Synthesis and crystal structures of the heptamagnesium cationic and mixed magnesium(II)/nickel(II) molecular 2-tetrahydrofurfuroxo aggregates

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Received* (*in Montpellier, France*) *5th October 1998, Accepted 23rd November 1998

Direct reaction of metallic magnesium with 2-tetrahydrofurfuryl alcohol (THFFOH) produces the alkoxo magnesium compound of composition $Mg(THFFO)_2$, **1**. Compound **1** reacts with $FeCl_2$ and $NiCl_2$ to create two different species: the ionic $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6][FeCl_4]\cdot 3CH_2Cl_2$, **2**, and the mixed $[(Mg^{II}/Ni^{II})_4(\mu_3,\eta^2\text{-THFFO})_4Cl_4(C_2H_5OH)_4]\cdot 0.5C_2H_5OH$ molecular complex **3**, respectively. Complexes **2** and **3** have been structurally characterized. The cation of compound **2** consists of a Mg_7 unit comprising a central Mg atom held within a Mg_6 puckered hexagon by six μ_3-O(alkoxo) groups from the THFFO ligands. Complex **3** consists of four crystallographically independent distorted octahedral metal sites, distributed unequally ($Mg_{0.7}$ and $Ni_{0.3}$), which together with alkoxo oxygen atoms form a cubane-like framework.

This work is a continuation of our systematic study on complexes of non- and transition metals with the *O*-donor function in the bidentate alkoxo ligand 2-tetrahydrofuryl methoxide (2-tetrahydrofurfuroxide, THFFO).[1] The use of functionalized alkoxo ligands may reduce molecularities sufficiently to allow soluble and high vapour pressure metal alkoxides to be obtained.[2] We are interested in determining the role of magnesium species in supported polymerization catalysts used extensively in the polyolefin industry.[3] It was found that catalysts containing crystalline alkoxo magnesium compounds as a component are capable of producing polymers with improved activity and morphological properties.[4] Previously we described the crystal structures of the tetranuclear compounds $[Mg_4(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_2]$[1d] and $[V_2Mg_2(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_4]$.[1e]

Here we report in detail the preparation of $[Mg(THFFO)_2]$, **1,** and the crystal structures of its derivatives $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6][FeCl_4]\cdot 3CH_2Cl_2$, **2**, and the mixed $[(Mg^{II}/Ni^{II})_4(\mu_3,\eta^2\text{-THFFO})_4Cl_4(C_2H_5OH)_4]\cdot 0.5C_2H_5OH$ complex **3**.

Results and discussion

The direct reaction of magnesium turnings with 2-tetrahydrofurfuryl alcohol under reflux in toluene yields an air-sensitive compound of composition $Mg(THFFO)_2$, **1**, which can be stored under N_2:

$$Mg + 2\ THFFOH \xrightarrow{\text{toluene}} \underset{\mathbf{1}}{[Mg(THFFO)_2]} + H_2 \quad (1)$$

The IR spectrum of compound **1** shows strong bands between 450 and 700 cm^{-1}, suggesting Mg—μ-O and Mg—μ_3-O alkoxide bridges. There are also Mg-O_{ether} modes in the range of 300 to 400 cm^{-1} due to co-ordinated THFFO ligand. These indicate a multinuclear character of **1** in the solid state. **1** is insoluble in THF and hydrocarbons and weakly soluble in ethyl acetate. Halohydrocarbons such as CH_2Cl_2 as well as $MgCl_2$ cause the chlorination of **1** and the tetranuclear $[Mg_4(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_2]$ compound was formed.[1d]

