Atom-efficient synthesis of a benchmark electrolyte for magnesium battery applications

Scott A. Brown,^{ac} Serena A. Cussen,^{b*} Rhiannon Kennard,^b Sofia Marchesini,^c Jethro J. Pryke,^b Annabel Rae,^a Stuart D. Robertson,^{a*} Rudra N. Samajdar,^{ac} and Andrew J. Wain^{c*}

a WestCHEM, Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, UK, G1 1XL

b Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, UK c Department of Electromagnetic and Electrochemical Technologies, National Physical Laboratory, Hampton Road, Teddington, UK, TW11 0LW

stuart.d.robertson@strath.ac.uk; andy.wain@npl.co.uk; s.cussen@sheffield.ac.uk

Supporting Information

Synthesis of MgPh₂·2THF

Dioxane (5 mL) was added to a solution of PhMgCl (10 mL, 20 mmol, 2 M in THF from Sigma-Aldrich) and stirred at room temperature overnight. The resulting white suspension (dioxane·MgCl₂) was then filtered and the THF and excess dioxane were removed *in vacuo* to concentrate the solution; crystals could then be grown from this solution of the product MgPh₂·2THF, confirmed by X-Ray diffraction. Isolated crystalline yield 39 % from a maximum of 50 %.

MgPh₂·2THF (0.064 g, 0.2 mmol) was added to an NMR tube fitted with a J Youngs tap and dissolved in 0.5 mL of d₈-THF. ¹H and ¹³C NMR was then carried out and the data are shown in Figures S1 and S2, below.

¹H NMR (400 MHz, 298 K, d₈-THF): δ = 7.69 (m, 4H, o-C*H*, Ar), 6.98 (t, 4H, m-C*H*, Ar), 6.89 (tt, 2H, p-C*H*, Ar), 3.63 (t, 8H, O-C*H*₂-CH₂), 1.76 (m, 8H, O-CH₂-C*H*₂)

¹³C NMR (400 MHz, 298 K, d₈-THF): δ = 140.12 (o-CH, Ar), 125.11 (m-CH, Ar), 123.25 (p-CH, Ar), 66.41 (O-CH₂-CH₂), 24.15 (O-CH₂-CH₂)



Figure S1 ¹H NMR spectrum of MgPh₂·2THF in d₈-THF



Figure S2 ¹³C NMR spectrum of MgPh₂·2THF in d_8 -THF

Synthesis of [Mg₂Cl₃·6THF]⁺ [AlPh₄]⁻

MgPh₂·2THF (0.646 g, 2 mmol) and AlCl₃ (0.133 g, 1 mmol) were added to the same Schlenk flask in an argon atmosphere glove box. 7 mL of THF was then added slowly at 0°C and the solution slightly heated to dissolve the reactants, the solution was then stirred at room temperature overnight. Colourless crystals were obtained by slowly layering hexane on top of the solution (0.288 g, 31 % crystalline yield). Excess hexane was then added to the filtrate after collection of the crystals resulting in another white precipitate. The precipitate was then collected via filtration and dried *in vacuo* and found to be $[Mg_2Cl_3\cdot 6THF]^+$ [AlPh₄]⁻ by NMR spectroscopy (0.631 g, 68 % yield). Total yield 99 %.

In situ preparation

In an argon filled glove box $AICl_3$ (0.013 g, 0.1 mmol) was weighed out in a small vial. The MgPh₂·2THF solution from the NMR tube was then syringed into the vial and stirred until all reactants had dissolved. The solution was then transferred back into the NMR tube and ¹H, ¹³C and ²⁷Al NMR was performed.

The data are shown in Figures S3-S8, below.

¹H NMR (400 MHz, 298 K, d₈-THF): δ = 7.67 (d, 8H, o-CH, Ar), 6.94 (t, 8H, m-CH, Ar), 6.89 (dt, 4H, p-CH, Ar), 3.58 (t, 16H, O-CH₂-CH₂), 1.71 (m, 16H, O-CH₂-CH₂)

¹³C NMR (400 MHz, 298 K, d₈-THF): δ = 138.68 (o-CH, Ar), 124.87 (m-CH, Ar), 123.50 (p-CH, Ar), 66.44 (O-CH₂-CH₂), 24.01 (O-CH₂-CH₂)

²⁷Al NMR (104.2 MHz, 298 K, d_8 -THF) δ = 132.90 ppm (s)

Microanalysis (crystals): Found (Calcd for $[Mg_2Cl_3 \cdot 5THF]^+$ [AlPh₄]⁻) C 61.77 (62.11), H 7.32 (7.11).

