Electronic Supplementary Material (ESI) for Dalton Transactions.

Crystalline magnesium chloride-electron donor complexes: new support materials for Ziegler–Natta catalysts

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Supplementary Information

Morphology of the crystals

The morphology of the products was analyzed using a Hitachi S-4800 scanning electron microscope (SEM). The acceleration voltage of electrons used in imaging was 3.0 kV. Samples were in contact with air for a few second as they were transferred into the loading chamber of SEM.

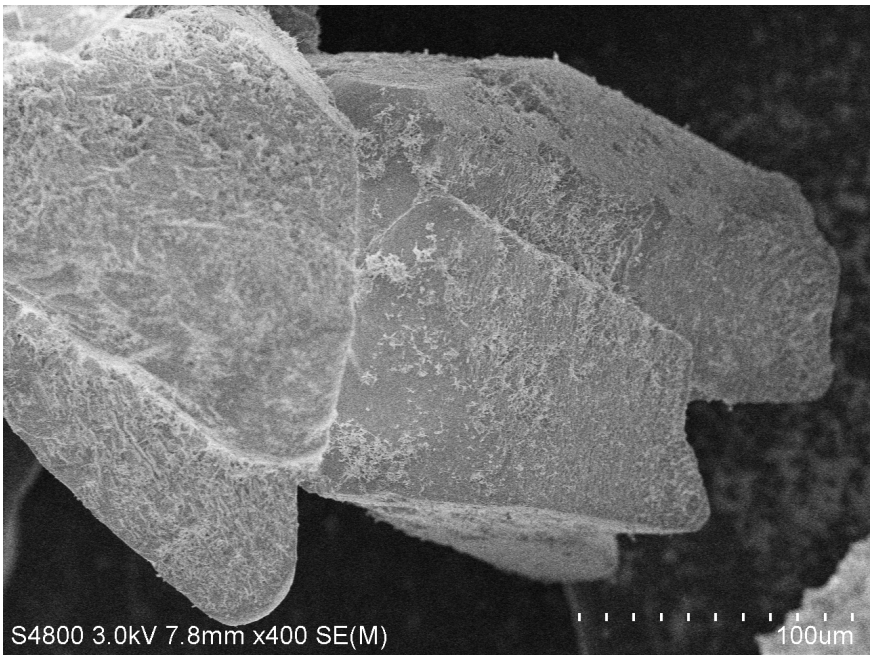

Figure S1. SEM image of $[MgCl_2(DME)]_n$ crystal.

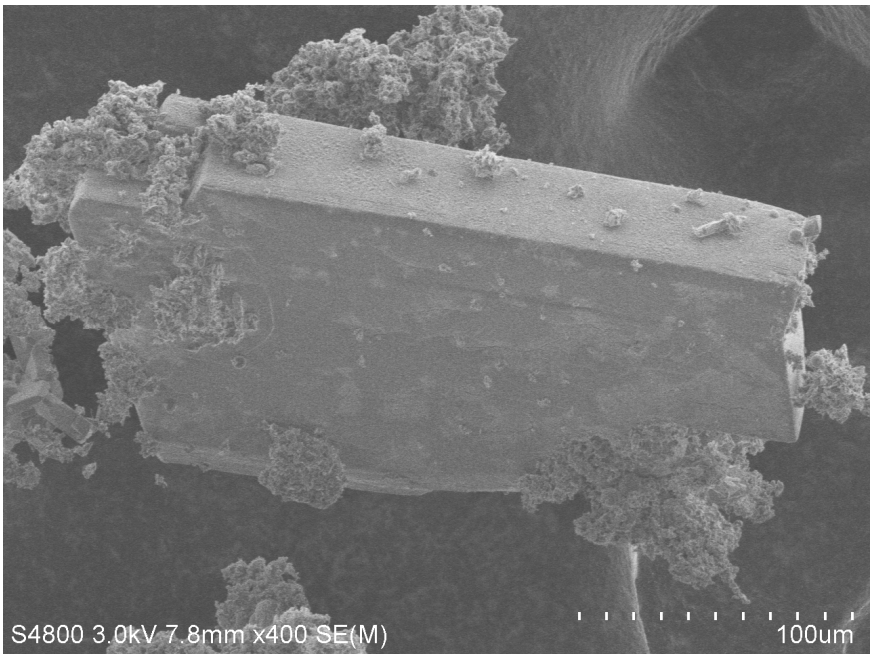

Figure S2. SEM image of $Mg_2Cl_4(DMP)_2(H_2O)$ crystal.