To explain the reaction of $[Mg(THFFO)_2]$ with $MgCl_2$, we extended this chemistry to transition metal dichlorides since MCl_2 (where M = Mg, Mn, Fe and Co) forms compounds of composition $[MCl_2(THF)_{1.5}]$ with tetrahydrofuran.[5] Until recently, the only well-documented structures of Fe and Co derivatives were of the remarkable $[M_4(\mu_3\text{-Cl})_2(\mu\text{-Cl})_4Cl_2(THF)_6]$.[6,7] Although the structure of $[MgCl_2(THF)_{1.5}]$ is unknown it seems most likely that its structure is similar to the Fe and Co analogues. The structure of $[Mg_4(\mu_3\text{-Cl})_2(\mu\text{-Cl})_4\ Et_2(THF)_6]$ confirms this suggestion.[8] We were interested in determining whether the $[FeCl_2(THF)_{1.5}]$ compound would react with $[Mg(THFFO)_2]$ *via* a similar pathway.

The reaction of $[FeCl_2(THF)_{1.5}]$ with 3 equiv. of $[Mg(THFFO)_2]$ in CH_2Cl_2 gave upon slow diffusion of THF into the solution colourless cubic-shaped crystals of composition $Mg_7Fe(THFFO)_{12}Cl_4\cdot 3CH_2Cl_2$. An X-ray diffraction study showed them to be the ionic compound $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6][FeCl_4]\cdot 3CH_2Cl_2$, **2**. The IR spectrum of **2** is very similar to that of **1**. The region where the Fe—Cl stretches of the $[FeCl_4]^{2-}$ anion generally appear is crowded due to absorption from the THFFO ligand, making identification of ν(Fe—Cl) impossible. The temperature independent (79–299 K) magnetic moment (μ_{eff} = 4.79 μ_B) per iron atom is consistent with high-spin d^6 Fe^{II} species.

The crystal lattice of **2** consists of centrosymmetric $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6]^{2+}$ cations (Fig. 1) as well as $[FeCl_4]^{2-}$ anions and CH_2Cl_2 molecules in a 1 : 1 : 3 molar ratio. The $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6]^{2+}$ cation is composed of seven magnesium atoms and twelve THFFO ligands. The magnesium atom Mg(1) lies on the threefold axis and is located in the centre of a flattened trigonal antiprism formed by the remaining six magnesium atoms [Mg(2)–Mg(7)]. In the the Mg_6 puckered hexagon Mg···Mg separations are very similar [average 3.159(5) Å]. Each of these six magnesium atoms is co-ordinated by four alkoxo oxygen atoms (two from Mg—μ-O and two from Mg—μ_3-O bridging THFFO ligands) and two ether oxygen atoms of the THFFO ligands. However the Mg(1) atom is surrounded by six oxygen atoms from the μ_3-O bridging THFFO ligand. The bridging Mg—μ-O and Mg—μ_3-O

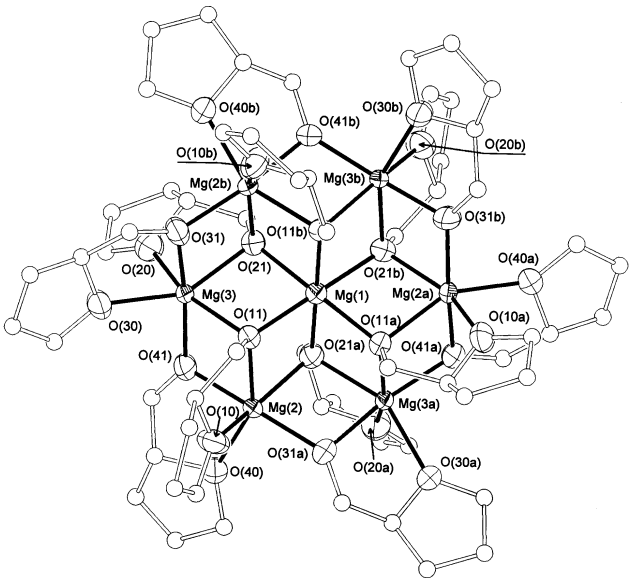

Fig. 1 The molecular structure of **2** with atom numbering scheme (*a* and *b* labels identify atoms that are related to the unlabeled atoms by symmetry: $-y, x-y, z$ and $-x+y, -x, z$, respectively). The displacement ellipsoids are drawn at the 30% probability level. For clarity, the C-bonded H atoms are not shown. The C atoms are represented by circles of arbitrary radii.

