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Polynuclear Aggregation of Manganese Dichloride. Syntheses, Properties, and Structures of Polymeric $[MnCl_2(THF)_{1.6}]_\infty$, Dimeric $[(THF)_4Mg(\mu\text{-}Cl)_2MnCl_2]$, and Ionic $[Mg(H_2O)_2(THF)_4][Mg(H_2O)_4(THF)_2][MnCl_4]_2\cdot 2THF$ Compounds

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Introduction

The properties and nature of anhydrous dichlorides with tetrahydrofuran (THF) which form compounds of composition $MCl_2(THF)_{1.5}$ are especially attractive for studying the factors which favor polynuclear aggregation in both the solid state and solution.[1] Moreover, interest in the chemistry of $MgCl_2(THF)_{1.5}$ has also been stimulated by the search for modern high-yield heterogeneous $TiCl_4/MgCl_2(THF)_{1.5}/ED/AlEt_3$ (ED = electron donor such as tetrahydrofuran or organic esters) olefin polymerization catalysts. Extremely active catalysts were prepared by treating $MgCl_2(THF)_{1.5}$ with $TiCl_4$ and ED.[2] Up to now, only the structures of $MCl_2(THF)_{1.5}$ for Fe and Co derivatives have been well documented.[3,4] The iron and cobalt species exist as $[M_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ (M = Fe,[3] Co[4]) centrosymmetric tetranuclear compounds with two different types of M(II) centers corresponding to six-coordinated octahedral MCl_4O_2 and five-coordinated trigonal bipyramidal MCl_4O chromophores. The structure of the $MgCl_2(THF)_{1.5}$ species is unknown, but probably it is similar to that found for $[Mg_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Et_2(THF)_6]$.[5] We are interested in determining the role of $MgCl_2$ in the supported polymerization catalyst used extensively in the polyolefin industry.[2] $MgCl_2(THF)_{1.5}$ has limited solubility and up to now was impossible to obtain in crystalline state. With this in mind, we have been studying the reactivity of manganese complexes, in particular $MnCl_2(THF)_{1.5}$.[1] It was expected that these investigations would help in understanding the behavior of metal dichlorides toward the transition metals and furnish useful relationships between structure and catalyst activity. Herein, we report the syntheses and crystal structures of polymeric $[MnCl_2(THF)_{1.6}]_\infty$ and dimeric $[(THF)_4Mg(\mu\text{-}Cl)_2MnCl_2]$ complexes and the $[Mg(H_2O)_2(THF)_4][Mg(H_2O)_4(THF)_2][MnCl_4]_2\cdot 2THF$ salt.

Experimental Section

Syntheses were carried out under dry dinitrogen by following standard Schlenk techniques. All solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds $MnCl_2$, $MgCl_2$, and $TiCl_4$ were purchased from Aldrich Chemical Co. Infrared spectra were recorded on a Perkin-Elmer 180 instrument in Nujol mulls.

Synthesis of $[MnCl_2(THF)_{1.6}]_\infty$ (1). $MnCl_2$ (0.2 g; 1.6 mmol) and $TiCl_4$ (0.05 g; 0.26 mmol) in a mixture of 120 cm^3 of THF and 20 cm^3 of toluene were refluxed for 4 h. The solution was filtered off and left to crystallize at room temperature. After 1 month, colorless crystals of **1** were collected, washed with *n*-hexane (3 × 5 cm^3), and dried in vacuo. Yield: 0.6 g (15%). Anal. Calcd for $C_{32}H_{64}Cl_{10}Mn_5O_8$: C, 31.97; H, 5.35; Cl, 29.40; Mn, 22.78. Found: C, 31.98; H, 5.19; Cl, 29.62; Mn, 22.64. IR (Nujol, cm^{-3}): 382 (m), 573 (m, br), 670 (m), 719 (s), 805 (vs, br), 865 (s, br), 914 (m), 1023 (vs, br), 1258 (m).

