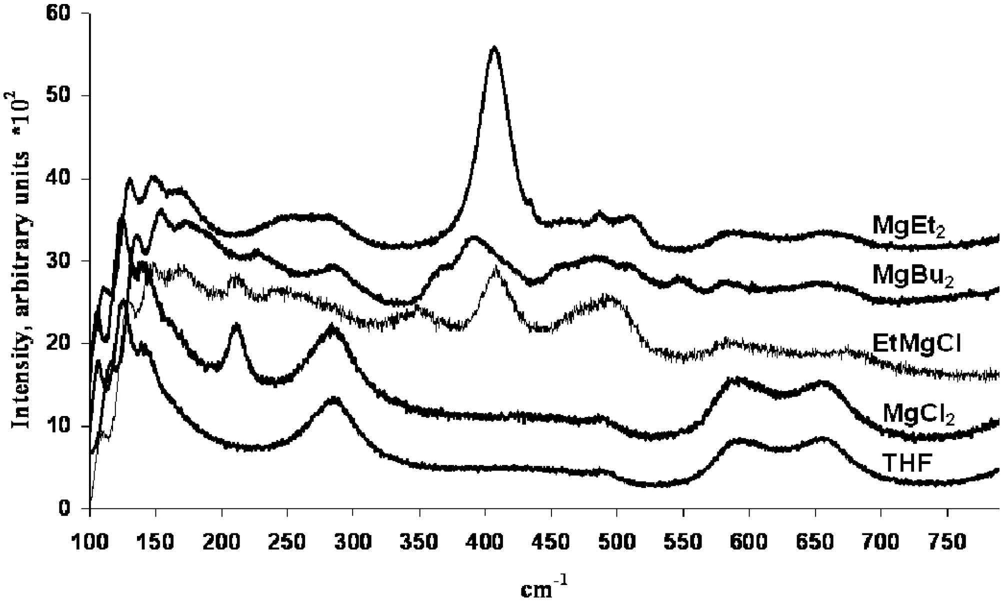

Figure 4. Raman spectra of organo−halo magnesium compounds in THF.

measurements, it was clearly observed that the higher the Cl/R ligand ratio, the higher the electrochemical stability of the solutions toward oxidation.

For reference data on the possible magnesium compounds, we acquired the Raman spectra of $MgCl_2$, Bu_2Mg, Et_2Mg, and EtMgCl, all as solutions in THF. Note that, from ^{25}Mg NMR analyses, it appears that in THF solutions all these magnesium compounds are hexacoordinated.[3,9] Nevertheless, we must stress that the literature data on Grignard reagents are very inconsistent and the actual species present in solution depend on the solvent, concentration, purity, and temperature.[8] Figure 4 presents the Raman spectra of the above compounds. The data are also compiled in Table 1.

As can be seen from these spectra in the 100−800 cm^{-1} region, the magnesium species show only a few features. $MgCl_2$, presumably coordinated by four THF molecules, shows only a single sharp peak at 212 cm^{-1}. Et_2Mg, at a high concentration in THF (2 M), shows one sharp and strong peak at 409 cm^{-1} and in two regions, 250−300 and 475−530 cm^{-1}, a multitude of small features can be discerned. The spectrum of Bu_2Mg is similar in this respect, although instead of a single strong peak it possesses two large peaks at 370 and 394 cm^{-1}, probably due to the existence of the two isomers of butyl as the organic ligands in the commercial product, namely *n*-butyl and 2-butyl. It is evident here that the use of Et_2Mg as the model system, instead of Bu_2Mg, is indeed highly advantageous for the spectroscopic analysis. The spectrum of EtMgCl in THF, which is expected to be a monomer in this solution, contains, as reported by others,[11] the features seen for both Et_2Mg and $MgCl_2$. This is consistent with the Schlenk equilibrium (i.e., ($2EtMgCl \leftrightarrows Et_2Mg + MgCl_2$). The spectra above are not strictly consistent with some of the literature data on identical or similar solutions (in other ethers). For instance, Kress et al. reports on a multitude of features for Et_2Mg in diethyl ether, although one of the main peaks, that at 410 cm^{-1}, and the multitude of small peaks around 500 cm^{-1} are in line with our findings. Note that in Kress' work the author stresses that the Raman spectra of EtMgCl in diethyl ether reflect the existence of dimers, while in a THF solution, as in our study, this material is a single moiety.[11] Salinger et al.[12] report a single feature for Et_2Mg in THF at 512 cm^{-1} and do not report any peak around 210 cm^{-1} for MeMgCl in THF, which is expected for the Mg−Cl band.