bonds range between 1.972(6)–2.029(6) Å and 2.076(6)–2.146(6) Å, respectively, and are similar to the corresponding bond lengths found in $[Mg_4(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_2]$.[1d]

The $[FeCl_4]^{2-}$ anion serves only to balance the positive charge and is not essential to the molecular structure. The bond lengths and angles for the $[FeCl_4]^{2-}$ anion are similar to those found in $[N(CH_3)_4]_2[FeCl_4]$.[9]

To examine whether the formation of the $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6]^{2+}$ cationic species is common in the presence of other $[MCl_4]^{2-}$ anions, the reaction of $NiCl_2$ with $[Mg(THFFO)_2]$ in THF–CH_2Cl_2 was carried out. Light green cubic-shaped crystals, insoluble in THF, CH_2Cl_2, CH_3CN and weakly soluble in ethanol were obtained. An X-ray structure analysis showed them to be the mixed $[(Mg^{II}/Ni^{II})_4(\mu_3,\eta^2\text{-THFFO})_4Cl_4(C_2H_5OH)_4]$ complex **3** containing an ethanol molecule of crystallization. **3** consists of four crystallographically independent distorted octahedral metal sites that, together with alkoxo oxygen atoms, form a cubane-like framework (Fig. 2, Table 1). Magnesium(II) and nickel(II) ions are distributed in unequal proportions ($Mg_{0.7}$ and $Ni_{0.3}$) in contrast to the earlier reported isostructural Mg^{II}/Mn^{II} tetranuclear complex $[(Mg_{0.5},Mn_{0.5})_4(\mu_3,\eta^2\text{-THFFO})_4Cl_4(C_2H_5OH)_4]\cdot 0.5C_2H_5OH$ in which the metal ions are equally distributed.[10]

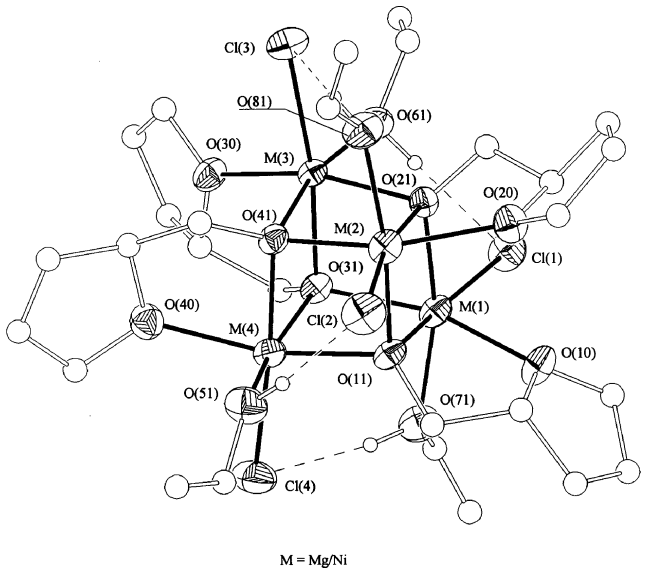

Fig. 2 The molecular structure of **3** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. For clarity the C-bonded H atoms are not shown. The C and H atoms are represented by circles of arbitrary radii. Intramolecular hydrogen bonds are shown by dashed lines.

