Supporting Information:

Identification of Highly Reactive $[Mg_2(\mu\text{-}Cl)_2(DME)_4]^{2+}$ Cation Complex for Rechargeable Mg Batteries and the Formation Mechanism

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Experimental Section

Materials and electrolyte synthesis: Magnesium dichloride ($MgCl_2$, 99.99%), aluminum trichloride ($AlCl_3$, 99.99%) and ethylaluminum dichloride ($AlEtCl_2$, 97%) were purchased from Sigma Aldrich. THF, DME, diglyme, triglyme and tetraglyme were purchased from BASF and were dried over molecular sieve for > 48 hours prior to use. $Mg(TFSI)_2$ (99.5%) was purchased from SOLVIONIC (France). The cathode material *Chevrel* phase nanocubes (Mo_6S_8) were synthesized using our reported method.[4] All electrolyte synthesis work was carried out inside an Ar-filled glove box. In a typical synthesis of 10 ml 0.4M $MgCl_2$-$AlEtCl_2$/DME electrolyte, $AlEtCl_2$ (0.518 g) was added dropwise to a suspension of $MgCl_2$ (0.38 g, in 10ml DME) in a 25 ml glass vial. The mixture was stirred at 60°C using a sand bath for 6 hours, and was cooled to room temperature. A clear solution was obtained with no precipitations. The $MgCl_2$-$AlCl_3$/DME electrolyte and $MgCl_2$-$Mg(TFSI)_2$/DME electrolyte were prepared using a similar procedure. $MgCl_2$-$AlEtCl_2$/THF electrolyte was synthesized by using our method

reported previously.[12] The synthesis protocol for electrolytes of $MgCl_2$-$AlEtCl_2$ in diglyme, triglyme and tetraglyme was the same as in DME.

Spectroscopy measurements: ^{25}Mg NMR spectra were obtained using a 600 MHz Varian-Agilent spectrometer (Agilent, USA). ^{27}Al NMR spectra were recorded using a 17.6 T Bruker Avance III spectrometer equipped with an HDX BBO probe. The ^{25}Mg and ^{27}Al spectra were referenced to external 1.0 M $Al(NO_3)_3$ in H_2O/D_2O(9:1) and 10M $MgCl_2$ in H_2O solutions, respectively. Raman spectra were measured on an inverted Raman microscope (Nikon Eclipse Ti). A red He-Ne laser (632.8 nm) was used as the excitation source. All experiments were performed at room temperature.

Single crystal X-ray diffraction: Single crystals for structural analysis were prepared by layering hexane onto the desired electrolyte. Each crystal was coated with Paratone-N, affixed to a nylon loop micromount and placed under streaming nitrogen at a temperature of 100 K in a Bruker KAPPA APEX II CCD diffractometer with 0.71073 Å Mo-Kα radiations. The space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved using direct methods and refined using full-matrix least-squares methods on F^2. Anisotropic displacement parameters were determined for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters, by using a riding model. The following programs were used: SAINT for data reduction and cell refinement; SADABS for scaling and multi-scan absorption correction; SHELXS-2013 and SHELXL-2013 for structure solution and refinement, respectively; and OLEX2 was used as the graphical user interface in which structure solution and refinement were performed.

Electrochemical and battery tests: All electrolytes were aged at room temperature for ~ 24 hours prior to testing. All electrochemical experiments were carried out inside an Ar-filled glove box at room temperature using a CHI660C potentiostat. The Mg deposition/stripping properties of each electrolyte were evaluated using cyclic voltammograms and the three electrodes configuration. The working electrode was 1.0 mm Pt (PEEK-encased) and was polished prior to each experiment. The reference and counter electrodes were two freshly polished Mg metal strips. The electrolyte conductivity was measured using a WP CP650 conductivity meter (OAKTON Instruments). Prototype Mg batteries were assembled as coin cells (type 2032) inside an Ar-purged glove box. A piece of polished Mg foil was used as the anode and the separator was glass fiber membrane. The cathode electrodes were prepared by mixing 80 wt% of Mo_6S_8, 10 wt% of super-C, and 10 wt% of poly(vinylidene fluoride) with N-methyl-2-pyrrolidone (NMP) as the dispersant. The slurry was mixed well and then coated onto a piece of stainless steel foil. Typical active material loading was ~1.0 mg/cm^2. Cell tests were performed on an Arbin battery tester BT-2000 (Arbin Instruments, TX).

SEM and XRD measurements: The morphology and structure of the deposited Mg was studied with scanning electron microscopy (SEM) and XRD. Samples were prepared by galvanostatic deposing Mg on a piece of Pt working electrode (ca. 1 cm × 1 cm) at 1.0 mA/cm^2, followed by washing with DME and drying under vacuum. SEM images were collected using a JEOL 5900 microscope. XRD patterns were obtained using a Philips Xpert X-ray diffractometer with Cu Kα radiation at λ =1.54 Å. Samples were sealed inside a XRD sample holder with kapton tape.