From the point of view of the objective of this study, although the Mg−R bands we found lay in the same region as some of the Al−Cl bands, this should not interfere with the analysis of the solutions of interest (i.e., with the DCC solutions comprising the Lewis acid−base reaction products), as we recognized from the multinuclear NMR study that in these solutions no Mg−R species exist.[3]

Identification of the Anion Structure in DCC-Type Solutions. As mentioned in the Introduction, the main objective of this study is the identification of the various species in the so-called DCC solutions, which were developed as optimal electrolyte solutions for use in rechargeable magnesium batteries (reacting 2 equiv of the ethylaluminum dichloride with 1 equiv of dibutylmagnesium). The basic understanding of the solution structures in the family of DCC-like electrolytes (made by a reaction in various proportions of the aluminum and magnesium compounds) was based on a multinuclear NMR study, which enabled the unambiguous identification of some of the aluminum-based structures.[3] Unfortunately, as was already mentioned, this study could not give an unambiguous identification for the aluminum species in the DCC solutions. However, on the basis of Raman spectroscopy we can discriminate between the different aluminum-based compounds present in these solutions. Moreover, since the study necessitated the analysis of whole spectra of DCC-based solutions, with various acid−base proportions, as well as analyses of various reference solutions, the present study achieved a thorough understanding of the chemistry of these systems. The spectral identifications also correlate well with the electrochemistry of these solutions: namely, their appreciable ionic conductivity due to the existence of dissociated aluminum-based anions and magnesium-based cations.

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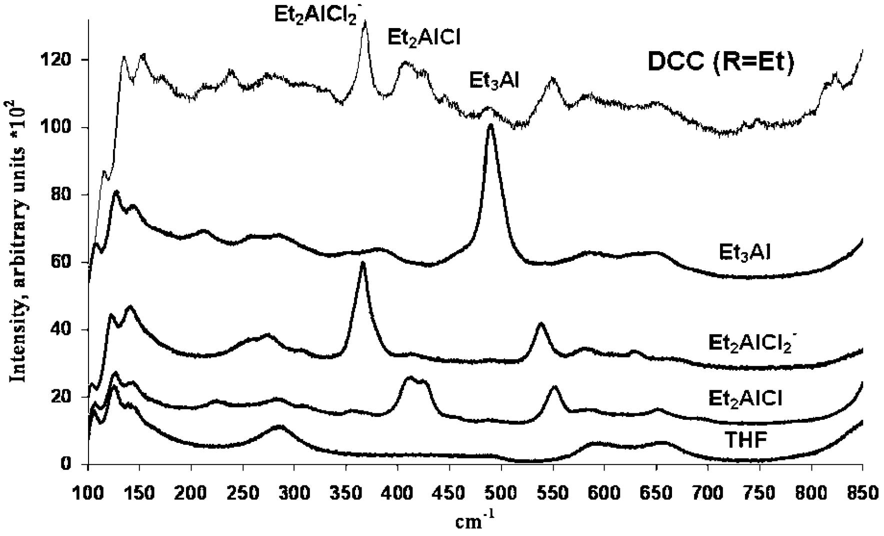

Figure 5. Raman spectrum of a 0.25 M all-ethyl DCC solution (top line) in comparison with appropriate reference spectra (from bottom to top), all in THF: Et_2AlCl, Et_3Al, and $Et_2AlCl_2^-$.

Figure 5 presents the spectra of the all-ethyl DCC species (i.e., the reaction product of Et_2Mg and $AlCl_2Et$) in THF, as well as the reference spectra of Et_3Al, Et_2AlCl, and $LiEt_2AlCl_2$ in THF.

From these spectra, it is possible to identify in the DCC solution the existence of the anion $Et_2AlCl_2^-$ (the large peak at 367 cm^{-1}), the neutral molecule Et_2AlCl−THF (the large double peak at 413−424 cm^{-1}), and, in a small concentration, Et_3Al−THF (a smaller feature at ca. 490 cm^{-1}). It is also discernible that the wide feature at around 540−550 cm^{-1} is a superposition of the relevant peaks of $Et_2AlCl_2^-$ and Et_2AlCl−THF (the magnesium features, observed at ca. 212 and 239 cm^{-1}, are not dealt with at this stage). This result supports the NMR data which showed that dialkylmagnesium exchanges ligands with the aluminum-based Lewis acid in such a way that magnesium takes up the chlorides, giving up the alkyl groups to which it is bound originally.[3] Interestingly, from the Raman spectra it is obvious that the DCC solution contains both the postulated anion, $Et_2AlCl_2^-$, as well as the neutral molecule, Et_2AlCl−THF. The Raman data show no indication of the existence of a dimer of these two molecules, as was suggested from the NMR data. Interestingly, it is also discernible that in DCC solution there is also a small concentration of Et_3Al−THF.