Microanalysis (precipitate): Found (Calcd for [Mg₂Cl₃·5THF]⁺ [AlPh₄]⁻) C 60.79 (62.11), H 7.16 (7.11).



Figure S3 ¹H NMR spectrum of Crystalised $[Mg_2Cl_3 \cdot 6THF]^+$ $[AIPh_4]^-$ in d_8 -THF



Figure S4 ¹³C NMR spectrum of Crystalised $[Mg_2CI_3 \cdot 6THF]^+$ $[AIPh_4]^-$ in d_8 -THF



Figure S5 ²⁷Al NMR spectrum of Crystalised $[Mg_2CI_3 \cdot 6THF]^+$ $[AIPh_4]^-$ in d_8 -THF



Figure S6 ¹H NMR spectrum of in situ mixture of 2MgPh₂·2THF and AlCl₃ in d₈-THF



Figure S7 ¹³C NMR spectrum of in situ mixture of $2MgPh_2 \cdot 2THF$ and $AlCl_3$ in d_8 -THF



Figure S8 ²⁷Al NMR spectrum of in situ mixture of $2MgPh_2 \cdot 2THF$ and $AlCl_3$ in d_8 -THF



Figure S9: (a) FTIR and (b) Raman spectra of pure THF with the major vibrational modes marked. Individual deconvoluted peaks in the FTIR spectrum are labelled as (P_i) .



Figure S10: Deconvoluted FTIR spectra at the low wavenumber region for (a) electrolyte synthesised with stoichiometric control (b) electrolyte synthesised without stoichiometric control. Major peaks are deconvoluted and labelled as (P_i) .

Deconvolution of FTIR spectra

FTIR absorption spectra were deconvoluted into individual component peaks as shown in **Figure S9a** and **Figure S10**. A Voigt waveform in Origin was used to fit the absorption peaks, iterating until $R^2 > 0.99$.

Peak	Position / cm ⁻¹ (all values include a measurement uncertainty of \pm 4 cm ⁻¹)	Vibration (major contributor marked in bold)
P1	1066	C-O-C asymmetric stretch + $C_{\alpha}C_{\beta}$ asymmetric stretch + ring bend (type B vibrations)
P2	1027	β CH ₂ wag + β CH ₂ twist + C-O-C symmetric stretch + $C_{\alpha}C_{\beta}$ symmetric stretch + C _{β} C _{β} stretch + ring bend (type A vibrations)
Р3	907	β CH ₂ twist + α CH ₂ rock + $C_{\alpha}C_{\beta}$ asymmetric stretch (type B vibrations)
P4	875	βCH2 rock + ring bend + C-O-C asymmetric stretch (type B vibrations)

For the pure THF solvent (Figure S9a), the following peaks were identified:

Note that the 33 normal modes of THF are classified into A and B modes according to the irreducible representation [Γ (C₂)=17A + 16B] of the C₂ point group which represents the symmetry of the THF molecule in equilibrium in solution. [1]

The ratio of the peak area of the satellite peaks (P_2 and P_4) compared to the primary peaks (P_1 and P_3 , respectively) was calculated from the fit, and for THF these were determined as:

$$\frac{A(P_2)}{A(P_1)} = 0.05...(i)$$
$$\frac{A(P_4)}{A(P_3)} = 0.06...(ii)$$

For the electrolyte synthesised in this paper (Figure S10a) the major peaks were identified as:

Peak	Position / cm^{-1} (all values include a measurement uncertainty of ± 4 cm^{-1})	Vibration (major contributor marked in bold)
P1	1066	C-O-C asymmetric stretch + $C_{\alpha}C_{\beta}$ asymmetric stretch + ring bend (type B vibrations)
P2	1028	β CH ₂ wag + β CH ₂ twist + C-O-C symmetric stretch + $C_{\alpha}C_{\beta}$ symmetric stretch + C _{β} C _{β} stretch + ring bend (type A vibrations)
Р3	909	β CH ₂ twist + α CH ₂ rock + $C_{\alpha}C_{\beta}$ asymmetric stretch (type B vibrations)
P4	889	β CH ₂ wag + β CH ₂ rock + α CH ₂ rock + C-O-C symmetric stretch (type A vibrations)
Р5	875	β CH2 rock + ring bend + C-O-C asymmetric stretch (type B vibrations)

The ratio of the peak area of the satellite peaks (P_2 and P_4+P_5) compared to the primary peaks (P_1 and P_3 , respectively) was calculated from the fit, and for the electrolyte synthesised in this paper these were determined as:

 $\frac{A(P_2)}{A(P_1)} = 0.26...(iii\mathbb{Z})$ $\frac{A(P_4 + P_5)}{A(P_3)} = 0.43...(iv)$

For electrolyte synthesised without stoichiometric control (Figure S10b), the major peaks were identified as:

Peak	Position / cm^{-1} (all values include a measurement uncertainty of ± 4 cm^{-1})	Vibration (major contributor marked in bold)
P1	1066	C-O-C asymmetric stretch + $C_{\alpha}C_{\beta}$ asymmetric stretch + ring bend (type B vibrations)
P2	1040	$C_{\alpha}C_{\beta}$ symmetric stretch (in distorted/ clustered local coordination)
Р3	1028	β CH ₂ wag + β CH ₂ twist + C-O-C symmetric stretch + $C_{\alpha}C_{\beta}$ symmetric stretch + $C_{\beta}C_{\beta}$ stretch + ring bend (type A vibrations)
P4	908	β CH ₂ twist + α CH ₂ rock + $C_{\alpha}C_{\beta}$ asymmetric stretch (type B vibrations)
Р5	875	$\beta CH_2 rock$ + ring bend + C-O-C asymmetric stretch (type B vibrations)
P6	845	$ \begin{array}{l} \pmb{\beta CH_2 \ rock} + \alpha CH_2 \ rock + \alpha CH_2 \ twist + C-O-C \ symmetric \\ stretch + C_\alpha C_\beta \ symmetric \ stretch + C_\beta C_\beta \ stretch \ (type \ A \\ vibrations) \end{array} $

The ratio of the peak area of the satellite peaks (P_2+P_3 and P_5+P_6) compared to the primary peaks (P_1 and P_4 , respectively) was calculated from the fit, and for the electrolyte synthesised without stoichiometric control these were determined as:

$$\frac{A(P_2 + P_3)}{A(P_1)} = 0.36...(v)$$
$$\frac{A(P_5 + P_6)}{A(P_4)} = 0.59...(vi)$$

Comparing ratios (iii) to (vi) with (i) and (ii) indicates that presence of the electrolyte increases the relative absorbance associated with satellite peaks of THF at around 1028 cm⁻¹ and between 840 cm⁻¹ and 890 cm⁻¹. This arises as a consequence of coordination of THF to species present in solution (generally the solvent is known to coordinate to the cationic species, i.e. Mg²⁺, present in solution; the other cation, Al³⁺, that gives rise to the anionic species in solution, is preferentially coordinated by organic ligands i.e. phenyl rings) which distorts the overall symmetry of the molecule in solution, thus affecting the normal modes of vibration. Comparison of (iii) and (iv) with (v) and (vi), respectively, indicates a higher absorbance associated with satellite peaks for the stoichiometrically non-controlled synthesis. We believe that this is due to (a) presence of multiple solvent coordinated species and (b) increase in concentration of solvent coordinated species in the solution obtained from non-stoichiometrically controlled synthesis.



Figure S11 Nyquist plots obtained from electrolyte synthesised by traditional method using Grignard reagent (1a), atom efficient method prepared in situ (1b), and crystallized pure electrolyte re-dissolved in THF (1c). The intercept of each trace at the high frequency regime, where Z''=0, is used to calculate the conductivity (the cell constant for the set-up is 1 cm^{-1})

Reference

1. B. Cadioli, E. Gallinella, E. Coulombeau, H. Jobic and G. Berthier, *J. Phys. Chem.*, 1993, **97**, 7844-7856.