$[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$

Table S1. Crystal data and structure refinement for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$

Identification code	$[Mg(DME)_2Cl]_2\ (AlEtCl_3)_2$
Empirical formula	$C_{18}H_{25}O_8Mg_2Al_2Cl_8$
Formula weight	809.86
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	20.4918(9)
b/Å	13.8611(6)
c/Å	15.1335(6)
α/°	90
β/°	117.1327(19)
γ/°	90
Volume/Å^3	3825.5(3)
Z	4
ρ_{calc}mg/mm^3	1.4060
m/mm^{-1}	0.705
F(000)	1696.2
Crystal size/mm^3	0.42 × 0.3 × 0.25
2Θ range for data collection	3.7 to 56.22°
Index ranges	$-27 \le h \le 26$, $-14 \le k \le 18$, $-19 \le l \le 19$
Reflections collected	21813
Independent reflections	4620[R(int) = 0.0265]
Data/restraints/parameters	4620/0/206
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0203, wR_2 = N/A
Final R indexes [all data]	R_1 = 0.0242, wR_2 = 0.0543
Largest diff. peak/hole / e Å^{-3}	0.41/-0.31

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl3	2739.25(15)	4875.29(19)	3642.4(2)	18.15(7)
Cl4	1619.69(18)	5857.0(2)	1304.2(2)	27.30(8)
Al1	1936.55(18)	5992.9(2)	2874.1(2)	14.10(8)
Mg1	5000	7225.0(4)	2500	10.47(10)
Mg2	5000	4695.5(4)	2500	10.31(10)
O2	3881.3(4)	7320.4(5)	1504.5(5)	14.24(15)
O1	4621.9(4)	8334.7(5)	3089.1(5)	13.67(15)
O3	6105.3(4)	4506.0(5)	3458.3(5)	13.98(15)
O4	4970.7(4)	3631.2(6)	3480.3(5)	13.90(15)
C3	3463.1(6)	8007.6(8)	1753.4(9)	18.1(2)
C2	3865.2(6)	8173.7(8)	2855.1(8)	16.9(2)
C7	5654.8(6)	3580.4(9)	4375.9(8)	17.8(2)
C5	6759.6(6)	4888.8(8)	3454.4(9)	17.6(2)
C4	3492.1(6)	7022.3(9)	482.9(8)	18.7(2)
C8	4355.4(6)	3483.7(9)	3680.9(9)	21.4(2)
C1	5035.0(7)	8764.5(9)	4046.9(8)	21.8(2)
C6	6255.1(6)	3655.7(8)	4071.3(8)	17.8(2)
C10	1232.9(8)	5929.9(10)	4203.2(11)	30.4(3)
Cl1	5198.58(13)	5968.89(17)	1512.74(18)	12.06(6)
Cl2	2508.08(15)	7350.9(2)	3377.0(2)	21.28(7)
C11	1076.4(6)	5897.2(8)	3125.1(9)	23.8(4)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Cl3	17.99(13)	15.93(13)	17.99(13)	2.76(10)	6.00(11)	4.14(10)
Cl4	30.58(16)	34.98(17)	12.79(13)	11.41(13)	6.82(12)	3.30(12)
Al1	13.82(16)	14.73(16)	13.24(16)	0.63(12)	5.74(13)	1.30(12)
Mg1	9.6(2)	10.6(2)	10.1(2)	-0	3.56(19)	0
Mg2	11.0(2)	10.6(2)	9.1(2)	-0	4.44(19)	0
O2	10.7(3)	16.4(4)	12.0(4)	2.4(3)	2.0(3)	-2.5(3)
O1	11.8(4)	14.8(4)	13.3(4)	-0.9(3)	4.7(3)	-3.4(3)
O3	11.6(3)	15.5(4)	14.4(4)	1.4(3)	5.5(3)	3.4(3)
O4	14.3(4)	16.3(4)	11.4(4)	-0.1(3)	6.1(3)	2.4(3)
C3	12.3(5)	19.2(6)	20.1(6)	4.8(4)	5.1(4)	-1.8(4)
C2	12.5(5)	18.8(5)	20.2(5)	2.0(4)	8.1(4)	-1.7(4)
C7	17.2(5)	22.8(6)	11.6(5)	3.1(4)	5.1(4)	5.1(4)
C5	11.9(5)	19.4(5)	21.3(6)	-0.4(4)	7.4(4)	0.7(4)
C4	15.4(5)	22.4(6)	11.7(5)	0.5(4)	0.5(4)	-2.4(4)
C8	18.8(6)	28.5(6)	19.3(6)	-4.4(5)	10.8(5)	5.0(5)
C1	21.4(6)	24.7(6)	15.5(5)	-2.1(5)	5.0(5)	-8.1(5)
C6	17.7(5)	20.0(6)	15.1(5)	6.4(4)	7.1(4)	6.9(4)
C10	36.9(8)	28.2(7)	34.2(8)	-3.5(6)	23.3(7)	0.1(6)
Cl1	14.99(12)	11.75(12)	11.03(11)	0.28(9)	7.3(1)	0.47(9)
Cl2	18.67(13)	14.52(13)	32.90(16)	-1.62(10)	13.71(12)	-0.22(11)
C11	16.4(5)	24.0(6)	34.1(7)	-3.1(4)	14.3(5)	-3.6(4)