Quantitative Analysis of the Aluminum Species in Equilibrium. As described above, DCC-type complex salts are prepared by reacting organo magnesium and organo−halo aluminum precursors, both as solutions in hydrocarbons (e.g., hexane). These reactions are rapid and exothermic and are accompanied by the immediate precipitation of solids. Elemental analyses of the precipitate and the above hydrocarbon solutions (the reaction medium) have shown that, in this preparative stage, the precipitate includes mainly $MgCl_2$ and the solution contains mostly aluminum species, with both chloride and organic ligands. Thus, it can be concluded that when the synthesis is carried out in a nonpolar hydrocarbon medium, the first reaction involves a rapid exchange of all the organic ligands of magnesium by chlorides. Since DCC solution synthesis involves the reaction of 2 equiv of ethyl aluminum chloride with 1 equiv of dialkylmagnesium, it is obvious that, after the complete exchange of organic for chlorine ligands on Mg, the aluminum species will attain an equilibrium among Et_2AlCl, $EtAlCl_2$, and Et_3Al ($AlCl_3$ was not detected by NMR and Raman analyses). Since our focus is on ionic conducting electrolyte solutions, the exact equilibrium concentration in the hydrocarbon solutions was not studied in detail. However, a knowledge of the actual equilibrium concentration of the various species in the THF solutions is of great importance, as it influences the electrochemical properties.

The main relevant aluminum species are the anion $R_2AlCl_2^-$ and the neutral molecule R_2AlCl, as was concluded in the previous section. Fortunately, the Raman spectra of these species in THF have several unique peaks, adequate for calculating their concentration ratio. For the quantitative analysis of these species, we prepared solutions with a known ratio of R_2AlCl to $R_2AlCl_2^-$. For this purpose, solutions of $Li^+R_2AlCl_2^-$ were prepared by reacting equimolar quantities of LiCl with R_2AlCl in THF. On the basis of the Raman spectrum of this solution, it contains only the desired anionic species. Carefully weighed amounts of R_2AlCl were added at various stoichiometric proportions to these $Li^+R_2AlCl_2^-$ solutions (R = Et). The Raman spectra of these solutions are presented in Figure 6 and the data summarized in Table 2.

From these spectra it can be judged that these solutions contain only the desired anions and neutral aluminum species. It can also be seen that there is a linear correlation between the species' concentration ratio and the corresponding peak height ratio (at 367 and 413 cm^{-1}), as demonstrated in Figure 7.

Identification of the Structures of the Cations in Solution. Although the identities of the anions and the aluminum-based neutral molecules in solution have an important influence on their electrochemical properties, the magnesium species in the solutions are of the greatest importance. In this respect, the information that could be gathered from ^{25}Mg NMR analysis was poor, mainly due to the broad nature of the peaks, their low intensities, and the very small chemical shifts that could be observed in these spectra. Nevertheless, our previous studies of DCC solutions by ^{25}Mg NMR[3] indicated that the magnesium species in the various solutions tested are hexacoordinated. Furthermore, from ^{13}C and ^{1}H NMR data, we could deduce that, in solutions in which the reactant ratio is greater than 1:1 (Al/Mg), no organic ligands are bound to magnesium. Thus, the remaining possibilities for the magnesium-based structures are combinations of chloride and THF ligands, adding up to six ligands per Mg ion.