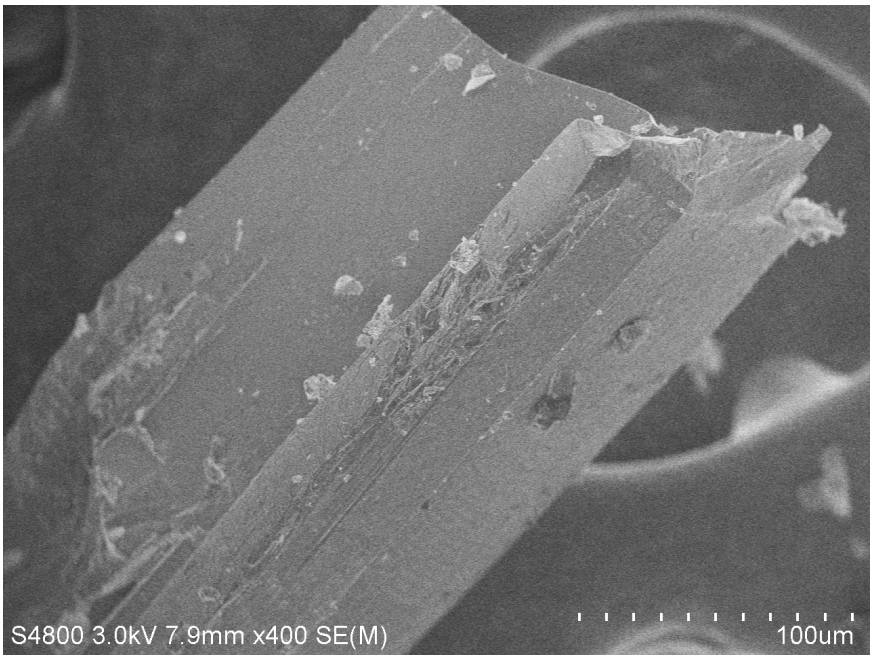

Figure S3. SEM image of $MgCl_2(DEEDA)_2$ crystal.

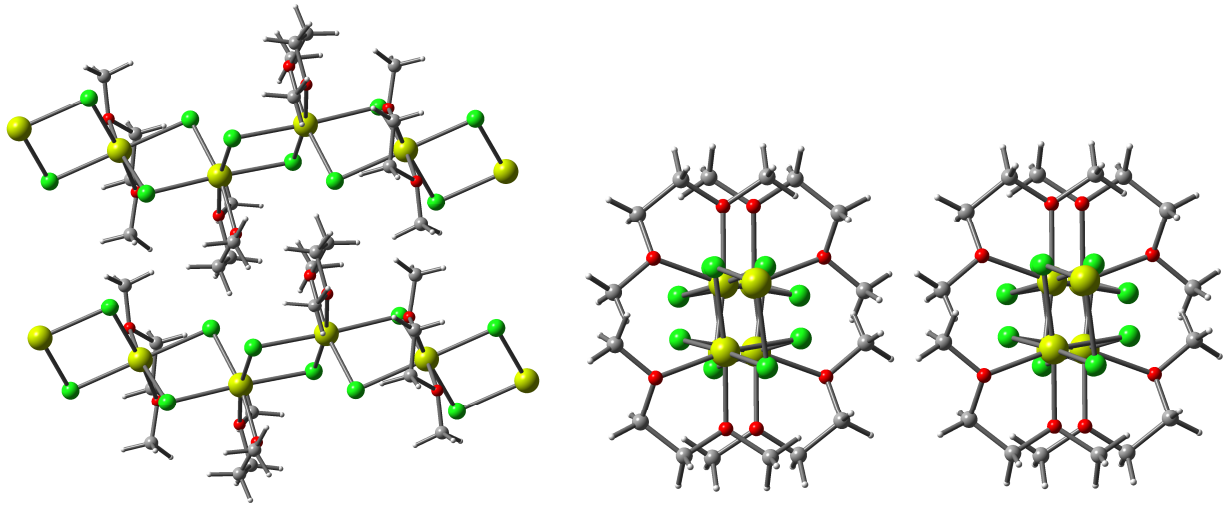

Figure S4. Packing of $[MgCl_2(DME)]_n$ polymeric chains from two different viewpoints.

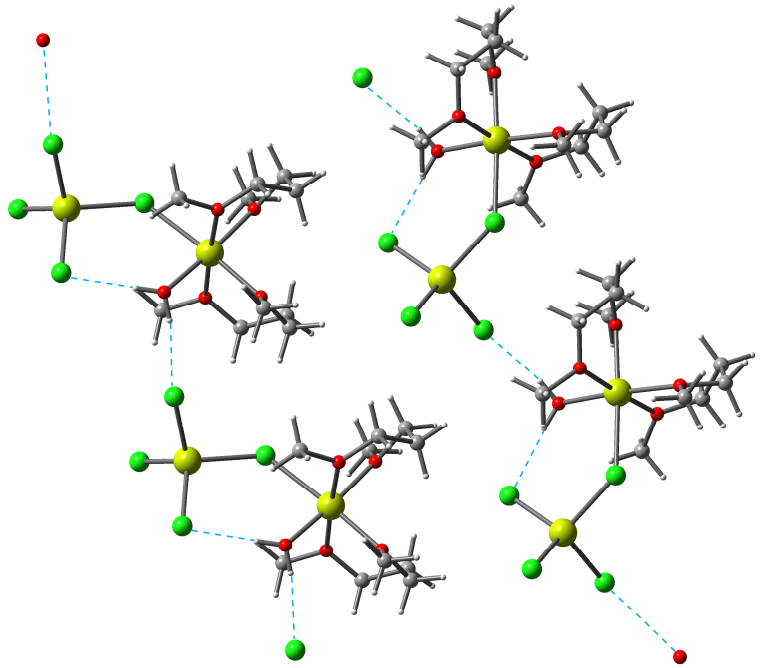

Figure S5. Packing of $Mg_2Cl_4(DMP)_2(H_2O)$ molecules. Hydrogen bonds are marked with light blue dashed lines.

