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Reaction of $MgCl_2$ with $AlCl_3$ in ethyl acetate. The crystal structure of $[Mg(CH_3OCOC_2H_5)_6][AlCl_4]_2$

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Abstract

The direct reaction of $[MgCl_2(CH_3OCOC_2H_5)_2]$ with $AlCl_3(CH_3OCOC_2H_5)_2$ in ethyl acetate yields the colourless crystalline salt formulated as $[Mg(CH_3OCOC_2H_5)_6][AlCl_4]_2$. The crystal structure of this compound has been determined by an X-ray diffraction study. Crystals are cubic, space group $Pa\bar{3}$ with a 16.61(1) Å and $Z = 4$. The structure was refined by full-matrix least squares to $R = 0.061$ for 806 independent non-zero reflections. The crystal contains $[Mg(CH_3OCOC_2H_5)_6]^{2+}$ cations, which show $\bar{3}$ (C_{3i}) symmetry, and $[AlCl_4]^-$ anions, which are in a three-fold axis.

Introduction

The Ziegler–Natta catalyst supported on $MgCl_2$ exhibits extremely high activity in α-olefin polymerizations [1]. In such systems the organometallic compounds $AlEt_2Cl$ or $AlEt_3$ are used as co-catalysts. By contrast, $AlEtCl_2$ is inert as an activator and probably poisons the titanium catalyst. It is formed during the synthesis of the catalyst in the reaction (eq. 1) [2].

$$AlEt_2Cl + AlCl_3 \rightarrow 2AlEtCl_2 \qquad (1)$$

$AlCl_3$ was found to react readily with $MgCl_2$ in polar solvents such as tetrahydrofuran (THF) [3] (eq. 2):

$$AlCl_3 + MgCl_2 \xrightarrow{THF} AlMgCl_5(THF)_6 \qquad (2)$$

Thus the aluminium trichloride could be effectively removed by magnesium dichloride [3] from the catalyst system which, in our opinion, prevents the formation of $AlEtCl_2$. The addition of Lewis bases such as esters is also important in preparation of the catalyst. For this reason it was interesting to see whether the reaction course

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between $MgCl_2$ and $AlCl_3$ in esters was similar to that of eq. 2 and whether the studies in THF would be relevant to esters.

Here we describe the results of a study of the reaction of $MgCl_2$ with $AlCl_3$ in ethyl acetate. The X-ray crystal structure of the $[Mg(CH_3OCOC_2H_5)_6]^{2+}[AlCl_4]^-{}_2$ compound is also described.

Experimental

All reactions were carried out under N_2 using dried solvents and Schlenk-tube techniques. $[MgCl_2(CH_3OCOC_2H_5)_2]$ was obtained by dissolving dry $MgCl_2$ in ethyl acetate [4]. Commercial $AlCl_3$ was sublimed before use. Microanalyses were performed at the University of Wrocław.

Hexa(ethyl acetate)magnesium(II) bis-tetrachloroaluminate(III)

$[MgCl_2(CH_3OCOC_2H_5)_2]$ (1.1 g; 4 mmol) and $AlCl_3$ (1.04 g; 8 mmol) were dissolved separately in 60 and 40 cm^3 ethyl acetate. The solutions were filtered, mixed and left for crystallization. After 12 h the colourless crystals were filtered off and washed with n-hexane (3×10 cm^3), and dried in vacuo. Yield 67%. The good quality, many-facetted crystals suitable for X-ray examination were taken from the post-reaction mixture.

X-Ray crystal structure determination

Crystal data. $[C_{24}H_{48}O_{12}Mg]^{2+} \cdot [AlCl_4]^-{}_2$, $M = 890.5$, a 16.61(1) Å, V 4583(5) Å^3, D_m (by flotation) 1.28 g cm^{-3}, $Z = 4$, D_c 1.29(1) g cm^{-3}, $F(000) = 1848$, space group $Pa\bar{3}$, Mo-K_α radiation, λ 0.71069 Å, μ 5.89 cm^{-1}, T 296(2) K.

