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Synthesis and crystal structure of the $MgCl_2(CH_3COOC_2H_5)_2 \cdot \frac{1}{2}(CH_3COOC_2H_5)$ adduct

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Abstract

The reaction of α-$MgCl_2$ with boiling ethyl acetate affords $MgCl_2(CH_3COOC_2H_5)_2 \cdot \frac{1}{2}(CH_3COOC_2H_5)$, which is obtained as crystals suitable for X-ray analysis only from the mother liquor. $M = 315.5$, orthorhombic, space group $P2_12_12_1$ (No. 18), $a = 25.077(3)$, $b = 8.616(1)$, $c = 7.345(1)$ Å, $V = 1587.0(3)$ Å^3, $Z = 4$, $D_x = 1.32$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 4.17$ cm^{-1}, $F(000) = 664$, $T = 298$ K, observed reflections: 1667, $R = 0.059$ and $R_w = 0.069$. The structure is composed of polymeric chains of $MgCl_2(CH_3COOC_2H_5)_2$ and the ethyl acetate molecules occupy a mutually *trans* position.

Introduction

Heterogeneous Ziegler–Natta catalysts for α-olefin polymerization, particularly when they are used for stereospecific polymerization of propylene, are based on activated $MgCl_2$ supports [1]. In view of the industrial interest of these catalysts, the crystallographic aspects of systems supported on $MgCl_2$ are a matter of intense investigation. After an initial period when the activation of $MgCl_2$ was carried out by mechanical methods (ball-milling) [2], new preparation routes of very active $MgCl_2$-based supports became more and more evident in the literature. Thus, 'chemical' methods began to develop and, in particular, the carefully controlled decomposition of compounds such as $MgCl_2 \cdot nB$, where B represents alcohols, esters or ethers. The structural investigations of these supports revealed, so far, that they are characterized by a particularly disordered structure [1].

The investigation of adducts formed among $MgCl_2$ and Lewis bases (also called 'donors') is interesting at least for two reasons: (i) for obtaining particularly active supports; (ii) for developing supported catalysts possessing activating and stereoregulating abilities, which can be 'tuned' on the basis of the particular choice of the donor molecules. Complete X-ray single crystal analyses have been reported for $[Mg(C_2H_5OH)_6]Cl_2$ (I) [3], $[Mg(THF)_6][MoOCl_4(THF)]_2$ (II) [4] and $[Mg(CH_3COOC_2H_5)_6][AlCl_4]_2$ (III) [5]. In these adducts ionic structures with the magnesium atoms octahedrically coordinated by the six oxygen atoms of the coordinating Lewis bases are observed.

We report here on the synthesis and the single crystal X-ray structure determination of the $MgCl_2(CH_3COOC_2H_5)_2 \cdot \frac{1}{2}(CH_3COOC_2H_5)$ (IV) adduct.

Experimental

Preparation and crystallization of $MgCl_2(CH_3COOC_2H_5)_2 \cdot \frac{1}{2}(CH_3COOC_2H_5)$

To 1.5 g of a sample of a disordered [1] $MgCl_2$ *c.* 60 ml of ethyl acetate (Aldrich A.C.S. reagent) were added. The ligand had been previously purified by standard methods. The addition of ethyl acetate and all manipulations were carried out in a strictly inert controlled atmosphere. The reaction was carried out at reflux temperature for 2 h, under stirring.

The obtained clear solution was slowly cooled in the dark for 12 h and very thin needle-like crystals of a pale-green colour were obtained. Elemental

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TABLE 1. Fractional coordinates and equivalent isotropic thermal parameters (Å)[a, b] for $MgCl_2(CH_3COOC_2H_5)_2 \cdot \frac{1}{2}(CH_3COOC_2H_5)$