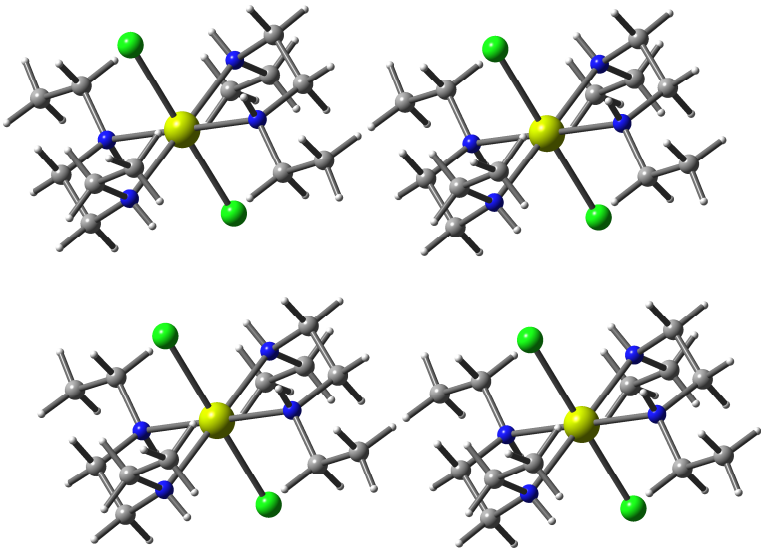

Figure S6. Packing of $MgCl_2(DEEDA)_2$ molecules.

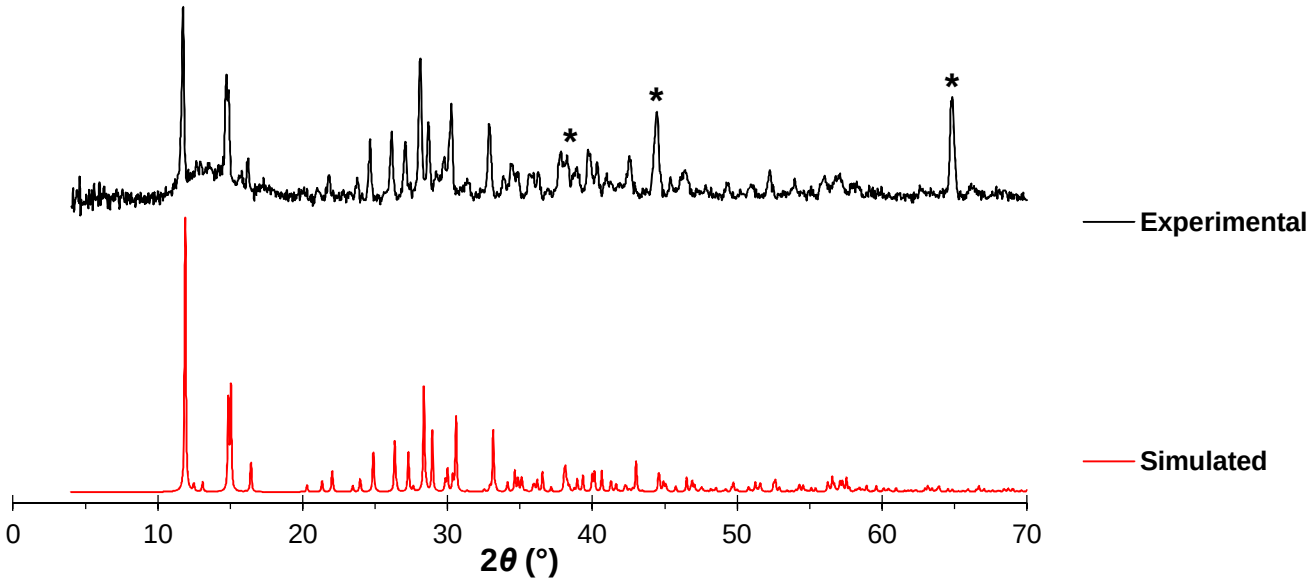

Figure S7. Experimental (black line) and simulated (red line) powder X-ray diffractograms of $[MgCl_2(DME)]_n$ complex. Reflections of the sample holder are marked with asterisks (*).