A sample of dimensions from 0.9 to 1.1 mm was cut from a large crystal and sealed in a capillary. The Weissenberg photographs revealed the space group $Pa\bar{3}$. The intensity data were measured on a Syntex P2$_1$ automated diffractometer with graphite-monochromatized Mo-K_α radiation. Intensities were collected by the 2θ–ω scan technique up to 2θ 60°. The intensities of two standard reflections, measured after every 50 scan intensities showed no evidence of crystal decay. 3339 reflections were collected of which 1809 with $I > 3\sigma(I)$ were used for the structure analysis. The structure was solved by use of random-start multisolution direct methods [5]. The H atoms were located from a difference-Fourier synthesis. An absorption correction carried out by use of the DIFABS procedure [6] was applied to isotropically refined data; minimum and maximum absorption corrections were 0.265 and 1.409, respectively. The symmetry related reflections were averaged after DIFABS to give 806 observations with $R_{int} = 0.034$. Full-matrix least-squares refinement, based on F values, was performed with SHELX76 on the positional and anisotropic (isotropic for H) thermal parameters. The H atoms were refined with the constraint that d(C–H) 1.08 Å. The isotropic extinction correction of the form $1 - xF_c^2/\sin\theta$ was applied and the final x parameter was $8.4(4) \times 10^{-8}$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 2.8617/\sigma^2(F_o)$. Final R and R_w were 0.061 and 0.054 respectively. The maximal value of Δ/σ in the final cycle of refinement was 0.01. The maximal and minimal residual electron densities in the difference Fourier map were to be found within -0.42 and 0.39 eÅ^{-3}. Neutral atom scattering factors were taken from ref. 7. Real and imaginary components of anomalous dispersion were included for all the non-H atoms. Final atom parameters are given in Table 1.

Table 1

Final positional and thermal parameters with e.s.d.s in parentheses for $[Mg(CH_3OCOC_2H_5)_6][AlCl_4]_2$

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg	4 b	0.5	0.5	0.5	0.039(2)	0.039(2)	0.039(2)	−0.004(2)	−0.004(2)	−0.004(2)
Al	8 c	0.2120(2)	0.2120(2)	0.2120(2)	0.052(1)	0.052(1)	0.052(1)	0.003(1)	0.003(1)	0.003(1)
Cl(1)	8 c	0.2848(2)	0.2848(2)	0.2848(2)	0.119(2)	0.119(2)	0.119(2)	−0.027(2)	−0.027(2)	−0.027(2)
Cl(2)	24 d	0.2108(2)	0.0951(2)	0.2608(2)	0.127(2)	0.060(2)	0.128(2)	0.024(2)	0.032(2)	0.007(2)
C(1)	24 d	0.5573(6)	0.6122(5)	0.3059(6)	0.089(7)	0.080(6)	0.077(6)	0.013(5)	0.004(6)	−0.041(5)
C(2)	24 d	0.5113(4)	0.5357(4)	0.3138(4)	0.039(4)	0.070(5)	0.054(5)	−0.003(4)	−0.003(4)	0.011(4)
C(3)	24 d	0.4437(5)	0.4299(5)	0.2441(5)	0.074(6)	0.081(6)	0.071(6)	−0.018(5)	−0.004(5)	−0.016(5)
C(4)	24 d	0.4337(7)	0.4060(9)	0.1580(7)	0.104(9)	0.18(2)	0.093(8)	−0.072(8)	0.008(6)	−0.046(9)
O(1)	24 d	0.4880(3)	0.5062(3)	0.3771(3)	0.060(3)	0.055(3)	0.043(3)	−0.001(3)	0.000(3)	−0.003(3)
O(2)	24 d	0.4932(3)	0.5031(3)	0.2444(3)	0.064(4)	0.088(4)	0.043(3)	−0.004(3)	−0.002(3)	−0.002(3)

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(11)	0.532(5)	0.660(4)	0.270(5)	0.19(5)	H(31)	0.476(3)	0.382(3)	0.275(4)	0.09(3)
H(12)	0.605(4)	0.609(5)	0.262(4)	0.15(4)	H(41)	0.401(5)	0.352(3)	0.143(5)	0.16(4)
H(13)	0.586(4)	0.631(4)	0.361(3)	0.13(3)	H(42)	0.489(4)	0.375(5)	0.142(6)	0.19(5)
H(3)	0.387(2)	0.436(4)	0.275(4)	0.12(3)	H(43)	0.417(7)	0.464(4)	0.134(6)	0.22(7)

Results and discussion

Solid $MgCl_2$ has a layer structure [8]. During the dissolution of $MgCl_2$, polar solvents are strong enough to break the chloride bridges between magnesium atoms. For this reason $MgCl_2$ forms molecular compounds with THF [9] and ethyl acetate [4]. Reaction of $MgCl_2$ with ethyl acetate directly gives the compound, $[MgCl_2(CH_3OCOC_2H_5)_2]$, which is in contrast to that $AlCl_3$ with THF (eq. 3).