Table 1 Selected bond lengths [Å] for **2** and **3**

Complex **2**			
Mg(1)—O(11)	2.076(6)	Mg(3)—O(21)	2.102(6)
Mg(1)—O(21)	2.078(6)	Mg(3)—O(20)	2.179(7)
Mg(2)—O(31a)	1.998(6)	Mg(3)—O(31)	2.027(7)
Mg(2)—O(11)	2.096(6)	Mg(3)—O(30)	2.182(7)
Mg(2)—O(10)	2.146(7)	Mg(3)—O(41)	1.972(6)
Mg(2)—O(21a)	2.146(6)	Mg(1)—Mg(2)	3.140(2)
Mg(2)—O(41)	2.029(6)	Mg(1)—Mg(3)	3.123(2)
Mg(2)—O(40)	2.117(7)	Mg(2)—Mg(3)	3.159(4)
Mg(3)—O(11)	2.134(6)	Mg(3)—Mg(2b)	3.158(4)
Complex **3**			
M(1)—Cl(1)	2.398(2)	M(3)—O(31)	2.062(3)
M(1)—O(10)	2.133(4)	M(3)—O(41)	2.142(3)
M(1)—O(11)	2.069(3)	M(3)—O(61)	2.184(4)
M(1)—O(21)	2.147(3)	M(4)—Cl(4)	2.409(2)
M(1)—O(31)	2.067(3)	M(4)—O(11)	2.071(3)
M(1)—O(71)	2.163(4)	M(4)—O(31)	2.143(3)
M(2)—Cl(2)	2.408(2)	M(4)—O(40)	2.107(4)
M(2)—O(20)	2.145(4)	M(4)—O(41)	2.066(3)
M(2)—O(21)	2.079(3)	M(4)—O(51)	2.162(4)
M(2)—O(41)	2.067(3)	M(1)—M(2)	3.242(2)
M(2)—O(81)	2.144(4)	M(1)—M(3)	3.104(2)
M(2)—O(11)	2.145(3)	M(1)—M(4)	3.119(2)
M(3)—Cl(3)	2.411(2)	M(2)—M(3)	3.113(2)
M(3)—O(21)	2.059(3)	M(2)—M(4)	3.119(2)
M(3)—O(30)	2.096(3)	M(3)—M(4)	3.224(2)

Symmetry transformations used to generate equivalent atoms in **2**: (a) $-y, x-y, z$; (b) $-x+y, -x, z$. In **3** M = Mg, Ni.

Preliminary results of an ethylene polymerization test on **1**/$TiCl_4$/$AlEt_3$ catalyst gives 13 kg polyethylene per g Ti h^{-1} (Mg : Ti = 10, $[Ti]_o = 0.01$ mmol dm^{-3} and [Al] = 5 mmol dm^{-3}); that is, ten-fold less when compared to a catalyst based on the chlorinated derivative $[Mg_4(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_2]$ (170 kg PE per g Ti h^{-1} under the same conditions).[1d] We suggest that the reason for the low catalytic activity of the catalyst supported on **1** is the lower incorporation of $AlEt_3$ with $TiCl_4$ and **1** when compared to $[Mg_4(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_2]$.[1d]

Conclusions

To our knowledge until recently there was only one structural report for magnesium alkoxides of the general formula $Mg(OR)_2$, where R = alkyl, that is $[Mg_4(\mu\text{-}OCH_3)_4(OCH_3)_4(CH_3OH)_8]$.[11] The reason is that Group 2 alkoxides with conventional, monodentate alkoxo ligands are generally poorly soluble in nondonor solvents,[2] probably as a result of nonmolecular, CdI_2-like structures.[12] The use of the bidentate THFFO ligand seems to allow soluble derivatives to be obtained; for example, interaction of calcium and 2-methoxyethanol gave $[Ca_9(OCH_2CH_2OCH_3)_{18}(HOCH_2CH_2OCH_3)_2]$, which is among the largest aggregates known for alkoxide complexes.[13] Direct reaction of metallic magnesium with tetrahydrofurfuryl alcohol produces $[Mg(THFFO)_2]$, **1**, which can be crystallized from CH_2Cl_2 to give the tetranuclear magnesium aggregate $[Mg_4(\mu_3,\eta^2\text{-THFFO})_2(\mu,\eta^2\text{-THFFO})_4Cl_2]$.[1d] Addition of $[FeCl_2(THF)_{1.5}]$ to a solution of **1** in CH_2Cl_2 results in the isolation of another magnesium salt, $[Mg_7(\mu_3,\eta^2\text{-THFFO})_6(\mu,\eta^2\text{-THFFO})_6][FeCl_4]\cdot 3CH_2Cl_2$, **2**. The aggregate size exhibited by the $[Mg_7(\mu_3,\eta^2\text{-}$