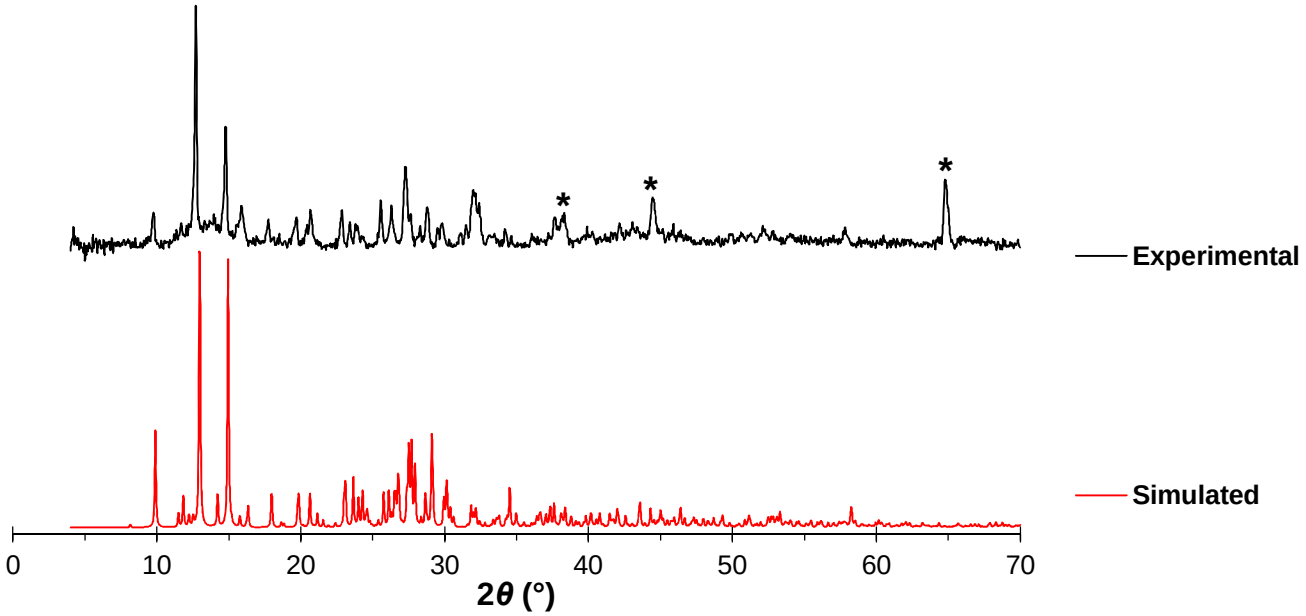

Figure S8. Experimental (black line) and simulated (red line) powder X-ray diffractograms of $Mg_2Cl_4(DMP)_2(H_2O)$ complex. Reflections of the sample holder are marked with asterisks (*).

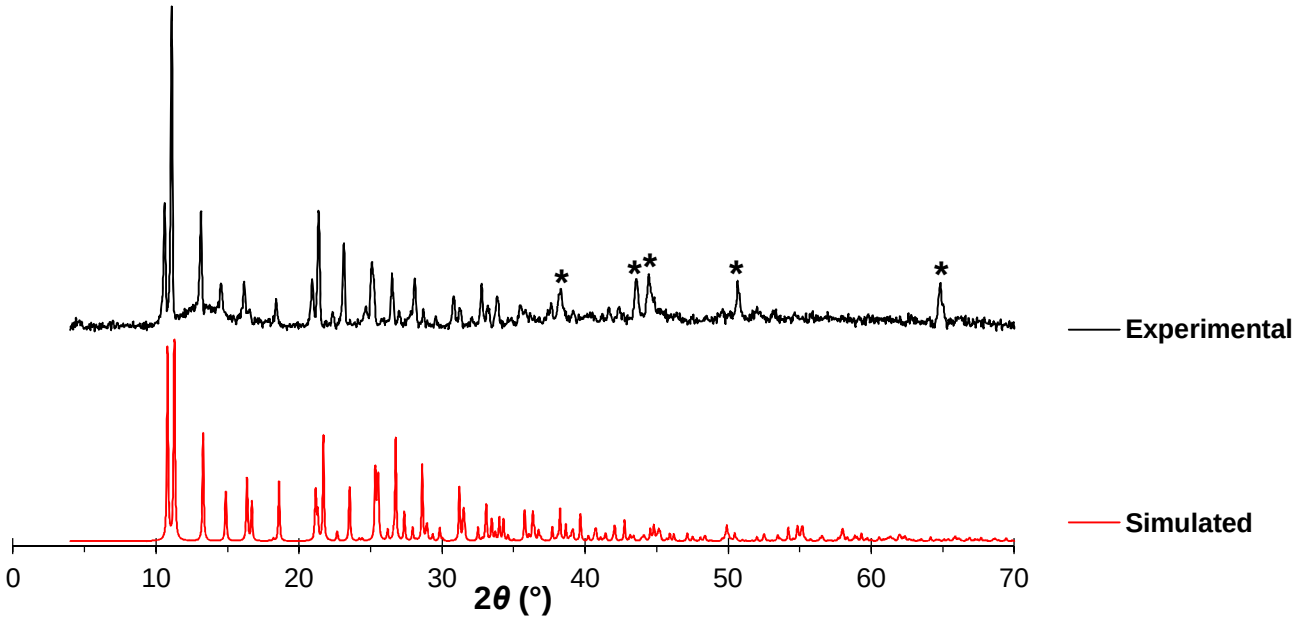

Figure S9. Experimental (black line) and simulated (red line) powder X-ray diffractograms of $MgCl_2(DEEDA)_2$ complex. Reflections of the sample holder are marked with asterisks (*).