Table S4. Bond Lengths for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl3	Al1	2.1709(4)	Mg2	Cl1	2.4633(4)
Cl4	Al1	2.1667(4)	Mg2	Cl1[1]	2.4633(4)
Al1	Cl2	2.1636(4)	O2	C3	1.4415(13)
Al1	C11	1.9696(10)	O2	C4	1.4397(13)
Mg1	O2	2.0957(7)	O1	C2	1.4418(13)
Mg1	O2[1]	2.0957(7)	O1	C1	1.4329(13)
Mg1	O1	2.0955(8)	O3	C5	1.4444(12)
Mg1	O1[1]	2.0955(8)	O3	C6	1.4436(13)
Mg1	Cl1	2.4462(4)	O4	C7	1.4402(13)
Mg1	Cl1[1]	2.4462(4)	O4	C8	1.4398(13)
Mg2	O3[1]	2.0751(7)	C3	C2	1.5029(16)
Mg2	O3	2.0751(7)	C7	C6	1.5013(15)
Mg2	O4	2.1123(8)	C10	C11	1.5131(18)
Mg2	O4[1]	2.1123(8)			

[1]1-X,+Y,1/2-Z

Table S5. Bond Angles for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl4	Al1	Cl3	107.471(18)	Cl1[1]	Mg2	O3[1]	94.88(2)
Cl2	Al1	Cl3	106.024(17)	Cl1[1]	Mg2	O3	95.53(2)
Cl2	Al1	Cl4	107.745(18)	Cl1	Mg2	O4	172.69(2)
O2	Mg1	O2[1]	172.76(5)	Cl1	Mg2	O4[1]	90.52(2)
O1[1]	Mg1	O2[1]	76.35(3)	Cl1[1]	Mg2	O4	90.52(2)
O1[1]	Mg1	O2	98.24(3)	Cl1[1]	Mg2	O4[1]	172.69(2)
O1	Mg1	O2[1]	98.24(3)	Cl1[1]	Mg2	Cl1	88.459(19)
O1	Mg1	O2	76.35(3)	C3	O2	Mg1[1]	116.08(6)
O1	Mg1	O1[1]	85.55(4)	C4	O2	Mg1[1]	129.98(6)
Cl1	Mg1	O2[1]	92.97(2)	C4	O2	C3	111.47(8)

Cl1	Mg1	O2	92.18(2)	C2	O1	Mg1[1]	110.29(6)
Cl1[1]	Mg1	O2[1]	92.18(2)	C1	O1	Mg1[1]	124.96(7)
Cl1[1]	Mg1	O2	92.97(2)	C1	O1	C2	112.70(8)
Cl1	Mg1	O1	168.26(2)	C5	O3	Mg2[1]	132.06(7)
Cl1	Mg1	O1[1]	93.78(2)	C6	O3	Mg2[1]	113.39(6)
Cl1[1]	Mg1	O1[1]	168.26(2)	C6	O3	C5	112.13(8)
Cl1[1]	Mg1	O1	93.78(2)	C7	O4	Mg2	111.58(6)
Cl1[1]	Mg1	Cl1	89.242(19)	C8	O4	Mg2	123.73(7)
O3	Mg2	O3[1]	165.45(5)	C8	O4	C7	111.39(8)
O4	Mg2	O3[1]	91.77(3)	C2	C3	O2	107.49(9)
O4	Mg2	O3	78.01(3)	C3	C2	O1	106.28(9)
O4[1]	Mg2	O3	91.77(3)	C6	C7	O4	106.85(8)
O4[1]	Mg2	O3[1]	78.01(3)	C7	C6	O3	106.87(9)
O4[1]	Mg2	O4	91.40(4)	Mg2	Cl1	Mg1	91.150(14)
Cl1	Mg2	O3[1]	95.53(2)	C10	C11	Al1	115.95(8)
Cl1	Mg2	O3	94.88(2)				

[1]1-X,+Y,1/2-Z

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$.