$$Al_2Cl_6 + 4THF \rightarrow [AlCl_2(THF)_4][AlCl_4] \qquad (3)$$

The ionic compound $[AlCl_2(THF)_4]^+[AlCl_4]^-$ [10] was found to crystallize from a solution of $AlCl_3$ in tetrahydrofuran [10]. We found [4] that a similar reaction between $AlCl_3$ and ethyl acetate is strongly exothermic and yields the $AlCl_3(CH_3OCOC_2H_5)$ (eq. 4).

$$AlCl_3 + 2CH_3OCOC_2H_5 \xrightarrow[223\ K]{} AlCl_3(CH_3OCOC_2H_5)_2 \qquad (4)$$

The IR spectrum of this compound shows the characteristic $AlCl_4^-$ band at 490 cm^{-1} (vs). This suggests that it has the ionic structure $[AlCl_2(CH_3OCOC_2H_5)_4]^+$ $[AlCl_4]^-$.

It was expected that $MgCl_2$ and $AlCl_3$ would react mutually in esters to produce compounds which could be separated and characterized, and that the product obtained from this reaction could provide useful in information on the structure and mechanism involved in the super high activity catalyst polymerization systems.

Reactions of $MgCl_2(CH_3OCOC_2H_5)_2$ with $AlCl_3(CH_3OCOC_2H_5)_2$ were carried out in ethyl acetate. Irrespective of the molar ratio of reactants, the compound formulated as $MgCl_2 \cdot 2AlCl_3 \cdot 6CH_3OCOC_2H_5$ was always obtained (eq. 5):

$$[MgCl_2(CH_3OCOC_2H_5)_2] + 2AlCl_3(CH_3OCOC_2H_5)_2 \rightarrow [Mg(CH_3OCOC_2H_5)_6][AlCl_4]_2 \qquad (5)$$

This was found by X-ray diffraction study, to have the $[Mg(CH_3OCOC_2H_5)_6]^{2+}$ cations and $[AlCl_4]^-$ anions present in the ratio of 1/2. The structure of the hexa(ethyl acetate)magnesium(II) cation is depicted in Fig. 1. Selected bond lengths and angles are listed in Table 2

The cation $[Mg(CH_3OCOC_2H_5)_6]^{2+}$ has $\bar{3}$ symmetry. The magnesium atoms are octahedrally coordinated by the carbonyl oxygen atom of each of the six ethyl acetate molecules. The Mg–O bond lengths were found to be 2.053(4) Å and are similar to the average magnesium–carbonyl-oxygen distance of 2.038(5) Å of the coordinated ethyl acetate molecules in $[(CH_3OCOC_2H_5)_4Mg(\mu\text{-}Cl)_2TiCl_4]$ [11]. The other bond lengths and angles of the ethyl acetate molecules (see Table 2) are similar to those found in $[(CH_3OCOC_2H_5)_4Mg(\mu\text{-}Cl)_2TiCl_4]$. The C and O atoms of each ethyl acetate are almost coplanar with the Mg atom situated at 0.31(1) Å above this plane. The torsion angles of Mg–O(1)–C(2)–O(2) and Mg–O(1)–C(2)–C(1) are 163.4(9) and $-20.3(14)°$, respectively.

The $[AlCl_4]^-$ anion lies on the three-fold axis. A number of structures containing $[AlCl_4]^-$ anions have been described previously. In all cases the $[AlCl_4]^-$ units have the same dimensions.

In all the reactions carried out in THF and in ethyl acetate solvent, $MgCl_2$ was found to act as a Cl^- donor. During the reaction (eq. 5) of $MgCl_2$ with $AlCl_3$ in