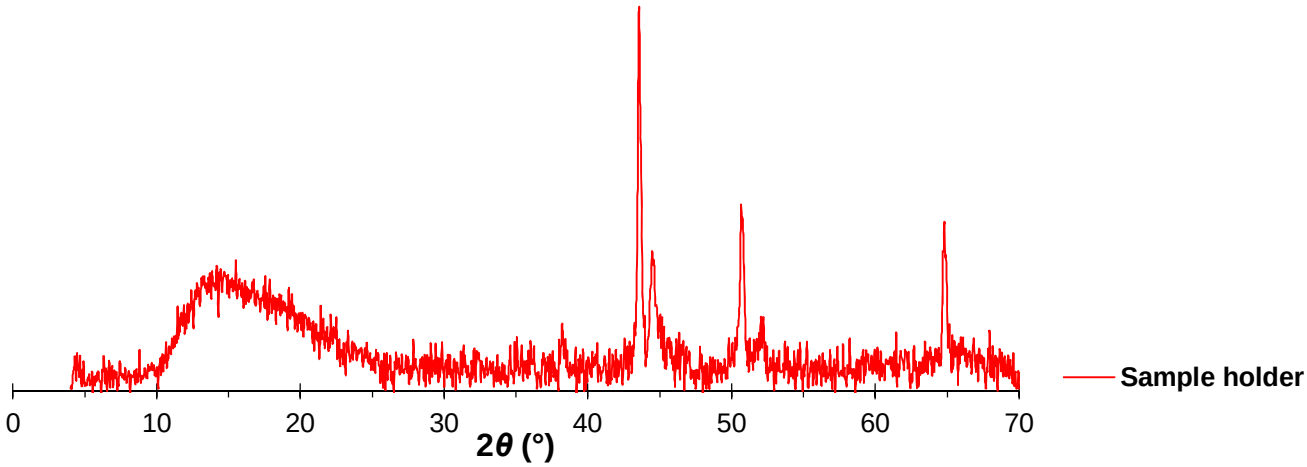

Figure S10. Powder X-ray diffractogram of the sample holder utilized in measurements.

Table S1. Crystal data and structure refinement for $[MgCl_2(DME)]_n$, $Mg_2Cl_4(DMP)_2(H_2O)$ and $MgCl_2(DEEDA)_2$.

	$[MgCl_2(DME)]_n$	$Mg_2Cl_4(DMP)_2(H_2O)$	$MgCl_2(DEEDA)_2$
Empirical formula	$C_4H_{10}Cl_2MgO_2$	$C_{10}H_{26}Cl_4Mg_2O_5$	$C_{12}H_{32}Cl_2MgN_4$
Formula weight	185.33	416.73	327.62
Color	white	brownish	white
T (K)	120(2)	120(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	9.2117(4)	8.1550(3)	6.7256(4)
b (Å)	13.5279(4)	17.8774(8)	7.9186(5)
c (Å)	13.0025(4)	14.0589(6)	8.2724(5)
α (deg)	90	90	84.028(2)
β (deg)	104.540(1)	103.905(2)	84.0440(10)
γ (deg)	90	90	84.4590(10)
Volume ($Å^3$)	1568.41(10)	1989.59(14)	434.17(5)
Z	8	4	1
ρ_{calc} (Mg/m^3)	1.570	1.391	1.253
μ (mm^{-1})	0.836	0.671	0.405
F(000)	768	872	178
Crystal size (mm^3)	0.139 x 0.123 x 0.093	0.143 x 0.093 x 0.064	0.803 x 0.612 x 0.536
θ range for data collection (deg.)	2.736 to 36.490	2.278 to 30.999	2.596 to 35.027
Index ranges	-15<=h<=15, -22<=k<=22, -21<=l<=21	-11<=h<=11, -25<=k<=25, -19<=l<=20	-10<=h<=10, -12<=k<=12, -12<=l<=12
Reflections collected	51157	25520	11005
Unique reflections	3854	6244	3531
R_{int}	0.0202	0.0358	0.0144
Completeness to θ= 25.242°	100.0 %	98.9 %	99.9 %
Absorption correction	Multi-scan	Multi-scan	Numerical

Max. and min. transmission	0.926 and 0.893	0.958 and 0.909	0.805 and 0.722
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	3854 / 0 / 82	6244 / 0 / 190	3531 / 0 / 88
GOOF on F^2	1.065	1.044	1.056
Final R indices [I>2sigma(I)][a]	R1 = 0.0179, wR2 = 0.0493	R1 = 0.0346, wR2 = 0.0781	R1 = 0.0221, wR2 = 0.0587
R indices (all data)	R1 = 0.0201, wR2 = 0.0504	R1 = 0.0552, wR2 = 0.0871	R1 = 0.0249, wR2 = 0.0603
Largest diff. peak and hole (e.Å^{-3})	0.629 and -0.393	0.435 and -0.413	0.398 and -0.161