THFFO)$_6$(μ,η^2-THFFO)$_6$]$^{2+}$ cationic species is the largest structurally characterized for magnesium alkoxides and the first M_7O_{24} core reported in the literature. Similar $[M_7X_{24}]^{2-}$ cationic species where X = O and N were found for $[Zn_7(L)_{12}][Cl]_2$ (L = pyridylmethanolate) by crystallization of ZnL_2 from CH_2Cl_2.[14] We postulate that in our case also, compound **1** reacts with CH_2Cl_2, incorporating chlorine with formation of at least two different alkoxo magnesium species: molecular [Mg$_4$(μ$_3$,η^2-THFFO)$_2$(μ,η^2-THFFO)$_4$Cl$_2$] and most likely ionic species such as [Mg$_7$(μ$_3$,η^2-THFFO)$_6$(μ,η^2-THFFO)$_6$][Cl]$_2$. The former, as the least soluble species, can be isolated directly from the mother solution. However, the latter species, which remains in solution, needs a suitable anion to be isolated as a solid. We have found $FeCl_2$ to be a good agent for crystallizing this ionic compound as the salt [Mg$_7$(μ$_3$,η^2-THFFO)$_6$(μ,η^2-THFFO)$_6$][FeCl$_4$]·3CH$_2$Cl$_2$, **2**. The use of $NiCl_2$ gave surprisingly the mixed Mg^{II}/Ni^{II} complex **3**. This suggests that alkoxo magnesium aggregates are formed by chance rather than by design. It is noteworthy that in the case of monodentate *O*-donor ligands such as tetrahydrofuran the following magnesium ionic species: $[MgCl(THF)_5]^+$, $[Mg(THF)_6]^{2+}$, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ and $[MgCl_4]^{2-}$ were isolated and well-documented.[15] The salt of the dinuclear cationic species, $[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_5(THF)]$, is used as a procatalyst in the industrial ethylene polymerization process.[16]

Experimental

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compound $[MgCl_2(THF)_2]$ was prepared by a published procedure.[17] $[FeCl_2(THF)_{1.5}]$ was prepared by heating under reflux $FeCl_3$ with $TiCl_3$ in THF.[18] The 2-tetrahydrofurfuryl alcohol, $FeCl_3$, $NiCl_2$ and metallic magnesium were obtained from Aldrich Chemical Co. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer in Nujol mulls. Magnetic moment determinations in the solid state used a Faraday balance.

Syntheses

Synthesis of [Mg(THFFO)$_2$], 1. To stirred magnesium turnings (2 g, 82.3 mmol) in toluene (200 cm^3), tetrahydrofurfuryl alcohol (16.8 g, 164.6 mmol) was added dropwise. Stirring was continued at room temperature to initiate exothermic reaction. Then the mixture was refluxed until all the magnesium had reacted. The solvent was evaporated *in vacuo* and the white residue was extracted with ethyl acetate (3 × 50 cm^3). The filtrate was concentrated (1/5 volume) and the white solid was filtered off, washed with hexane and dried *in vacuo*. Yield: 17.7 g (95% based on Mg). Anal. calcd for $C_{10}H_{18}MgO_4$: C, 53.0; H, 8.0; Mg, 10.7; found: C, 52.9; H, 8.1; Mg, 10.5. IR (Nujol mull) ν/cm^{-1}: 1325 (m), 1255 (m), 1180 (m), 1130 (s), 1070 (s), 1015 (s), 995 (m), 955 (w), 935 (w), 915 (m), 877 (w), 845 (w), 804 (m), 723 (w), 600 (w), 549 (m, br), 470 (s, sh), 390 (w), 354 (m), 336 (m).