Atom	***x***	***y***	***z***	**U(eq)**
H3a	3415.0(6)	8620.9(8)	1393.4(9)	21.7(3)
H3b	2965.7(6)	7752.4(8)	1565.2(9)	21.7(3)
H2a	3819.7(6)	7603.7(8)	3217.4(8)	20.3(3)
H2b	3663.0(6)	8742.5(8)	3041.9(8)	20.3(3)
H7a	5690.7(6)	4116.1(9)	4828.6(8)	21.3(3)
H7b	5691.9(6)	2962.0(9)	4723.0(8)	21.3(3)
H5a	6983(3)	4393(2)	3218(6)	26.4(3)
H5b	6631.2(9)	5450(4)	3013(5)	26.4(3)
H5c	7108(2)	5083(6)	4129.2(14)	26.4(3)
H4a	3415(4)	7581.0(15)	49.4(8)	28.0(3)

H4b	3780(2)	6534(5)	346.0(19)	28.0(3)
H4c	3017(2)	6749(6)	357.8(18)	28.0(3)
H8a	4344(3)	3997(4)	4119(6)	32.1(4)
H8b	3900.3(7)	3496(7)	3055.8(11)	32.1(4)
H8c	4404(3)	2857(3)	4005(6)	32.1(4)
H1a	5055(4)	8319(3)	4561.5(9)	32.8(4)
H1b	5534.0(16)	8901(6)	4150(3)	32.8(4)
H1c	4799(3)	9367(3)	4084(2)	32.8(4)
H6a	6260.9(6)	3075.2(8)	3693.8(8)	21.3(3)
H6b	6737.9(6)	3713.6(8)	4663.8(8)	21.3(3)
H11a	729(9)	6479(12)	2738(12)	38(4)
H11b	782(9)	5326(12)	2767(12)	36(4)
H10a	1544(9)	5310(12)	4591(12)	42(4)
H10b	1558(9)	6508(12)	4592(13)	42(5)
H10c	757(10)	5945(12)	4286(13)	47(5)

Experimental

Single crystals of $C_{18}H_{25}O_8Mg_2Al_2Cl_8$ ($[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$) were immersed in Paratone-N. A suitable crystal was selected and fixed to a nylon loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. olex2.solve (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)
3. olex2.refine (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)

Crystal structure determination of $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlEtCl_3)_2$

Crystal Data for $C_{18}H_{25}O_8Mg_2Al_2Cl_8$ (M =809.86): monoclinic, space group C2/c (no. 15), a = 20.4918(9) Å, b = 13.8611(6) Å, c = 15.1335(6) Å, β = 117.1327(19)°, V = 3825.5(3) Å^3, Z = 4, T = 100 K, μ(Mo) = 0.705 mm^{-1}, *Dcalc* = 1.4060 g/mm^3, 21813 reflections measured ($3.7 \leq 2\Theta \leq 56.22$), 4620 unique ($R_{int}$ = 0.0265) which were used in all calculations. The final R_1 was 0.0203 (I>=2u(I)) and wR_2 was 0.0543 (all data).

This report has been created with Olex2, compiled on 2013.03.22 svn.r2654. Please let us know if there are any errors or if you would like to have additional features.

$[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$

Table S7. Crystal data and structure refinement for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$.

Identification code	$[Mg(DME)_2Cl]_2(AlCl_4)_2$
Empirical formula	$C_{16}H_{40}Al_2Cl_{10}Mg_2O_8$
Formula weight	817.59
Temperature/K	100
Crystal system	orthorhombic
Space group	$Pc2_1b$
a/Å	7.2711(5)
b/Å	19.1328(14)
c/Å	26.492(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3685.5(5)
Z	4
ρ_{calc}mg/mm^3	1.4734
m/mm^{-1}	0.872
F(000)	1687.3
Crystal size/mm^3	2.932 × 0.697 × 0.478
2Θ range for data collection	3.74 to 55.84°
Index ranges	$-9 \le h \le 9$, $-25 \le k \le 25$, $-34 \le l \le 34$
Reflections collected	74448
Independent reflections	8791[R(int) = 0.0275]
Data/restraints/parameters	8791/0/351
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = N/A
Final R indexes [all data]	R_1 = 0.0370, wR_2 = 0.0934
Largest diff. peak/hole / e Å^{-3}	1.00/-0.38
Flack parameter	-0.01(4)