Atom	x	y	z	U_{eq}
Mg	0.75014(4)	0.5022(1)	0.1580(2)	0.0370(4)
Cl(1)	0.79330(4)	0.3484(2)	0.4054(1)	0.0447(3)
Cl(2)	0.70670(4)	0.6513(1)	0.4125(1)	0.0451(3)
O(1)	0.8148(1)	0.6582(3)	0.1584(5)	0.0491(9)
O(2)	0.8749(1)	0.8441(4)	0.1808(6)	0.058(1)
O(3)	0.6863(1)	0.3442(4)	0.1603(5)	0.050(1)
O(4)	0.6119(1)	0.2081(4)	0.1778(6)	0.060(1)
C(1)	0.8251(2)	0.7945(5)	0.1696(6)	0.045(1)
C(2)	0.7861(2)	0.9252(5)	0.1741(9)	0.059(1)
C(3)	0.9166(2)	0.7283(7)	0.172(1)	0.070(2)
C(4)	0.9670(2)	0.802(1)	0.243(1)	0.096(3)
C(5)	0.6383(2)	0.3399(5)	0.1681(7)	0.048(1)
C(6)	0.6032(2)	0.4786(6)	0.159(1)	0.066(2)
C(7)	0.6440(2)	0.0650(7)	0.173(1)	0.073(2)
C(8)	0.6064(3)	−0.0629(8)	0.167(2)	0.139(5)
O(5)	0.498(3)	−0.208(1)	0.523(12)	0.131(9)
O(6)	0.5732(7)	−0.257(2)	0.623(3)	0.142(7)
C(9)	0.5106(3)	−0.459(1)	0.533(4)	0.108(2)
C(10)	0.4702(7)	−0.310(2)	0.422(2)	0.193(9)
C(11)	0.447(2)	−0.263(3)	0.254(5)	0.22(2)
C(10′)[c]	0.5298(7)	−0.310(2)	0.578(2)	0.193(9)

[a] In this and the following Table standard deviations in the last significant digit(s) are given in parentheses. [b] The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter, defined as $\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. [c] Prime (′) = $1-x, y, 1-z$; population parameter: 0.5.

TABLE 2. Selected bond lengths (Å) and angles (°) for $MgCl_2(CH_3COOC_2H_5)_2 \cdot \frac{1}{2}(CH_3COOC_2H_5)$ with e.s.d.s in parentheses

Mg–Cl(1)	2.496(2)	Mg–Cl(2)	2.516(2)
Mg′–Cl(1)[a]	2.515(2)	Mg′–Cl(2)[a]	2.477(2)
Mg–O(1)	2.107(3)	Mg–O(3)	2.101(3)
O(1)–C(1)	1.205(5)	O(2)–C(1)	1.322(5)
O(2)–C(3)	1.447(6)	O(3)–C(5)	1.206(5)
O(4)–C(5)	1.316(5)	O(4)–C(7)	1.473(7)
C(1)–C(2)	1.492(6)	C(3)–C(4)	1.509(9)
C(5)–C(6)	1.485(6)	C(7)–C(8)	1.45(1)
O(1)–Mg–O(3)	179.1(1)	Cl(2)–Mg–O(3)	89.7(1)
Cl(2)–Mg–O(1)	90.4(1)	Cl(1)–Mg–O(3)	88.9(1)
Cl(1)–Mg–O(1)	90.2(1)	Cl(1)–Mg–Cl(2)	85.3(1)
Cl(1)–Mg′–Cl(2)[a]	83.7(1)	Mg–Cl(1)–Mg′[a]	94.3(1)
Mg–Cl(2)–Mg′[a]	94.7(1)	C(1)–O(2)–C(3)	117.2(4)
Mg–O(1)–C(1)	141.8(3)	C(5)–O(4)–C(7)	116.5(4)
Mg–O(3)–C(5)	141.3(3)	O(2)–C(1)–C(2)	112.0(4)
O(1)–C(1)–O(2)	121.4(4)	O(2)–C(3)–C(4)	107.4(5)
O(1)–C(1)–C(2)	126.6(4)	O(4)–C(5)–C(6)	113.5(4)
O(3)–C(5)–O(4)	122.1(4)	O(4)–C(7)–C(8)	106.4(5)
O(3)–C(5)–C(6)	124.4(4)		

[a] Prime (′) = $\frac{3}{2}-x, 1-y, 1+z$.