Synthesis of $[(THF)_4Mg(\mu\text{-}Cl)_2MnCl_2]$ (2). $MnCl_2$ (0.88 g; 7 mmol) and $[MgCl_2(THF)_2]$ (1.67 g; 7 mmol) in 80 cm^3 of THF were stirred vigorously. After 24 h, the white precipitate was filtered off, washed with *n*-hexane (3 × 5 cm^3), and dried in vacuo. Anal. Calcd for $C_{16}H_{32}Cl_4MgMnO_4$: C, 37.72; H, 6.33; Cl, 27.83; Mn, 10.78; Mg, 4.77. Found: C, 37.68; H, 6.11; Cl, 27.67; Mn, 10.71; Mg, 4.69. IR (Nujol, cm^{-3}): 308 (vs), 339 (vs), 592 (w), 691(m), 678 (w), 862 (sh), 884 (vs), 937 (s), 975 (vs), 1120 (m), 1198 (w). Crystals suitable for structure determination were obtained by heating 2 g of the white solid and 0.4 g (1.2 mmol) of $[TiCl_4(THF)_2]$ in 80 cm^3 of THF under reflux up to dissolution of the solid and then placing the solution in a Dewar vessel for slow cooling. After 24 h, colorless crystals of **2** were collected, washed with *n*-hexane (3 × 5 cm^3), and dried in vacuo.

Synthesis of $[Mg(H_2O)_2(THF)_4][Mg(H_2O)_4(THF)_2][MnCl_4]_2\cdot 2THF$ (3). To a suspension of $[MgCl_2(THF)_2]$ (0.96 g; 4 mmol) and $MnCl_2$ (0.5 g; 4 mmol) in 60 cm^3 of THF was added 0.22 cm^3 (12 mmol) of H_2O, and the mixture was stirred for 12 h at room temperature. The yellow-green powder that settled was filtered off and washed with *n*-hexane (3 × 5 cm^3). Yield: 1.65 g (84%). The filtrate was reduced in volume under vacuum to 40 cm^3 and left to crystallize at room temperature. After 2 weeks, the colorless crystals were filtered off and washed with *n*-hexane. Anal. Calcd for $C_{32}H_{76}Cl_8Mg_2Mn_2O_{14}$: C, 34.10; H, 6.80; Cl, 25.17; Mn, 9.75; Mg, 4.31. Found: C, 34.23; H, 6.72; Cl, 25.28; Mn, 9.71; Mg, 4.29. IR (Nujol, cm^{-3}): 310 (vs, br), 405 (w), 575 (m), 641 (m), 673 (m), 229 (m), 860 (vs, br), 880 (sh), 919 (s), 957 (m), 1010 (vs), 1032 (vs), 1038 (w), 1173 (m).

X-ray Data Collection and Refinement of the Structures. Data Collection Processing. The crystals were sealed in glass capillaries under a dinitrogen stream. Preliminary examination and intensity data collections were carried out on a KUMA KM-4 four-circle diffractometer[6] using graphite-monochromated Mo Kα radiation (0.710 73 Å). Cell parameters were obtained from a least-squares fit of the setting angles of 25 reflections in the ranges $16° < 2\theta < 30°$ for **1**, $16° < 2\theta < 30°$ for **2**, and $17° < 2\theta < 26°$ for **3**. Intensities were collected with the $\omega-2\theta$ scan mode up to 2θ = 30, 46, and 50° for **1**−**3**, respectively. After each group of 100 reflections, three standard intensities were monitored and no evidence of crystal decay was observed for **1**. In the cases of **2** and **3**, the intensities of the standard reflections decreased by 14 and 18%, respectively, and the recorded data for **2** and **3** were rescaled according to the intensities of the control reflections. For **1**, an absorption correction following the DIFABS[7] procedure was applied, but no changes to the geometric data resulted; because of this, for all data Lorentz and polarization corrections were applied only. The structures were solved by direct methods (SHELXS86)[8] and refined on F^2 by a full-matrix least-squares program

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Table 1. Crystal Data and Structure Refinement Details for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{16}H_{32}Cl_5Mn_{2.5}O_4$	$C_{16}H_{32}Cl_4MgMnO_4$	$C_{16}H_{38}Cl_4MgMnO_7$
fw	603.04	509.48	563.51
T, K	299(2)	299(2)	299(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	9.547(2)	15.025(3)	8.576(3)
b, Å	11.191(2)	9.715(2)	10.613(4)
c, Å	12.667(3)	16.647(3)	15.634(4)
α, deg	74.19(3)		84.84(3)
β, deg	76.16(3)	92.46(2)	74.49(3)
γ, deg	77.62(3)		81.03(3)
V, Å^3	1248.1(8)	2427.7(8)	1352.7(8)
Z	2	4	2
D_c, g/cm^3	1.605	1.394	1.388
μ, mm^{-1}	1.807	1.027	0.936
cryst size, mm	0.5 × 0.5 × 0.4	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.4
$R_1{}^a$	0.0342	0.0551	0.0411
w$R_2{}^b$	0.0953	0.1557	0.1157