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl2	-1884.4(7)	3646.0(3)	3793.6(2)	14.97(11)
Cl1	2665.3(7)	3887.0(3)	3573.23(19)	16.91(11)
Cl7	5085.2(9)	6585.6(4)	4511.1(3)	27.34(15)
Cl10	8828.7(9)	7071.7(4)	3770.1(3)	25.56(14)
Cl3	2867.4(10)	6391.9(3)	5780.2(3)	27.32(15)
Al7	5881.0(11)	7098.1(4)	3833.9(3)	17.65(16)
Mg1	-24(1)	3840.7(4)	3032.8(3)	10.93(15)
Mg2	755.5(11)	3825.2(4)	4344.1(3)	11.16(15)
Cl5	6789(1)	5332.1(4)	5798.9(3)	30.91(16)
Cl6	5322.8(12)	6138.2(4)	6898.8(3)	31.73(16)
Al12	4427.5(11)	5665.7(4)	6213.9(3)	15.48(15)
Cl4	2754.0(11)	4784.2(4)	6379.0(3)	33.38(17)
Cl8	4706.1(12)	6605.4(4)	3193.2(3)	38.66(19)
O5	204(3)	4897.7(9)	4403.3(7)	17.8(4)
O1	1529(2)	3822.0(9)	2354.6(6)	13.8(3)
O7	-776(2)	3581.6(9)	4998.4(6)	15.9(3)
O3	-279(3)	4933.3(9)	3026.0(7)	20.7(4)
O8	1395(3)	2766.5(9)	4450.1(7)	21.6(4)
O2	-1(3)	2778.6(9)	2850.4(7)	19.4(4)
O4	-2425(2)	4004.2(10)	2617.4(7)	20.3(4)
O6	2959(2)	4204.5(10)	4777.8(7)	19.3(4)
C5	1061(5)	5473.0(15)	3132.1(12)	29.5(6)
C7	-3283(4)	4657.0(16)	2739.4(11)	26.3(6)
C9	-1577(4)	5235.1(14)	4384.5(11)	23.8(6)
C13	-280(4)	3814.8(15)	5497.6(9)	22.5(5)
C2	1135(4)	3200.6(15)	2066.7(10)	24.5(6)
C1	1858(4)	4405.5(15)	2022.9(10)	22.9(5)
C11	3305(4)	4933.2(15)	4669.1(12)	25.9(6)
C16	2880(5)	2347.0(18)	4243.0(13)	38.0(8)
C12	4636(4)	3834.6(18)	4858.2(11)	28.1(6)
C14	-1195(4)	2842.9(13)	4980.5(11)	22.1(5)
C10	1478(4)	5305.5(15)	4695.6(12)	26.5(6)
C8	-3781(4)	3472.0(18)	2529.8(12)	30.6(7)
C6	-1790(4)	5204.9(15)	2737.2(11)	27.9(6)
C15	535(4)	2441.2(14)	4878.4(11)	24.2(6)
C3	1163(4)	2600.3(15)	2430.2(11)	25.1(6)
C4	-394(6)	2175.7(15)	3157.5(13)	36.1(8)
Cl9	5018.3(11)	8161.2(4)	3880.4(3)	29.17(16)

Table S9. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl2	11.0(2)	23.8(3)	10.1(2)	-1.4(2)	0.19(18)	2.0(2)
Cl1	10.5(2)	30.3(3)	10.0(2)	0.6(2)	0.09(18)	0.2(2)
Cl7	25.1(3)	29.5(3)	27.5(3)	-4.1(3)	5.4(3)	9.4(3)
Cl10	23.6(3)	26.3(3)	26.8(3)	-3.4(3)	8.0(2)	0.9(3)
Cl3	33.3(3)	25.1(3)	23.5(3)	9.0(3)	-2.2(3)	3.6(3)
Al7	22.1(4)	18.7(4)	12.1(3)	0.1(3)	-1.2(3)	-0.3(3)
Mg1	11.4(3)	13.3(4)	8.2(3)	0.1(3)	0.1(3)	-0.1(3)
Mg2	11.7(3)	13.4(4)	8.4(3)	1.1(3)	-0.8(3)	-0.8(3)
Cl5	28.0(3)	36.1(4)	28.6(4)	10.3(3)	7.8(3)	-1.6(3)
Cl6	42.8(4)	34.0(4)	18.4(3)	-4.2(3)	-6.2(3)	-5.8(3)
Al12	20.4(4)	15.3(3)	10.7(3)	0.9(3)	1.2(3)	0.2(3)
Cl4	38.9(4)	24.1(3)	37.2(4)	-10.7(3)	3.1(3)	3.1(3)
Cl8	44.6(4)	40.4(4)	30.9(4)	6.7(4)	-16.7(3)	-19.3(3)
O5	19.1(9)	11.4(8)	22.9(9)	-1.1(7)	2.0(7)	-0.7(7)
O1	16.7(7)	15.7(8)	8.9(7)	-3.1(7)	2.1(6)	1.2(6)
O7	18.6(8)	16.7(8)	12.3(8)	-2.4(7)	0.7(6)	1.3(7)
O3	23.6(9)	13.6(9)	24.9(10)	1.2(7)	1.6(8)	3.6(7)
O8	30.4(10)	14.6(8)	19.8(9)	10.0(8)	-0.7(8)	-0.7(7)
O2	25.8(10)	15.5(9)	16.9(9)	-2.8(7)	3.3(7)	-2.0(7)
O4	14.1(8)	31.2(11)	15.7(8)	1.4(7)	-1.0(6)	3.0(7)
O6	15.4(8)	26.5(10)	16.1(9)	-0.7(7)	-0.3(7)	-2.1(7)
C5	39.7(17)	17.3(13)	31.3(15)	-5.3(12)	1.3(13)	-1.0(11)
C7	19.2(13)	37.3(16)	22.4(13)	13.5(11)	2.9(10)	5.8(12)
C9	22.5(13)	20.1(13)	28.8(14)	6.5(11)	4.1(11)	0.3(11)
C13	30.8(13)	25.9(14)	10.8(11)	1.8(11)	2.2(9)	-3.9(10)
C2	33.2(15)	26.4(14)	13.9(12)	-7.5(12)	6.1(11)	-9.2(10)
C1	22.4(13)	26.4(13)	19.8(13)	1.5(11)	5.6(10)	7.0(11)
C11	20.8(13)	28.4(15)	28.5(14)	-7.9(11)	-1.7(11)	-2.7(11)
C16	52(2)	31.3(17)	30.5(17)	28.4(15)	6.7(14)	1.5(13)
C12	16.5(11)	45.9(17)	21.8(13)	2.4(12)	-4.4(10)	4.4(13)
C14	25.3(13)	18.4(12)	22.7(13)	-3.9(10)	-0.8(10)	3.1(10)
C10	27.1(14)	19.4(13)	33.1(15)	-4.0(11)	-1.4(12)	-8.5(12)
C8	16.2(12)	50.1(19)	25.5(14)	-6.5(12)	-4.5(11)	-3.1(13)
C6	29.2(15)	28.0(15)	26.6(14)	14.2(12)	4.2(12)	8.2(11)
C15	34.6(15)	16.6(13)	21.5(13)	2.7(11)	-4.9(11)	4.5(10)
C3	30.6(14)	21.9(13)	22.9(14)	0.1(11)	9.6(12)	-6.1(11)
C4	61(2)	16.5(14)	30.8(16)	-4.2(14)	14.7(15)	2.4(12)