Synthesis of [Mg$_7$(μ$_3$,η^2-THFFO)$_6$(μ,η^2-THFFO)$_6$][FeCl$_4$]·3CH$_2$Cl$_2$, 2. A suspension of $[FeCl_2(THF)_{1.5}]$ (0.42 g, 1.8 mmol) and $[Mg(THFFO)_2]$ (1.29 g, 5.4 mmol) in CH_2Cl_2 (50 cm^3) was stirred overnight. A white solid of unreacted $[FeCl_2(THF)_{1.5}]$ was filtered off and hexane (10 cm^3) was added. After standing overnight at 269 K a white solid of **2** had precipitated. Colourless cubic-shaped crystals suitable for X-ray study were obtained by slow diffusion of THF into a solution of the crude product in CH_2Cl_2. Yield 2.63 g (46% based on $[Mg(THFFO)_2]$). Anal. calcd for $C_{63}H_{114}Cl_{10}FeMg_7O_{24}$: Cl, 12.8; Fe, 3.4; Mg, 10.2; found: Cl, 12.8; Fe, 3.5; Mg 9.9. IR (Nujol mull) ν/cm^{-1}: 1325 (m), 1290 (w), 1255 (m), 1180 (m), 1057 (s, br), 956 (m), 940 (m), 915 (m), 875 (m), 820 (s, sh), 665 (m), 595 (m), 540 (s), 460 (s), 410 (s), 387 (s), 360 (s), 336 (s). μ_{eff} = 4.79 μ_B (79–299 K).

Synthesis of [(Mg^{II}/Ni^{II})$_4$(μ$_3$,η^2-THFFO)$_4$Cl$_4$(C$_2$H$_5$OH)$_4$]·0.5C$_2$H$_5$OH, 3. A suspension of $NiCl_2$ (1.13 g, 8.7 mmol) and $[Mg(THFFO)_2]$ (6.59 g, 29.1 mmol) in a mixture of CH_2Cl_2–THF (1 : 1, 100 cm^3) was refluxed until the colour changed from pink-orange to light green. The solid was filtered off, washed with THF and dried *in vacuo*. Then, the crude product was extracted with C_2H_5OH in a Soxhlet apparatus to give a light green solution from which, after cooling and standing overnight at room temperature, the light green cubic-shaped crystals of compound **3** precipitated. Yield: 3.3 g (51% based on $NiCl_2$). Anal. calcd for $C_{29}H_{63}Cl_4Mg_{2.8}Ni_{1.2}O_{12.5}$: C, 39.0; H, 7.1; Cl, 15.9; Mg, 7.6; Ni, 7.9; found: C, 39.1; H, 6.9; C, 15.5; Mg, 7.3; Ni, 8.0. IR (Nujol mull) ν/cm^{-1}: 3248 (s), 1304 (w), 1273 (w), 1052 (s, br), 1016 (s), 990 (m), 962 (m), 994 (m), 924 (w), 882 (m), 824 (m), 662 (m, br), 596 (m), 560 (m), 534 (m), 424 (s, sh), 380 (w), 358 (w), 272 (w), 212 (w). μ_{eff} = 2.81 μ_B (79–299 K).

Polymerization test

A slurry of $[Mg(THFFO)_2]$ (6.77 g, 30 mmol) in *n*-hexane was milled under argon in a glass mill (capacity 250 cm^3, with 20 balls of 5–15 mm diameter) at room temperature for 6 h. Then $TiCl_4$ (0.57 g, 3 mmol) and *n*-hexane (50 cm^3) were added and the mixture was milled for 24 h. The sample of precatalyst suspension (containing 0.01% titanium) was activated with $AlEt_3$ (2.28 g, 20 mmol) for 15 min at 323 K under argon to form the active catalyst. The polymerization of ethylene was carried out at 303–343 K in a stainless-steel reactor (1 dm^3) equipped with a stirrer, in *n*-hexane at an ethylene pressure 0.6 MPa. The polymerization was quenched with a 5% solution of HCl in methanol (150 cm^3) and the polymer was filtered off, washed with methanol and dried under vacuum.