^{a} $R_1 = \sum(F_o - F_c)/\sum F_o$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

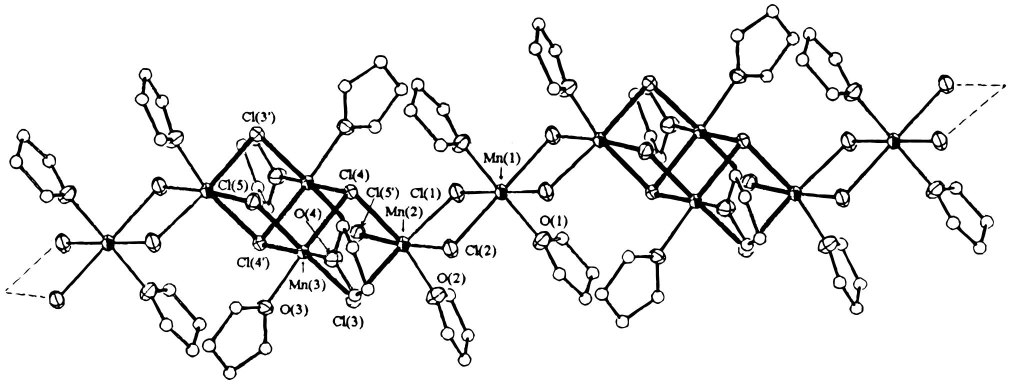

Figure 1. Molecular structure of **1** with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C-bonded H atoms are excluded for clarity. The C and H atoms are represented by circles of arbitrary radii. Primed atoms are related to unprimed by $-x + 1$, $-y$, $-z$.

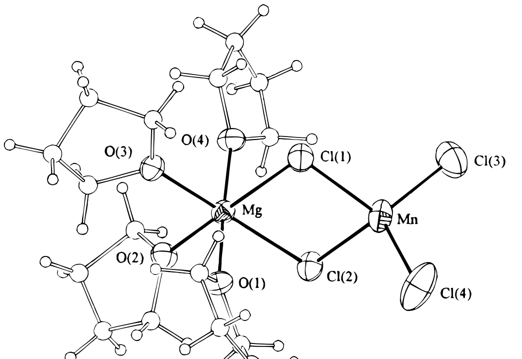

Figure 2. Molecular structure of **2** with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C and H atoms are represented by circles of arbitrary radii.

(SHELXL93).[9] The carbon-bonded H atoms were included in calculated the positions and refined using a riding model with isotropic displacement parameters equal to 1.2 × U_{eq} of the attached C atom. In structure **3**, the H atoms of water molecules were located from a difference Fourier map and refined with a restraints. Weighting schemes of the forms $w = 1/\sigma^2(F_o^2) + (0.0662P)^2 + 0.026P$, $w = 1/\sigma^2(F_o^2) + (0.101P)^2 + 5.38P$, and $w = 1/\sigma^2(F_o^2) + (0.077P)^2 + 0.95P$ (where P is defined as $(F_o^2 + 2F_c^2)/3$) were applied for **1**−**3**, respectively. The final difference maps showed generally featureless backgrounds within −0.41 and 0.32 e Å^{-3} for **1**, −0.48 and 0.28 e

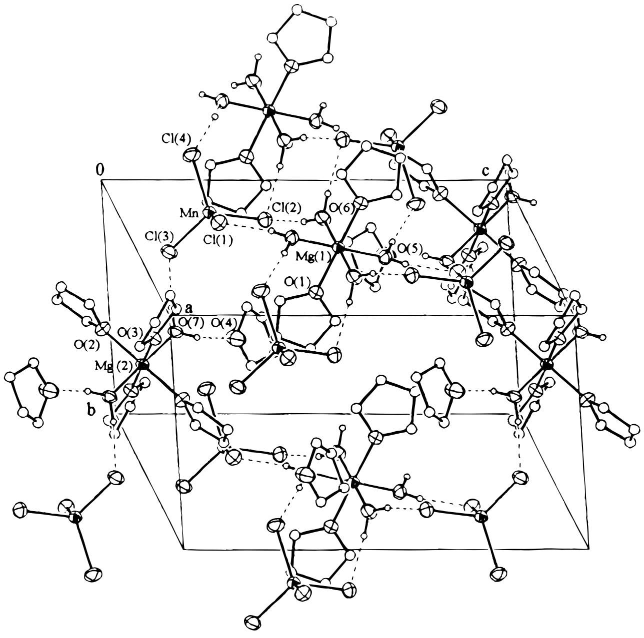

Figure 3. View of the packing in compound **3**. The displacement ellipsoids are drawn at the 30% probability level. The C-bonded H atoms are excluded for clarity. The C and H atoms are represented by circles of arbitrary radii. Hydrogen bonds are shown by dashed lines.