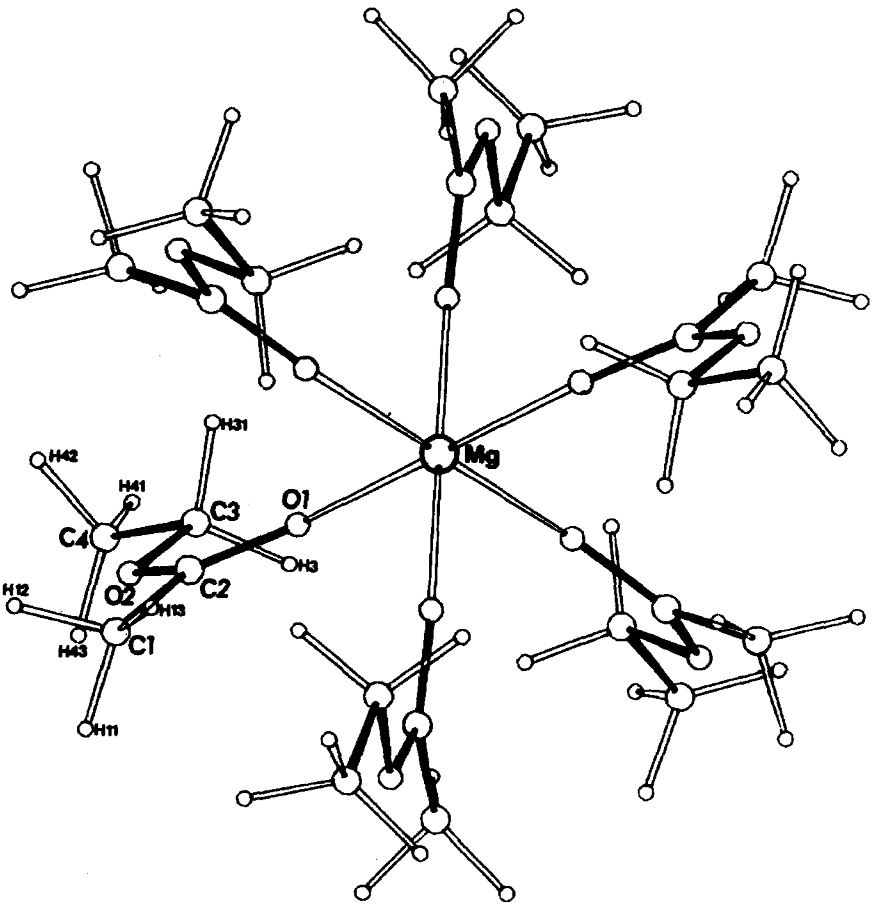

Fig. 1. The structure of the $[Mg(CH_3OCOC_2H_5)_6]^{2+}$ cation viewed along the $\bar{3}$ axis.

ethyl acetate, magnesium dichloride donates Cl^- to $AlCl_3$, and so the cations $[Mg(CH_3OCOC_2H_5)_6]^{2+}$, and the anions $[AlCl_4]^-$ result. Similarly reaction of $TiCl_4$ with $MgCl_2$ in ethyl acetate [11] is as shown in eq. 7.

$$TiCl_4 + MgCl_2 + 4CH_3OCOC_2H_5 \rightarrow [(CH_3OCOC_2H_5)_4Mg(\mu\text{-}Cl)_2TiCl_4] \qquad (7)$$

In $[(CH_3OCOC_2H_5)_4Mg(\mu\text{-}Cl)_2TiCl_4]$ the titanium atom is surrounded by six

Table 2

Selected bond lengths (Å) and angles (°) for $[Mg(CH_3OCOC_2H_5)_6][AlCl_4]_2$ [a]

Al–Cl(1)	2.095(2)	Al–Cl(2)	2.104(2)
Mg–O(1)	2.053(4)	O(1)–C(2)	1.224(7)
C(1)–C(2)	1.489(10)	C(2)–O(2)	1.308(7)
C(3)–O(2)	1.468(9)	C(3)–C(4)	1.495(13)
Cl(1)–Al–Cl(2)	108.4(2)	Cl(2)–Al–Cl(2^i)	110.5(2)
O(1)–Mg–O(1^i)	87.6(2)	Mg–O(1)–C(2)	147.6(4)
C(1)–C(2)–O(1)	125.4(6)	C(1)–C(2)–O(2)	113.2(6)
O(1)–C(2)–O(2)	121.3(6)	C(4)–C(3)–O(2)	106.6(7)
C(2)–O(2)–C(3)	118.3(5)		

[a] Symmetry code: (i) *z*, *x*, *y*.

chlorines [11]. It is evident that the Ti^{4+} and Al^{3+} anions, being more powerful Lewis acids, prefer the Cl^- anion, and because of this, the $CH_3OCOC_2H_5$ and THF molecules are dislodged from the coordination sphere of the titanium and aluminium atoms.

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