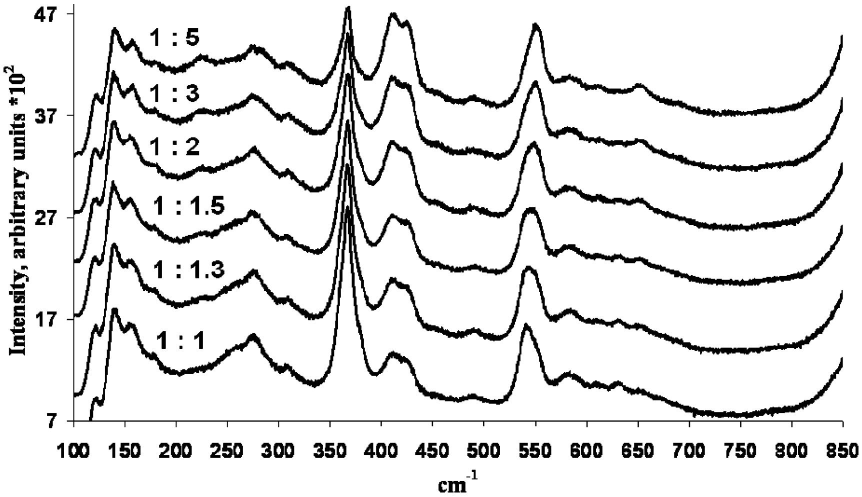

Figure 6. Raman spectra of THF solutions containing mixtures of Et_2AlCl and $Et_2AlCl_2^-$ at different concentration ratios, as indicated in the figure.

Table 2. Correlation between $Et_2AlCl_2^-$ and Et_2AlCl Concentration Ratio and the Corresponding Peak Height Ratio (at 367 and 413 cm^{-1})

organic ligand	ion−molecule ratio	peak height ratio
ethyl	1:1	2.06
	1:1.3	1.80
	1:1.5	1.76
	1:2	1.47
	1:3	1.25
	1:4	1.13
	1:5	1.03
methyl	1:1	2.00
	1:1.3	1.35
	1:1.5	1.31
	1:2	1.21
	1:3	1.14

Figure 8 presents the spectra of $MgCl_2$, $MgCl^+AlEt_4^-$, and $Mg_2Cl_3^+AlEt_4^-$ in THF. $MgCl^+$ was prepared by the reaction of an equimolar quantity of EtMgCl with Et_3Al, while $Mg_2Cl_3^+$ was synthesized by reacting 2 equiv of EtMgCl with 1 equiv of Et_2AlCl.

The expected reaction sequence is presented in eqs 1 and 2 (the THF presence was omitted for clarity).

$$\mathrm{EtMgCl} + \mathrm{Et_3Al} \leftrightarrows \mathrm{MgCl^+} + \mathrm{Et_4Al^-} \qquad (1)$$

$$\mathrm{2EtMgCl} + \mathrm{Et_2AlCl} \leftrightarrows \mathrm{MgCl^+} + \mathrm{MgCl_2} + \mathrm{Et_4Al^-} \leftrightarrow \mathrm{Mg_2Cl_3^+} + \mathrm{Et_4Al^-} \qquad (2)$$

An indication that reactions take place between the reactants as described in eqs 1 and 2 was obtained from the dramatic increase in the solution's ionic conductivity compared to those of the solutions of the reactants alone. The sharp peak at 460 cm^{-1} in the Raman spectra, measured from solutions in which reactions (1) and (2) took place, testifies that from the viewpoint of aluminum species only Et_4Al^- is present in the solution. No other known spectral features were observed, which could indicate the existence of any other aluminum species. From these reference spectra, it is possible to learn that $MgCl_2$ has a single characteristic peak at 212 cm^{-1}, that $MgCl^+$ does not have discernible features in the spectral window of our Raman setup, and that $MgCl^+$ and $MgCl_2$ form a dimer, namely, $Mg_2Cl_3^+$, which shows a characteristic peak at 239 cm^{-1}. Indeed, solutions with varying ratios of $MgCl_2$ to $MgCl^+$ have shown the anticipated trend in the peak height ratio.[7]

Interestingly, the spectra of the DCC solutions invariably contain two peaks, at 212 and 239 cm^{-1}. This provides evidence for the existence of both $MgCl_2$ and $Mg_2Cl_3^+$ moieties in solution. The peak height ratio was found to be dependent both on the exact reactant ratio (the exact Al to Mg ratio) and, to a lesser degree, on the reaction conditions. Since $MgCl^+$ does not have a fingerprint in the Raman spectra that we could measure, we deduce its existence on the basis of the reactant ratio. For instance, in DCC solutions that were prepared with an Al to Mg ratio of 1, only the peak at 212 cm^{-1} is observed, testifying for the existence of only $MgCl_2$ in the solution as a single magnesium-based species. This is in line with the ^{27}Al NMR spectra, ionic conductivity data (minimum in conductivity), and the rest of the Raman spectra, which demonstrate the existence of only the neutral aluminum species Et_3Al.