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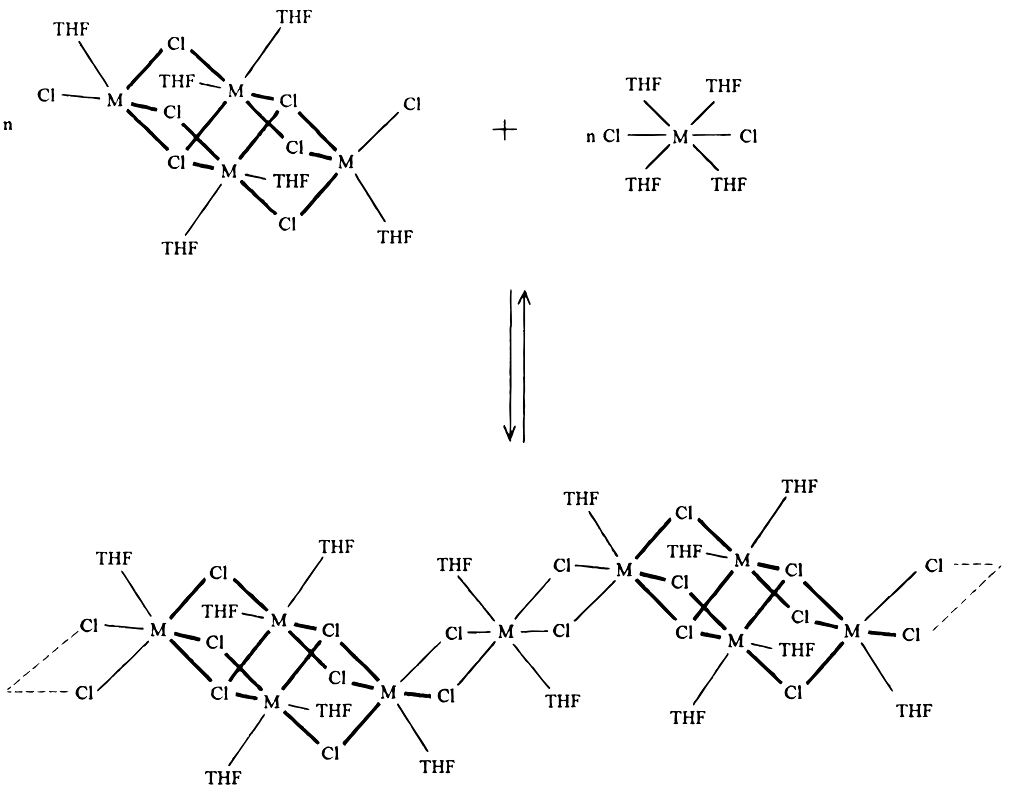
(9) Sheldrick, G. M. *SHELXL93: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

Scheme 1



$\mathrm{\AA}^{-3}$ for **2**, and −0.48 and 0.46 e $\mathrm{\AA}^{-3}$ for **3**. The crystal data and some features of the structure refinement are summarized in Table 1.

Results and Discussion

Anhydrous $MnCl_2$, when heated under reflux in tetrahydrofuran, yields a colorless compound of approximate composition $MnCl_2(THF)_{1.5}$. This compound is insoluble in halogenated solvents and hydrocarbons. Direct recrystallization of the manganese−THF species from tetrahydrofuran or by slow diffusion of *n*-hexane into its solution in THF yields an amorphous powder. To increase the solubility of $MnCl_2$, $[TiCl_4(THF)_2]$ was added in a 1:1 molar ratio to a 6:1 THF/toluene solvent mixture.[10] These efforts were successful, and colorless crystals of composition $MnCl_2(THF)_{1.6}$ precipitated from the solution. An X-ray study revealed **1** to be the polymer $[MnCl_2(THF)_{1.6}]_\infty$ formed by tetranuclear $[Mn_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ units linked by $MnCl_2(THF)_2$ moieties (Figure 1). On the basis of bond distances and analyses, the tetranuclear $[Mn_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ unit is best described as a nearly regular Mn_4 rhombus bridged by two μ_3-chlorine atoms and Cl(4) and Cl(4′), one above and one below the Mn_4 plane, in addition to μ_2-chlorine atoms bridging Mn−Mn edges. The tetranuclear units contain two types of manganese centers: the six-coordinate Mn(3) and five-coordinate Mn(2) atoms. We suppose that the $[Mn_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ unit has a structure similar to those of the iron and cobalt complexes and that the two five-coordinated Mn(2) atoms are linked by μ-chlorine atoms of Mn(1)−$Cl_2(THF)_2$ moieties to form the polymer as outlined in Scheme 1. The reaction equilibrium (1)