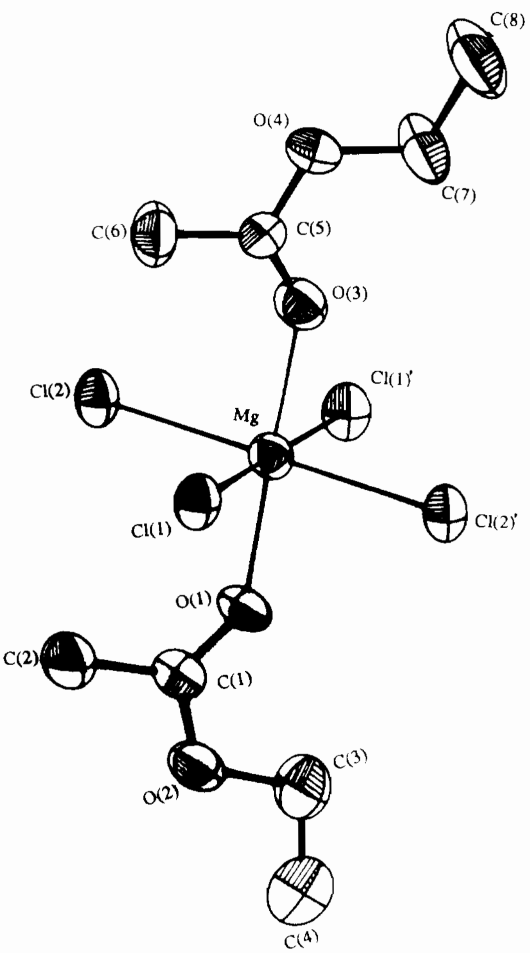

Fig. 1. A perspective view showing the coordination around the Mg atom with the numbering scheme of the asymmetric part.

analysis (AA spectrometry) gave a magnesium content equal to 7.6%, and FT-IR attenuated total reflectance spectrometry [6] revealed a content of ethyl acetate equal to 68.4%. The analytical data agree with the stoichiometry: $MgCl_2(CH_3COOOC_2H_5)_{2.48}$.

These crystals, in the form of regularly shaped parallelepipeds, are very unstable and instantaneously become opaque if removed in a dry-box from the mother liquor. Every attempt to recrystallize the compound failed, but after eight months of ripening in the dark and in the mother liquid, some crystals suitable for XRD analysis were obtained. Owing to their high instability, these crystals were quickly transferred from the solution into dry and oxygen free vaseline petroleum (OBAT-55-ROL OIL) and finally into a Lindemann capillary previously filled with the same oil. The crystal examined in the present work had the dimensions of 0.2×0.3×0.3 mm and,