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[MgCl_2(DME)]_n$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8826(1)	5532(1)	1032(1)	18(1)
C(2)	8070(1)	7092(1)	1591(1)	16(1)
C(3)	6748(1)	7779(1)	1315(1)	17(1)
C(4)	4126(1)	7823(1)	1149(1)	17(1)
Mg(1)	5477(1)	5689(1)	1230(1)	10(1)
Cl(1)	5786(1)	3988(1)	689(1)	11(1)
Cl(2)	3165(1)	5438(1)	1833(1)	11(1)
O(1)	7604(1)	6201(1)	993(1)	12(1)
O(2)	5471(1)	7244(1)	1465(1)	12(1)

Table S3. Selected bond lengths and angles for $[MgCl_2(DME)]_n$.

bond lengths (Å)		bond angles (°)	
C(1)-O(1)	1.4353(8)	O(2)-Mg(1)-O(1)	74.879(19)
C(2)-O(1)	1.4402(8)	O(2)-Mg(1)-Cl(1)	167.899(17)
C(2)-C(3)	1.5023(10)	O(1)-Mg(1)-Cl(1)	94.887(15)
C(3)-O(2)	1.4350(8)	O(2)-Mg(1)-Cl(2)	93.255(15)
C(4)-O(2)	1.4369(8)	O(1)-Mg(1)-Cl(2)	165.677(17)
Mg(1)-O(2)	2.1261(5)	Cl(1)-Mg(1)-Cl(2)	97.729(9)
Mg(1)-O(1)	2.1723(5)	O(2)-Mg(1)-Cl(1)#1	87.332(15)
Mg(1)-Cl(1)	2.4426(3)	O(1)-Mg(1)-Cl(1)#1	90.753(15)
Mg(1)-Cl(2)	2.4705(3)	Cl(1)-Mg(1)-Cl(1)#1	86.349(8)
Mg(1)-Cl(1)#1	2.5123(3)	Cl(2)-Mg(1)-Cl(1)#1	96.775(9)
Mg(1)-Cl(2)#2	2.5382(3)	O(2)-Mg(1)-Cl(2)#2	90.452(15)
		O(1)-Mg(1)-Cl(2)#2	86.900(15)
		Cl(1)-Mg(1)-Cl(2)#2	95.499(9)
		Cl(2)-Mg(1)-Cl(2)#2	85.174(8)
		Cl(1)#1-Mg(1)-Cl(2)#2	177.125(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z #2 -x+1,y,-z+1/2

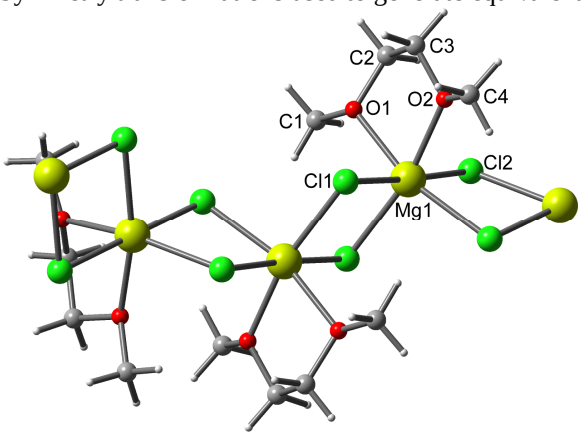

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[MgCl_2(DME)]_n$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	12(1)	20(1)	21(1)	3(1)	4(1)	4(1)
C(2)	15(1)	16(1)	17(1)	0(1)	4(1)	-5(1)
C(3)	20(1)	12(1)	20(1)	2(1)	7(1)	-3(1)
C(4)	18(1)	13(1)	17(1)	1(1)	2(1)	5(1)
Mg(1)	10(1)	9(1)	10(1)	0(1)	3(1)	0(1)
Cl(1)	14(1)	10(1)	10(1)	0(1)	2(1)	2(1)
Cl(2)	10(1)	14(1)	10(1)	-2(1)	3(1)	-1(1)
O(1)	10(1)	13(1)	14(1)	0(1)	3(1)	0(1)
O(2)	13(1)	9(1)	14(1)	1(1)	3(1)	0(1)