$$4MnCl_2 + 6THF \rightleftharpoons [M_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6] \underset{-MnCl_2(THF)_2}{\overset{+MnCl_2(THF)_2}{\rightleftharpoons}} \mathbf{1} \quad (1)$$

is relatively complex and would depend on the least soluble species formed in the tetrahydrofuran solution. The $[Mn_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ complex is probably an intermediate in the formation of **1**. From the data presented in Table 2 it follows that compound **1** gives the least soluble species which precipitates preferentially so driving the equilibrium to its final position. In the case of iron and cobalt, the least soluble compound is tetranuclear $[M_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$. The same structural M_4X_6 (X = Cl, OR) core is seen in $[Mg_4(\mu_3\text{-}\eta^2\text{-}THFFO)_2(\mu\text{-}\eta^2\text{-}THFFO)_4Cl_2]$[11] and $[V_2Mg_2(\mu_3\text{-}\eta^2\text{-}THFFO)_2(\mu\text{-}\eta^2\text{-}THFFO)_4Cl_4]$,[12] where THFFO = 2-tetrahydrofurfuroxide, but a comparison is not justified here because of the very different bridging properties of the chlorides compared to alkoxide ligands.

We expect that the $MCl_2(THF)_{1.6}$ type of heterometallic polymeric species which contain $[M_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ (M = Co, Fe, Cu, Mn, Mg) units linked by $M'Cl_n$ (e.g., M′ = Mg, Zn, Sn, Ti, Zr) could also be obtained. Our efforts to prepare the magnesium−manganese compound have been partially successful. Compound **2** was obtained from the reaction of $MgCl_2$ with $MnCl_2$ in tetrahydrofuran under reflux.

$$MnCl_2(THF)_{1.5} + MgCl_2(THF)_{1.5} \xrightarrow{THF} \underset{\mathbf{2}}{[(THF)_4Mg(\mu\text{-}Cl)_2MnCl_2]} \quad (2)$$

An X-ray study revealed **2** to be $[(THF)_4Mg(\mu\text{-}Cl)_2MnCl_2]$ (Figure 2). The magnesium atom is six-coordinate and the manganese atom four-coordinate, the octahedron and tetrahedron being linked by two chloride bridges. The bimetallic molecular species **2** has an approximate 2-fold rotational axis of symmetry

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**3**[a]