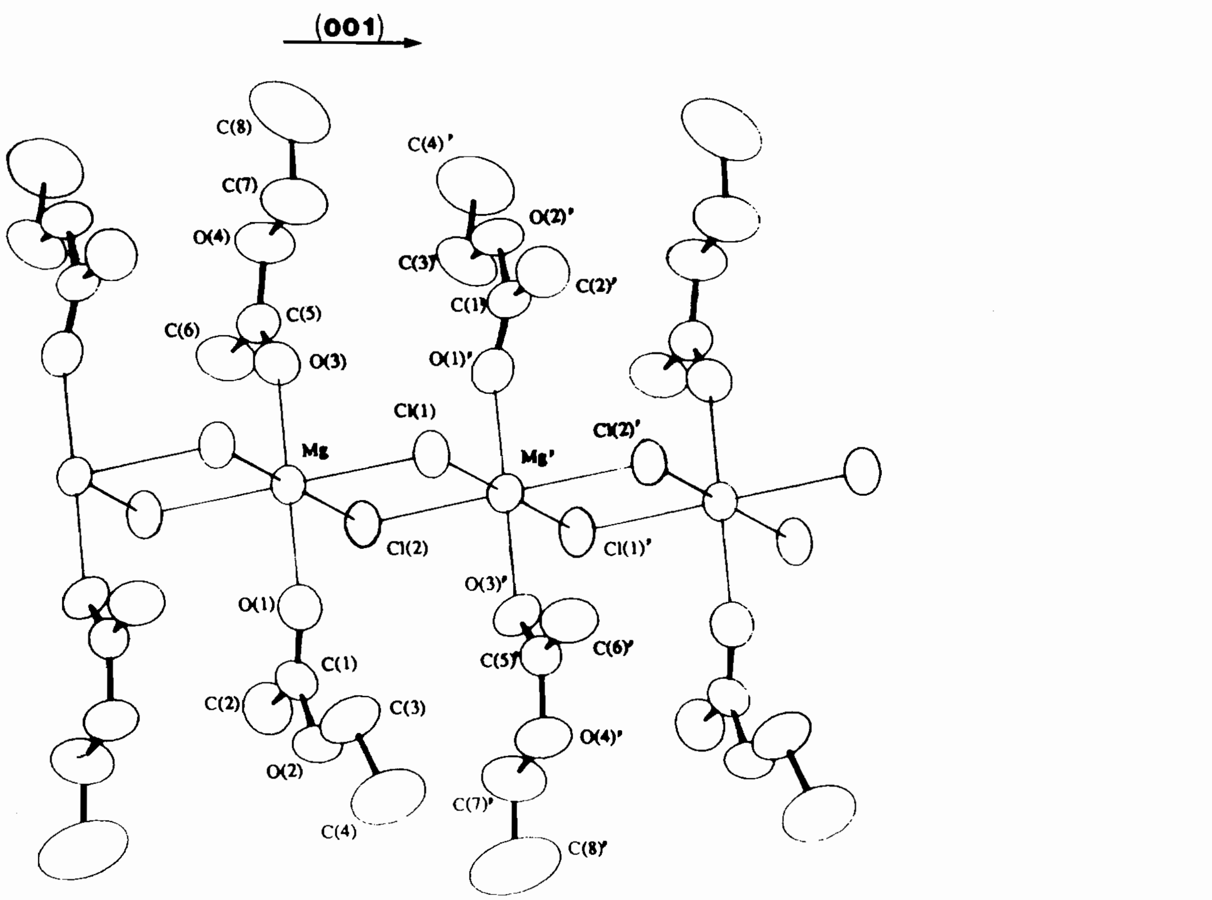

Fig. 2. View of a polymeric chain along the [001] direction showing the regularity of the octahedron.

under the above conditions, it remained indefinitely stable.

X-ray analysis

The cell parameters were determined by least-squares refinement of the setting angles of 25 reflections with 2θ from 12 to 20°. A total of 2202 independent reflections was collected for $0 \leqslant h \leqslant 33$, $0 \leqslant k \leqslant 11$ and $0 \leqslant l \leqslant 9$ on a Philips PW 1100 four-circle diffractometer in the ω-scanning mode up to $2\theta = 56°$, using graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. The data were corrected for Lorentz and polarization but not for absorption effects. The structure was phased by direct methods using SHELX86 [7] programs and it was refined by full-matrix least-squares methods using anisotropic temperature factors for all non-hydrogen atoms. During the refinement of the structure, the difference Fourier synthesis gave evidence of four strong maxima around the crystallographic 2 axis. The interpretation is that some included molecules of ethyl acetate are present in the structure, whose presence is justified by the chemical synthesis and by the chemical analysis of the adduct. This solvate molecule is disordered around the crystallographic twofold axis but it does not respect this symmetry; in fact for the solvent molecule, $Z = 2$. Moreover, apart from the occupancy parameters, which were applied in agreement with this hypothesis, no constraints were applied to the refinement of the ethyl acetate molecule. The full-matrix least-squares refinement based on F using weights $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ where $g = 7.28 \times 10^{-3}$, gave final values of $R = 0.059$, $R_w = 0.069$, $S = 1.10$ for 204 variables and 1667 considered observed reflections having $F_o > 7\sigma(F_o)$; $(\Delta/\sigma)_{av} = 0.30$. We wish to underline that the high value 7σ is due to the need to carry out the data collection with an adequate high speed, because the crystal in time undergoes decomposition.

The organic part of the molecule shows a disorder in the atomic positions. This disorder is higher for the solvate than for the coordinating molecules and is responsible for the value of $(\Delta/\sigma)_{max} = 1.59$. The final maximum residual electron density is $(\Delta\rho)_{max} = 0.45$ e Å^{-3} in the region of the solvate ethyl acetate. The atomic scattering factors for Mg atom were taken from the International Tables for