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Mg_2Cl_4(DMP)_2(H_2O)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-298(2)	1127(1)	780(1)	32(1)
C(2)	-802(2)	1370(1)	2344(1)	29(1)
C(3)	-27(2)	1402(1)	3431(1)	27(1)
C(4)	468(2)	655(1)	3904(1)	24(1)
C(5)	2281(2)	-384(1)	4020(1)	29(1)
C(6)	4526(2)	663(1)	678(1)	31(1)
C(7)	3881(3)	1915(1)	989(2)	44(1)
C(8)	3317(3)	2431(1)	1698(2)	42(1)
C(9)	4308(2)	2362(1)	2743(2)	37(1)
C(10)	4634(3)	1671(1)	4218(1)	37(1)
O(1)	453(1)	1163(1)	1817(1)	22(1)
O(2)	1877(1)	341(1)	3580(1)	21(1)
O(3)	3759(1)	1149(1)	1269(1)	26(1)
O(4)	3853(1)	1685(1)	3185(1)	26(1)
O(5)	2045(1)	-219(1)	1659(1)	23(1)
Mg(1)	2862(1)	724(1)	2421(1)	17(1)
Mg(2)	6574(1)	-1061(1)	2586(1)	19(1)
Cl(1)	5721(1)	115(1)	3116(1)	22(1)
Cl(2)	4212(1)	-1593(1)	1547(1)	26(1)
Cl(3)	8534(1)	-807(1)	1676(1)	30(1)
Cl(4)	7733(1)	-1776(1)	3925(1)	35(1)

Table S6. Selected bond lengths and angles for $Mg_2Cl_4(DMP)_2(H_2O)$.

bond lengths (Å)		bond angles (°)	
C(1)-O(1)	1.441(2)	O(5)-Mg(1)-O(3)	91.41(5)
C(2)-O(1)	1.4476(18)	O(5)-Mg(1)-O(4)	176.31(5)
C(2)-C(3)	1.509(3)	O(3)-Mg(1)-O(4)	86.24(5)
C(3)-C(4)	1.503(2)	O(5)-Mg(1)-O(1)	86.59(5)
C(4)-O(2)	1.4483(17)	O(3)-Mg(1)-O(1)	91.06(5)
C(5)-O(2)	1.438(2)	O(4)-Mg(1)-O(1)	96.28(5)
C(6)-O(3)	1.445(2)	O(5)-Mg(1)-O(2)	90.02(5)
C(7)-O(3)	1.435(2)	O(3)-Mg(1)-O(2)	177.17(5)
C(7)-C(8)	1.509(3)	O(4)-Mg(1)-O(2)	92.45(5)
C(8)-C(9)	1.501(3)	O(1)-Mg(1)-O(2)	86.60(4)
C(9)-O(4)	1.449(2)	O(5)-Mg(1)-Cl(1)	90.11(4)
C(10)-O(4)	1.440(2)	O(3)-Mg(1)-Cl(1)	89.65(4)
O(1)-Mg(1)	2.0965(11)	O(4)-Mg(1)-Cl(1)	87.04(4)
O(2)-Mg(1)	2.0971(11)	O(1)-Mg(1)-Cl(1)	176.64(4)
O(3)-Mg(1)	2.0749(12)	O(2)-Mg(1)-Cl(1)	92.78(4)
O(4)-Mg(1)	2.0835(12)	Cl(4)-Mg(2)-Cl(1)	109.21(2)
O(5)-Mg(1)	2.0218(12)	Cl(3)-Mg(2)-Cl(1)	106.88(3)
Mg(1)-Cl(1)	2.5455(6)	Cl(2)-Mg(2)-Cl(1)	107.25(2)
Mg(2)-Cl(4)	2.2839(7)	Mg(2)-Cl(1)-Mg(1)	124.38(2)
Mg(2)-Cl(3)	2.3197(6)		
Mg(2)-Cl(2)	2.3225(6)		
Mg(2)-Cl(1)	2.3899(6)		