X-Ray crystallography

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[19] using graphite-monochromated Mo-Kα radiation. Cell parameters were obtained from a least-squares fit of the setting angles of 35 reflections in the ranges: 7.8 < θ < 13.4 for **2** and 8.5 < θ < 13.0 for **3**. Intensities were collected in the ω–2θ scan mode up to 2θ = 60° and 46° for **2** and **3**, respectively. For **2** the data indicated a primitive trigonal cell. Lack of systematic absences and intensity statistics indicated that the space group was the noncentrosymmetric *P*3, which was subsequently shown to be correct from the successful refinement of the structure. The alternative space group $P\bar{3}$ was also checked and found to give significantly worse results than *P*3. After each group of 100 reflections three standard intensities were monitored and no evidence of crystal decay was observed for **3**. In the case of **2** the intensities of the standard reflections decreased by 48.6% and the recorded data for this crystal were rescaled according to the intensities of the control reflections. For all data Lorentz and polarization corrections were applied. For **3** the absorption corrections following the ABSORB[20] procedure were also used: minimum and maximum absorption corrections were 0.89–1.08. The structures were solved by direct methods (SHELXS 86)[21] and refined on F^2 with a full-matrix least-squares program (SHELXL 93).[22] For both compounds the carbon-bonded hydrogen atoms were included in calculated positions and refined using a riding model. It was found that in the structure of **2** one magnesium atom [Mg(1)], the iron atom

Table 2 Crystal data for complexes **2** and **3**.

	2	**3**
Formula	$C_{21}H_{38}Cl_{3.33}Fe_{0.33}Mg_{2.33}O_8$	$C_{29}H_{62.50}Cl_4Mg_{2.80}Ni_{1.20}O_{12.50}$
FW	612.02	891.61
T/K	298(2)	298(2)
Crystal system	Trigonal	Triclinic
Space group	$P3$	$P\bar{1}$
a/Å	16.058(2)	12.079(3)
b/Å	16.058(2)	12.150(3)
c/Å	10.286(2)	17.641(4)
α/deg	90	87.02(3)
β/deg	90	78.00(3)
γ/deg	120	60.87(3)
U/Å^3	2297.0(6)	2208.4(9)
Z	3	2
D_c/g cm^{-3}	1.327	1.341
μ/mm^{-1}	0.566	0.855
F(000)	964	943
Theta range for data collection	2–30	2–23
Reflections collected	4420	3986
Independent reflections	2912 [R(int) = 0.0369]	3847 [R(int) = 0.0376]
Parameters/data	317/2912	476/3847
R_1[a]	0.0666	0.0416
wR_2[b]	0.1726	0.1129

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

(Fe) and one chlorine atom of the $FeCl_4^{2-}$ anion [Cl(3)] lie on the threefold axis. The high degree of anisotropy observed for the CH_2Cl_2 atoms in **2** indicate possible disorder, but this could not be resolved. Crystals of **3** are isomorphous with those of $[(Mg_{0.5},Mn_{0.5})_4(\mu_3,\eta^2\text{-THFFO})_4Cl_4(C_2H_5OH)_4]\cdot 0.5C_2H_5OH$.[10] The refined occupancy of the metal sites suggests mixed cation occupancy; the final structure model was then refined on the basis of Mg (0.7) and Ni (0.3) populations. Moreover, during refinement of **3** it was found that this structure is isostructural with the Mg,Mn analogue and because of this the same treatment of disordered atoms was applied.[10] The crystal data and some features of the structure refinement for both compounds **2** and **3** are summarized in Table 2.

CCDC reference number 440/084. See http://www.rsc.org/suppdata/nj/1999/185/ for crystallographic files in .cif format.

Acknowledgements

The authors thank the State Committee for Scientific Research for financial support of this work (Grant No. 3 T09A 13115).

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Paper 8/07745B