Cl9	42.6(4)	18.3(3)	26.7(3)	6.8(3)	-3.9(3)	-2.0(3)

Table S10. Bond Lengths for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	Mg1	2.4558(9)	O5	C9	1.448(3)
Cl2	Mg2	2.4348(9)	O5	C10	1.438(3)
Cl1	Mg1	2.4251(9)	O1	C2	1.441(3)
Cl1	Mg2	2.4724(9)	O1	C1	1.441(3)
Cl7	Al7	2.1248(10)	O7	C13	1.442(3)
Cl10	Al7	2.1505(11)	O7	C14	1.447(3)
Cl3	Al12	2.1299(10)	O3	C5	1.447(3)
Al7	Cl8	2.1211(10)	O3	C6	1.436(3)
Al7	Cl9	2.1322(10)	O8	C16	1.453(3)
Mg1	O1	2.1223(17)	O8	C15	1.437(3)
Mg1	O3	2.0987(19)	O2	C3	1.439(3)
Mg1	O2	2.0889(19)	O2	C4	1.440(3)
Mg1	O4	2.0872(19)	O4	C7	1.433(3)
Mg2	O5	2.0966(19)	O4	C8	1.436(3)
Mg2	O7	2.1121(18)	O6	C11	1.446(3)
Mg2	O8	2.0973(19)	O6	C12	1.425(3)
Mg2	O6	2.1010(19)	C7	C6	1.509(4)
Cl5	Al12	2.1365(10)	C2	C3	1.499(4)
Cl6	Al12	2.1291(10)	C11	C10	1.509(4)
Al12	Cl4	2.1252(11)	C14	C15	1.499(4)

Table S11. Bond Angles for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Mg2	Cl2	Mg1	92.06(3)	Cl5	Al12	Cl3	110.21(4)
Mg2	Cl1	Mg1	91.89(3)	Cl6	Al12	Cl3	110.22(4)
Cl10	Al7	Cl7	109.08(4)	Cl6	Al12	Cl5	108.64(5)
Cl8	Al7	Cl7	111.15(5)	Cl4	Al12	Cl3	108.89(5)
Cl8	Al7	Cl10	109.15(5)	Cl4	Al12	Cl5	109.20(5)
Cl9	Al7	Cl7	108.14(4)	Cl4	Al12	Cl6	109.67(4)
Cl9	Al7	Cl10	108.67(4)	C9	O5	Mg2	127.23(16)
Cl9	Al7	Cl8	110.59(5)	C10	O5	Mg2	116.63(16)
Cl1	Mg1	Cl2	88.00(3)	C10	O5	C9	110.7(2)
O1	Mg1	Cl2	170.16(6)	C2	O1	Mg1	110.89(14)
O1	Mg1	Cl1	94.10(5)	C1	O1	Mg1	126.28(16)