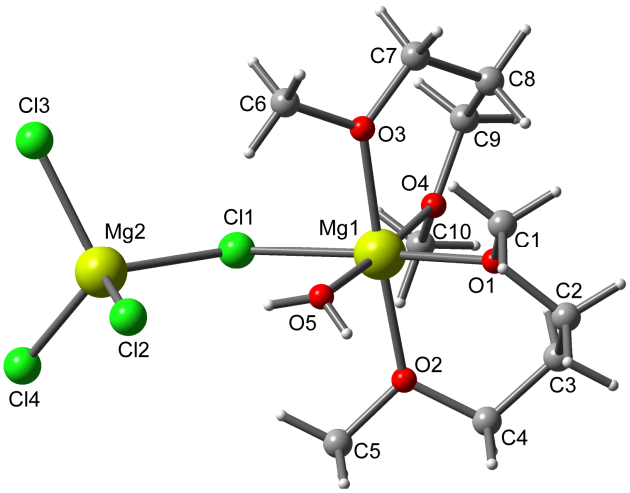

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Mg_2Cl_4(DMP)_2(H_2O)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	26(1)	44(1)	25(1)	11(1)	4(1)	5(1)
C(2)	23(1)	30(1)	36(1)	9(1)	15(1)	9(1)
C(3)	25(1)	25(1)	37(1)	-5(1)	18(1)	2(1)
C(4)	24(1)	28(1)	24(1)	-3(1)	13(1)	-1(1)
C(5)	34(1)	27(1)	28(1)	10(1)	12(1)	4(1)
C(6)	27(1)	48(1)	20(1)	-1(1)	12(1)	0(1)
C(7)	56(1)	34(1)	48(1)	15(1)	26(1)	-7(1)
C(8)	43(1)	20(1)	67(2)	14(1)	23(1)	0(1)
C(9)	34(1)	17(1)	65(1)	-5(1)	24(1)	-7(1)
C(10)	40(1)	39(1)	34(1)	-18(1)	11(1)	-7(1)
O(1)	19(1)	28(1)	22(1)	4(1)	7(1)	3(1)
O(2)	23(1)	21(1)	21(1)	3(1)	11(1)	2(1)
O(3)	27(1)	28(1)	26(1)	6(1)	14(1)	1(1)
O(4)	26(1)	20(1)	35(1)	-7(1)	12(1)	-5(1)
O(5)	17(1)	24(1)	29(1)	-6(1)	6(1)	-1(1)
Mg(1)	17(1)	17(1)	18(1)	0(1)	7(1)	-1(1)
Mg(2)	18(1)	19(1)	19(1)	-1(1)	6(1)	2(1)
Cl(1)	18(1)	22(1)	24(1)	-5(1)	4(1)	2(1)
Cl(2)	22(1)	21(1)	36(1)	-7(1)	6(1)	-2(1)
Cl(3)	22(1)	38(1)	33(1)	-1(1)	14(1)	-4(1)
Cl(4)	51(1)	32(1)	21(1)	3(1)	6(1)	12(1)

Table S8. Atomic coordinates ($x\ 10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for $MgCl_2(DEEDA)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2359(1)	8975(1)	1657(1)	26(1)
C(2)	2347(1)	7291(1)	2699(1)	21(1)
C(3)	1971(1)	4259(1)	2783(1)	20(1)
C(4)	3914(1)	3416(1)	3386(1)	20(1)
C(5)	7332(1)	2318(1)	2485(1)	20(1)
C(6)	7434(1)	644(1)	3570(1)	26(1)
N(1)	2322(1)	5838(1)	1715(1)	16(1)
N(2)	5310(1)	2908(1)	1989(1)	16(1)
Mg(1)	5000	5000	0	14(1)
Cl(1)	7333(1)	6658(1)	1227(1)	20(1)

Table S9. Selected bond lengths and angles for $MgCl_2(DEEDA)_2$.

bond lengths (Å)		bond angles (°)	
C(1)-C(2)	1.5107(9)	N(2)#1-Mg(1)-N(1)	98.620(18)
C(2)-N(1)	1.4791(8)	N(2)-Mg(1)-N(1)	81.380(19)
C(3)-N(1)	1.4780(8)	N(2)-Mg(1)-Cl(1)	90.635(14)
C(3)-C(4)	1.5165(9)	N(1)-Mg(1)-Cl(1)	93.411(14)
C(4)-N(2)	1.4753(8)	N(2)-Mg(1)-Cl(1)#1	89.365(14)
C(5)-N(2)	1.4798(8)	N(1)-Mg(1)-Cl(1)#1	86.589(14)
C(5)-C(6)	1.5211(9)		
N(1)-Mg(1)	2.2654(5)		
N(2)-Mg(1)	2.2209(5)		
Mg(1)-Cl(1)	2.49463(16)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

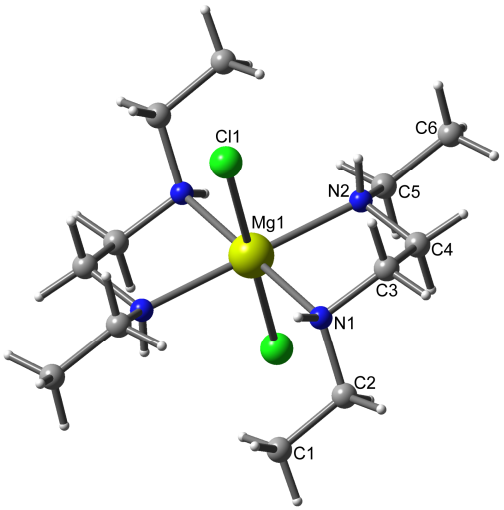

Table S10. Anisotropic displacement parameters ($Å^2x\ 10^3$) for $MgCl_2(DEEDA)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	30(1)	19(1)	28(1)	-4(1)	0(1)	0(1)
C(2)	23(1)	20(1)	20(1)	-6(1)	-1(1)	0(1)
C(3)	15(1)	21(1)	23(1)	-1(1)	3(1)	-3(1)
C(4)	22(1)	21(1)	17(1)	1(1)	1(1)	0(1)
C(5)	16(1)	24(1)	21(1)	0(1)	-4(1)	-1(1)
C(6)	28(1)	23(1)	25(1)	0(1)	-6(1)	5(1)
N(1)	14(1)	17(1)	18(1)	-3(1)	-2(1)	-1(1)
N(2)	14(1)	17(1)	17(1)	-2(1)	-2(1)	-2(1)
Mg(1)	12(1)	15(1)	15(1)	-1(1)	-1(1)	-2(1)
Cl(1)	16(1)	21(1)	27(1)	-7(1)	-5(1)	-3(1)