Complex **1**

Mn(1)−O(1)	2.194(3)	Mn(2)−Cl(4)	2.619(2)
Mn(1)−Cl(1)	2.522(2)	Mn(3)−O(4)	2.199(3)
Mn(1)−Cl(2)	2.551(2)	Mn(3)−O(3)	2.222(3)
Mn(2)−O(2)	2.216(3)	Mn(3)−Cl(3)	2.478(2)
Mn(2)−Cl(2)	2.520(2)	Mn(3)−Cl(5)	2.481(2)
Mn(2)−Cl(1)	2.521(2)	Mn(3)−Cl(4)	2.591(2)
Mn(2)−Cl(3)	2.548(2)	Mn(3)−Cl(4′)	2.606(2)
Mn(2)−Cl(5′)	2.550(2)		
O(1)−Mn(1)−Cl(1)	90.0(1)	O(3)−Mn(3)−Cl(3)	88.7(1)
O(1)−Mn(1)−Cl(2)	89.9(1)	O(4)−Mn(3)−Cl(5)	89.8(1)
Cl(1)−Mn(1)−Cl(2)	85.1(1)	O(3)−Mn(3)−Cl(5)	93.2(1)
O(2)−Mn(2)−Cl(2)	93.4(1)	Cl(3)−Mn(3)−Cl(5)	177.8(1)
O(2)−Mn(2)−Cl(1)	89.9(1)	O(4)−Mn(3)−Cl(4)	95.8(1)
Cl(2)−Mn(2)−Cl(1)	85.8(1)	O(3)−Mn(3)−Cl(4)	175.1(1)
O(2)−Mn(2)−Cl(3)	86.6(1)	Cl(3)−Mn(3)−Cl(4)	86.5(1)
Cl(2)−Mn(2)−Cl(3)	92.6(1)	Cl(5)−Mn(3)−Cl(4)	91.6(1)
Cl(1)−Mn(2)−Cl(3)	176.0(1)	O(4)−Mn(3)−Cl(4′)	173.8(1)
O(2)−Mn(2)−Cl(5′)	89.3(1)	O(3)−Mn(3)−Cl(4′)	91.3(1)
Cl(2)−Mn(2)−Cl(5′)	175.4(1)	Cl(3)−Mn(3)−Cl(4′)	93.7(1)
Cl(1)−Mn(2)−Cl(5′)	90.4(1)	Cl(5)−Mn(3)−Cl(4′)	85.2(1)
Cl(3)−Mn(2)−Cl(5′)	91.4(1)	Cl(4)−Mn(3)−Cl(4′)	87.9(1)
O(2)−Mn(2)−Cl(4)	168.3(1)	Mn(2)−Cl(1)−Mn(1)	94.8(1)
Cl(2)−Mn(2)−Cl(4)	94.5(1)	Mn(2)−Cl(2)−Mn(1)	94.1(1)
Cl(1)−Mn(2)−Cl(4)	99.3(1)	Mn(3)−Cl(3)−Mn(2)	96.7(1)
Cl(3)−Mn(2)−Cl(4)	84.5(1)	Mn(3)−Cl(4)−Mn(3′)	92.1(1)
Cl(5′)−Mn(2)−Cl(4)	83.5(1)	Mn(3)−Cl(4)−Mn(2)	92.3(1)
O(4)−Mn(3)−O(3)	85.4(2)	Mn(3′)−Cl(4)−Mn(2)	93.3(1)
O(4)−Mn(3)−Cl(3)	91.5(1)	Mn(3)−Cl(5)−Mn(2′)	98.1(1)

Complex **2**

Mn−Cl(1)	2.414(3)	Mg−O(2)	2.069(6)
Mn−Cl(2)	2.412(3)	Mg−O(3)	2.084(6)
Mn−Cl(3)	2.302(4)	Mg−O(4)	2.109(7)
Mn−Cl(4)	2.301(4)	Mg−Cl(1)	2.522(3)
Mg−O(1)	2.108(6)	Mg−Cl(2)	2.539(3)
Cl(4)−Mn−Cl(3)	116.9(2)	O(2)−Mg−Cl(1)	175.2(2)
Cl(4)−Mn−Cl(2)	109.7(2)	O(3)−Mg−Cl(1)	91.5(2)
Cl(3)−Mn−Cl(2)	110.0(2)	O(1)−Mg−Cl(1)	89.5(2)
Cl(4)−Mn−Cl(1)	109.2(2)	O(4)−Mg−Cl(1)	88.1(2)
Cl(3)−Mn−Cl(1)	115.3(2)	O(2)−Mg−Cl(2)	88.6(2)
Cl(2)−Mn−Cl(1)	93.2(1)	O(3)−Mg−Cl(2)	178.9(2)
O(2)−Mg−O(3)	92.2(3)	O(1)−Mg−Cl(2)	89.9(2)
O(2)−Mg−O(1)	93.7(3)	O(4)−Mg−Cl(2)	89.3(2)
O(3)−Mg−O(1)	89.3(2)	Cl(1)−Mg−Cl(2)	87.7(2)
O(2)−Mg−O(4)	88.7(3)	Mn−Cl(1)−Mg	89.6(1)
O(3)−Mg−O(4)	91.5(3)	Mn−Cl(2)−Mg	89.3(1)
O(1)−Mg−O(4)	177.5(3)		