O3	Mg1	Cl2	96.29(6)	C1	O1	C2	110.45(19)
O3	Mg1	Cl1	92.29(6)	C13	O7	Mg2	123.57(15)
O3	Mg1	O1	93.23(8)	C14	O7	Mg2	107.46(15)
O2	Mg1	Cl2	92.69(6)	C14	O7	C13	112.6(2)
O2	Mg1	Cl1	99.53(6)	C5	O3	Mg1	130.51(18)
O2	Mg1	O1	77.49(7)	C6	O3	Mg1	115.63(17)
O2	Mg1	O3	165.40(9)	C6	O3	C5	111.1(2)
O4	Mg1	Cl2	89.70(6)	C16	O8	Mg2	130.4(2)
O4	Mg1	Cl1	168.58(7)	C15	O8	Mg2	115.30(15)
O4	Mg1	O1	90.06(7)	C15	O8	C16	112.5(2)
O4	Mg1	O3	76.84(8)	C3	O2	Mg1	114.48(15)
O4	Mg1	O2	91.76(8)	C4	O2	Mg1	130.30(17)
Cl1	Mg2	Cl2	87.41(3)	C4	O2	C3	111.3(2)
O5	Mg2	Cl2	91.82(6)	C7	O4	Mg1	112.09(16)
O5	Mg2	Cl1	97.04(6)	C8	O4	Mg1	123.58(17)
O7	Mg2	Cl2	92.57(6)	C8	O4	C7	110.8(2)
O7	Mg2	Cl1	169.88(6)	C11	O6	Mg2	110.91(16)
O7	Mg2	O5	93.08(8)	C12	O6	Mg2	124.23(18)
O8	Mg2	Cl2	96.84(6)	C12	O6	C11	111.1(2)
O8	Mg2	Cl1	91.84(6)	C6	C7	O4	106.9(2)
O8	Mg2	O5	167.87(8)	C3	C2	O1	106.8(2)
O8	Mg2	O7	78.10(8)	C10	C11	O6	107.0(2)
O6	Mg2	Cl2	167.79(7)	C15	C14	O7	109.2(2)
O6	Mg2	Cl1	90.39(6)	C11	C10	O5	106.6(2)
O6	Mg2	O5	76.53(8)	C7	C6	O3	107.3(2)
O6	Mg2	O7	91.69(7)	C14	C15	O8	106.6(2)
O6	Mg2	O8	95.23(8)	C2	C3	O2	107.9(2)

Table S12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$.

Atom	***x***	***y***	***z***	**U(eq)**
H5a	2126(16)	5266(3)	3303(8)	44.2(9)
H5b	1460(30)	5689(9)	2815.0(14)	44.2(9)
H5c	507(11)	5829(7)	3350(8)	44.2(9)
H7a	-4239(4)	4772.4(16)	2486.6(11)	31.6(7)
H7b	-3869(4)	4631.4(16)	3076.2(11)	31.6(7)
H9a	-2390(11)	4974(7)	4157(7)	35.7(8)
H9b	-2113(14)	5245(11)	4723.8(18)	35.7(8)
H9c	-1433(6)	5714(4)	4260(8)	35.7(8)
H13a	809(19)	3559(9)	5613(4)	33.8(8)

H13b	-10(30)	4316(3)	5489.6(19)	33.8(8)
H13c	-1304(12)	3728(11)	5730(2)	33.8(8)
H2a	-86(4)	3238.6(15)	1903.9(10)	29.4(7)
H2b	2075(4)	3132.9(15)	1800.6(10)	29.4(7)
H1a	707(7)	4537(7)	1855(6)	34.3(8)
H1b	2320(30)	4802(4)	2219.5(16)	34.3(8)
H1c	2770(20)	4274(4)	1768(5)	34.3(8)
H11a	4171(4)	5131.8(15)	4919.5(12)	31.1(7)
H11b	3850(4)	4984.8(15)	4328.6(12)	31.1(7)
H16a	3540(20)	2618(5)	3987(8)	57.0(12)
H16b	3730(20)	2216(13)	4514(2)	57.0(12)
H16c	2370(6)	1924(7)	4088(9)	57.0(12)
H12a	4362(4)	3348(4)	4947(9)	42.1(9)
H12b	5375(15)	3846(11)	4549(3)	42.1(9)
H12c	5322(16)	4055(8)	5134(6)	42.1(9)
H14a	-1733(4)	2692.3(13)	5306.2(11)	26.6(6)
H14b	-2105(4)	2750.5(13)	4710.7(11)	26.6(6)
H10a	1585(4)	5782.9(15)	4554.6(12)	31.8(7)
H10b	1057(4)	5340.8(15)	5050.0(12)	31.8(7)
H8a	-3166(4)	3032(4)	2443(9)	45.9(10)
H8b	-4520(20)	3406(10)	2836(3)	45.9(10)
H8c	-4580(20)	3615(6)	2251(6)	45.9(10)
H6a	-2247(4)	5644.1(15)	2889.9(11)	33.5(8)
H6b	-1394(4)	5304.3(15)	2386.9(11)	33.5(8)
H15a	247(4)	1946.2(14)	4803.8(11)	29.1(7)
H15b	1361(4)	2458.6(14)	5175.3(11)	29.1(7)
H3a	2434(4)	2513.6(15)	2548.4(11)	30.2(7)
H3b	705(4)	2171.2(15)	2263.4(11)	30.2(7)
H4a	762(6)	1965(8)	3272(8)	54.2(12)
H4b	-1120(30)	2318(3)	3451(5)	54.2(12)
H4c	-1090(30)	1834(6)	2959(3)	54.2(12)