To complete the picture, spectra were also acquired for Et_2Mg, Bu_2Mg, BuMgCl, and EtMgCl solutions in THF. These spectra are not presented, as they do not add to the identification of the species in solution. Nevertheless, it is worth mentioning that in THF solutions which contain species having organo−magnesium bonds, significant peaks were seen around 350, 400, and 490 cm^{-1}, along with a peak at 212 cm^{-1} for the Grignard solutions. These results are in agreement with literature data and are in accordance with the expected Schlenk equilibrium existing in all of these solutions, in which the presence of $MgCl_2$ is postulated.[9] The data related to these spectra are also given in Table 1, along with a compilation of the data for other solutions containing magnesium species.

Conclusion

Raman spectroscopy was proven to be a powerful tool for the identification of various organo−halo metallic species in solutions. These spectroscopic measurements were used for the identification of the various species in ethereal electrolyte solutions for rechargeable magnesium batteries on the basis of complexes obtained by reactions between R_xMgCl_{2-x} (Mg Lewis base) and Al-based Lewis acids−R'_yAlCl_{3-y} (R and R′ are organic ligands, $x = 0-2$, $y = 0-3$). From the Raman spectroscopic studies presented herein, it was proven that magnesium ion conducting ethereal solutions that comprise the

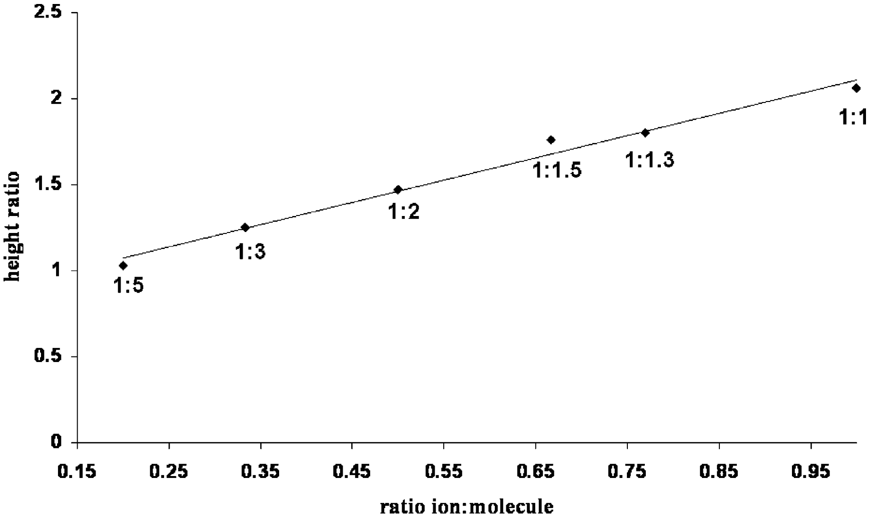

Figure 7. Correlation between various $Et_2AlCl_2^-$ and Et_2AlCl concentration ratios and the corresponding ratio between the heights of their main Raman peaks, at 367 and 413 cm^{-1}, respectively, which belong to Et−Al stretching vibrations.

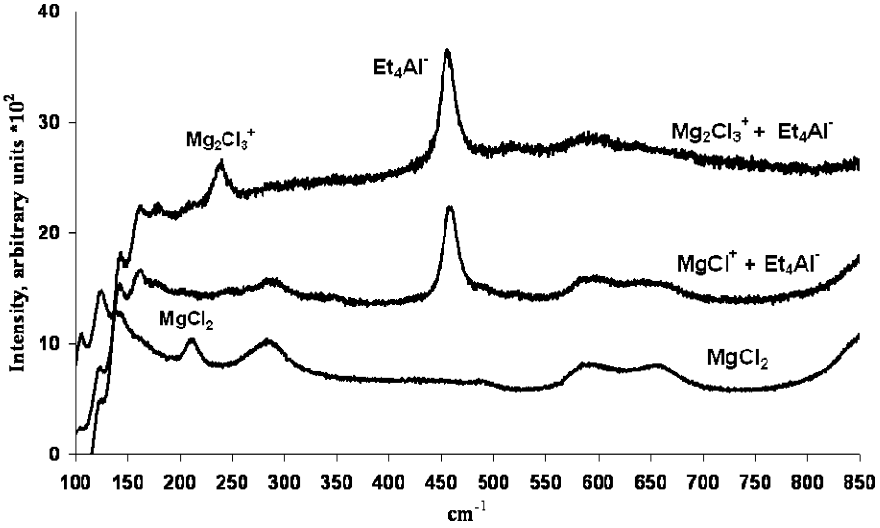

Figure 8. Raman spectra of $MgCl_2$, $MgCl^+AlEt_4^-$, and $Mg_2Cl_3^+AlEt_4^-$ solutions in THF.