Complex **3**

Mn−Cl(1)	2.354(2)	Mg(2)−O(2)	2.094(3)
Mn−Cl(2)	2.383(2)	Mg(2)−O(3)	2.132(3)
Mn−Cl(3)	2.363(2)	Mg(1)−O(5)	2.064(3)
Mn−Cl(4)	2.357(2)	Mg(1)−O(6)	2.045(3)
Mg(1)−O(1)	2.103(3)	Mg(2)−O(7)	2.037(3)
Cl(1)−Mn−Cl(3)	112.0(1)	O(2)−Mg(2)−O(3)	87.8(2)
Cl(1)−Mn−Cl(2)	106.6(1)	O(5)−Mg(1)−O(1)	90.5(2)
Cl(1)−Mn−Cl(4)	111.8(1)	O(6)−Mg(1)−O(5)	89.9(2)
Cl(3)−Mn−Cl(2)	109.8(1)	O(6)−Mg(1)−O(1)	91.3(2)
Cl(4)−Mn−Cl(3)	109.6(1)	O(7)−Mg(2)−O(2)	89.6(2)
Cl(4)−Mn−Cl(2)	107.0(1)	O(7)−Mg(2)−O(3)	90.0(2)

[a] Primed atoms are related to unprimed by −*x* + 1, −*y*, −*z*.

Table 3. Hydrogen-Bonding Scheme for **3** (Distances, Å; Angles, deg)[a]

O	H	A	O···A	H···A	O−H···A
O(5)	H(51)	Cl(1)^{i}	3.192(3)	2.24(2)	168(5)
O(5)	H(52)	Cl(4)^{ii}	3.149(3)	2.19(1)	170(5)
O(6)	H(61)	Cl(2)	3.169(3)	2.21(2)	168(5)
O(6)	H(62)	Cl(2)^{ii}	3.207(3)	2.26(2)	165(7)
O(7)	H(71)	O(4)	2.704(4)	1.75(1)	168(4)
O(7)	H(72)	Cl(3)	3.134(3)	2.17(1)	173(5)

[a] Symmmetry codes: (i) 1 − *x*, −*y*, 1 − *z*, (ii) −*x*, −*y*, 1 − *z*.

passing through both metals, and the $MgMnCl_4O_4$ core has approximate C_{2v} molecular symmetry. There is a remarkable similarity in the molecular structures of $[(THF)_4Mg(\mu\text{-}Cl)_2MnCl_2]$, $[(THF)_4Mg(\mu\text{-}Cl)_2FeCl_2]$,[13] and $[(THF)_4V(\mu\text{-}Cl)_2ZnCl_2]$.[14] Although the vanadium compound involves an inverted role for the transition metal and the electropositive metal, the structure similarity even extends to very similar (±0.08(1) Å) metal−ligand bond lengths.

The salt $[Mg(H_2O)_2(THF)_4][Mg(H_2O)_4(THF)_2][MnCl_4]_2\cdot 2THF$ (**3**) was obtained by two routes, the first accidental. Treatment of $MgCl_2$ with $MnCl_2$ in THF yields salt **3**. The origin of the water in **3** is probably moistness of the $MnCl_2$ used. Having established the structure of salt **3** (Figure 3), we sought a rational synthesis of it and found that it can be obtained in high yield by treatment of anhydrous $MgCl_2$ and $MnCl_2$ in THF with 3 equiv of H_2O. The crystals of **3** are composed of centrosymmetric $[Mg(H_2O)_2(THF)_4]^{2+}$ and $[Mg(H_2O)_4(THF)_2]^{2+}$ cations and $[MnCl_4]^{2-}$ anions in a 1:1:2 ratio as well as uncoordinated THF molecules. The main role in the crystal packing of **3** is played hydrogen bonds in which all hydrogen atoms of coordinated water molecules participate (see Table 3).

At present we see (1) the great tendency of manganese, iron, cobalt, magnesium, and vanadium atoms to form tetranuclear species with M_4X_6 cores, (2) that manganese tends to form polymeric species **1** (Figure 1) while cobalt, iron, and magnesium prefer the formation of tetranuclear $[M_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_4Cl_2(THF)_6]$ compounds, (3) that the magnesium atom shows a clear preference for six-coordination and manganese, iron, and zinc atoms prefer four-coordination, and (4) that the raised solubility of the Mg or Mn halogenides leads to a coordination of $MCl_2(THF)_2$ at the five-coordinate metal center in the M_4X_6 core (Scheme 1), thus blocking the reactive coordination sites needed for interaction with $TiCl_4$ and alkene polymerization. Which of these trends will emerge as the primary reason for the high activity observed with $TiCl_4/MgCl_2(THF)_{1.5}/ED/AlEt_3$ catalysts can only be determined by further studies.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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