Experimental

Single crystals of $C_{16}H_{40}Al_2Cl_{10}Mg_2O_8$ ($[Mg(DME)_2Cl]_2(AlCl_4)_2$) were grown from layering hexanes over a DME solution of the compound. A suitable crystal was selected and fixed to a nylon loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. olex2.solve (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)
3. olex2.refine (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)

Crystal structure determination of $[Mg_2(\mu\text{-}Cl)_2(DME)_4](AlCl_4)_2$

Crystal Data for $C_{16}H_{40}Al_2Cl_{10}Mg_2O_8$ (M =817.59): orthorhombic, space group $Pc2_1b$ (no. 29), a = 7.2711(5) Å, b = 19.1328(14) Å, c = 26.492(2) Å, V = 3685.5(5) Å^3, Z = 4, T = 100 K, μ(Mo) = 0.872 mm^{-1}, *Dcalc* = 1.4734 g/mm^3, 74448 reflections measured ($3.74 \leq 2\Theta \leq 55.84$), 8791 unique ($R_{int}$ = 0.0275) which were used in all calculations. The final R_1 was 0.0345 (I>=2u(I)) and wR_2 was 0.0934 (all data).

This report has been created with Olex2, compiled on 2013.03.22 svn.r2654. Please let us know if there are any errors or if you would like to have additional features.

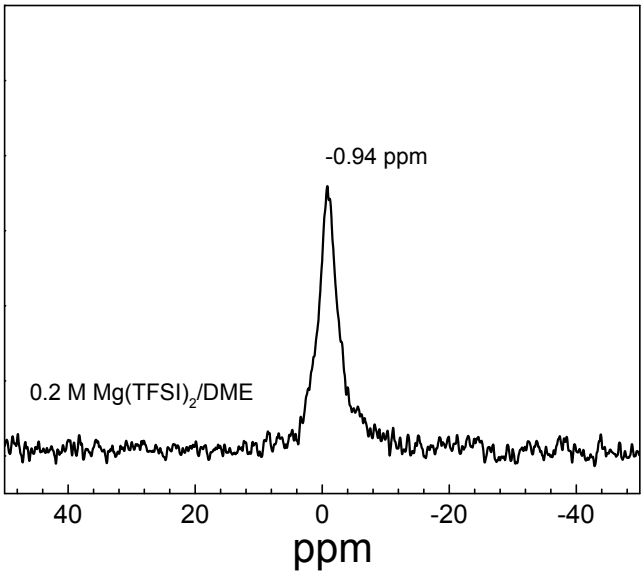

Figure S1. ^{25}Mg NMR spectrum of 0.2 M $Mg(TFSI)_2$ dissolved in DME at room temperature.

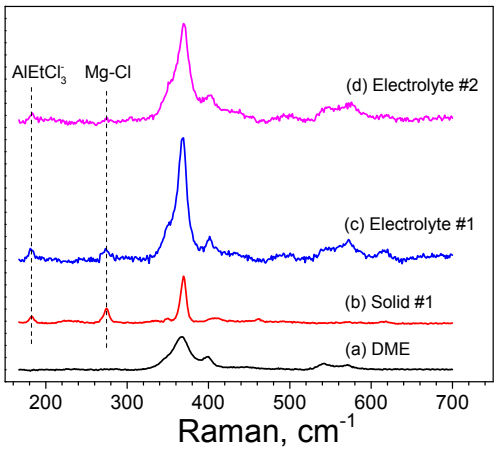

Figure S2. Raman spectra of (a) DME, (b) Solid powder precipitated from solution consists of 0.4 M $MgCl_2$ and 0.4 M $AlEtCl_2$ in DME by evaporating DME, (c) Electrolyte consists of 0.4 M $MgCl_2$ and 0.4 M $AlEtCl_2$ in DME, and (d) Electrolyte consists of 0.4 M $MgCl_2$ and 0.8 M $AlEtCl_2$ in DME.