reaction products between R_2Mg or RMgCl Lewis bases and $AlCl_2R$ Lewis acids contain various species in multiple equilibria, including $MgCl_2$, $Mg_2Cl_3^+$, $AlCl_{3-n}R_n$, and $AlCl_{4-n}R_n^-$ ($1 \leq n \leq 3$). The exact composition of these solutions is determined mostly by the Lewis base−Lewis acid reagent ratio. It was demonstrated that the Raman spectroscopy of these solutions enables their quantitative analysis. The exact species and their relative concentration ratio, as determined by Raman spectroscopy, come in line with the relatively high ionic conductivity of the DCC solutions, and their appreciable anodic stability. This Raman spectroscopy study enables accurate and simple analysis for practical, DCC-like solutions, for battery applications.

Experimental Section

All chemical preparations and electrochemical measurements were carried out under a pure argon atmosphere in M. Braun, Inc. gloveboxes (less than 1 ppm of water and oxygen).

Chemicals and Synthesis. One method of preparation of the complex salt solution consisted of the dropwise addition of a chosen amount of 1 M ethylaluminum dichloride ($EtAlCl_2$) solution in hexane (Aldrich, 97%) to a vigorously stirred, carefully measured amount of filtered 1 M dibutylmagnesium (Bu_2Mg) in heptane (Aldrich, 97%) or to an appropriate amount of 2 M ethylmagnesium chloride (EtMgCl) in THF (Aldrich, 99%). In these cases, a mildly exothermic reaction took place, yielding immediately a powdery white precipitate. The suspension thus formed was stirred at room temperature for an additional 48 h, after which it was vacuum-dried. Extra-dry tetrahydrofuran (THF, Merck, Selectipure) was then added to the dry, white solid, usually to a desired concentration of 0.25 or 0.5 M. The solutions thus obtained were clear and colorless.

Another method of electrolyte synthesis consisted of the preparation of a 1 M ethylaluminum dichloride ($EtAlCl_2$) solution in THF by vacuum-drying hexane from an ethylaluminum dichloride ($EtAlCl_2$) solution in hexane (Aldrich, 97%) and then adding an appropriate amount of THF (the same as above). After the obtained solution was stirred fir 30 min, it was added dropwise to an appropriate amount of 2 M ethylmagnesium chloride (EtMgCl) in THF (Aldrich, 99%).

Solutions of diethylmagnesium (Et_2Mg) in hexane were prepared by the addition of dry distilled 1,4-dioxane (Aldrich, 99.9%) to an ethylmagnesium chloride (EtMgCl) solution in THF (Aldrich, 97%), which caused the precipitation of $MgCl_2$•(dioxane), leaving out the Et_2Mg solution (which was obtained in a very pure form by filtration through a fine glass frit). A $MgCl_2$•4THF solution in THF was prepared by reacting an excess of pure magnesium foil (Merck, 99.95%) with a dry solution of $HgCl_2$ in THF.

Triethylaluminum (Et_3Al, Aldrich, 97%), diethylaluminum chloride (Et_2AlCl, Aldrich, 97%), and ethylaluminum dichloride ($EtAlCl_2$, Aldrich, 97%) were all used as received after their former solvent (hexane or heptane) was exchanged by THF, as described for ethylaluminum dichloride. The solution of $AlCl_3$ in THF was obtained by dissolving solid $AlCl_3$ (Aldrich, 99.99%) in this solvent. Lithium chloride (LiCl, Aldrich) was dried under vacuum over P_2O_5 at 75 °C for 72 h.

Spectral Studies. Raman spectra were measured with a JY Horiba spectrometer using an He−Ne excitation laser (632.817 nm) in a standard screw-cap rectangular spectrozile quartz cuvette (Aldrich). All of the experiments were performed at room temperature (25 ± 2 °C).

The theoretical Raman spectra were calculated at the HF/6-31G* level of theory, using the Gaussian 03 package.[13] A solvent molecule (THF) has been added to the neutral species as the fourth legand on the aluminum atom. The solvent (THF, $\epsilon = 7.58$) has been accounted for via the IEFPCM[14] model. The calculated vibrational eigenvectors were used to create animation files, to assist in assigning the vibrational modes.

Supporting Information Available: Tables giving QM calculation data for the various compounds studied in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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