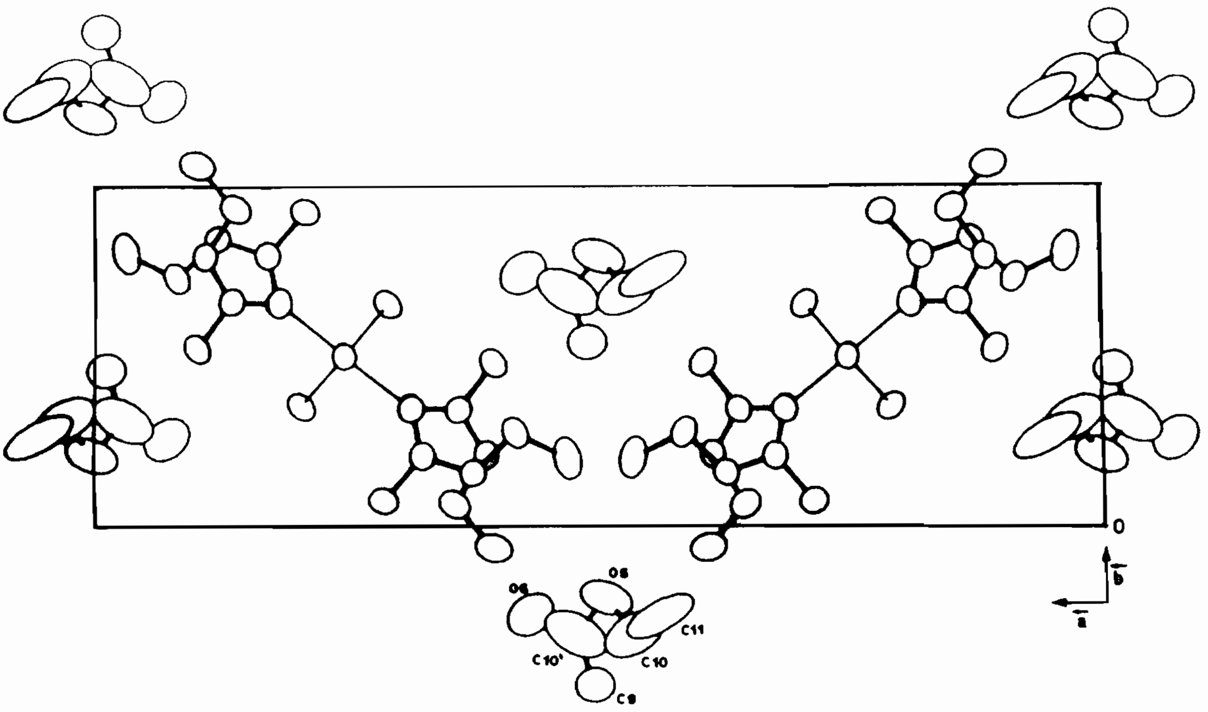

Fig. 3. The packing of the polymeric chains in the unit cell (viewed down *c*).

X-ray Crystallography [8] and all computations were performed using the SHELX76 [9] program.

Discussion

Table 1 gives the fractional coordinates with equivalent isotropic thermal parameters and Table 2 gives selected bond lengths and angles.

The magnesium atom of the $MgCl_2(CH_3COOC_2H_5)_2$ adduct appears to be octahedrally coordinated by four chlorine atoms and by two oxygen atoms of the ethyl acetate carbonyl groups, Fig. 1.

The strictly octahedral coordination around the Mg atom is a consequence of the co-planarity among all the Mg and Cl atoms and by the orthogonality to the Mg–Cl plane of the C=O bond of the ethyl acetate group.

The oxygen atoms located at the apical positions are mutually *trans* with respect to Mg. Furthermore, the C and O atoms of the ethyl acetate are also located on a plane which is perpendicular to the equatorial plane of the $(MgCl_4O_2)$ octahedron. The structure of **IV** is based on polymeric chains having repeat units $MgCl_2(CH_3COOC_2H_5)_2$ joined by double chlorine bridges along the [001] crystallographic direction (see Fig. 2). In Fig. 2 it is also possible to observe that the Mg–Cl–Mg bonds along the polymeric chain give rise to perfect squares, whose center appears as a pseudo-inversion center. As a matter of fact, the Mg atom is located in a particular position, $(\frac{3}{4}, \frac{1}{2}, z)$, along the chain and the ethyl acetate molecules are arranged in an alternated fashion along the [001] direction. This typical arrangement is likely due to steric and electrostatic intermolecular interactions.

The solvent molecules trapped by the polymeric chains show a strong thermal and positional disorder and this seems to be likely connected to the high crystal unstability.

Figure 3 shows the projection of the unit cell content onto the *ab* plane.

All the drawings have been obtained by means of the ORTEP [10] computing and drawing program.

The comparison between the structures of the adduct **IV** and $[MgCl_2(HCOOC_2H_5)_2]_n$ (**V**) [11] reveals some remarkable differences: compound **V** is based on a polymeric chain conformation also characterized by chlorine bridges, but it differs from the ethyl acetate adduct. In fact, the Mg and Cl atoms do not lie on the same plane, but are located along a 3_1 helix; thus producing a *cis* arrangement of the ethyl formate molecules with respect to the Cl and Mg atoms.

The adducts **IV** and **V** appear as the first examples of Mg complexes containing Cl and esters as ligands and showing covalent metal–chlorine bonds with negligible ionic character [11]. The crystal structures determined for such complexes have shown some utility as models for a refined interpretation of X-ray powder diffraction patterns of some related precursors for catalytic supports previously described in the patent and scientific literature [12].

The removal of the Lewis base from **IV** gives a $MgCl_2$-based support for Ziegler–Natta catalysis characterized by a high surface area [11], where it is now reasonable to suppose the presence of identical 'active' sites suitable for the generation of the Ziegler–Natta ones, after titanation.

Supplementary material

Tables of thermal parameters, complete listing of bond lengths, complete listing of bond angles, and observed and calculated structure factors are available from the authors on request.

Acknowledgements

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