

The crystal structure and properties of $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$

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Abstract

The direct reaction of AlCl_3 with ethyl benzoate in *n*-hexane gives the colourless crystalline compound $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$, the crystal structure of which has been determined by X-ray single crystal diffraction methods. Crystals are orthorhombic, space group *Pnma* with $a = 15.016(9)$, $b = 7.166(6)$, $c = 12.009(8)$ Å, and $Z = 4$. The structure was refined by block-diagonal least-squares to $R = 0.049$ for 1293 independent non-zero reflections. The aluminium atom is tetrahedrally coordinated by three chlorine atoms and by the carbonyl oxygen atom of ethyl benzoate.

Introduction

Most of the research in the field of olefin polymerization process has been focused on Ziegler–Natta titanium catalysts on a MgCl_2 support. In order to combine a high polymer yield with good stereoselectivity, a complexed co-catalyst is used. Most frequently it is a mixture of AlEt_2Cl or AlEt_3 and an electron donor such as ethyl benzoate. Polymerization studies have revealed that the interaction of ethyl benzoate with the catalyst ensures high isotacticity. Ethyl benzoate is believed to improve isotacticity by inactivating the non-stereospecific polymerization sites on the titanium atom [1].

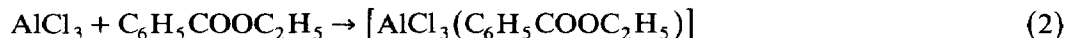
It has been found that the reaction of TiCl_4 with an ester produces dimeric compound $[(\text{L})\text{Cl}_3\text{Ti}(\mu\text{-Cl})_2\text{TiCl}_3(\text{L})]$ [2], where $\text{L} = \text{C}_2\text{H}_5\text{COOC}_6\text{H}_4\text{OCH}_3$ or $\text{CH}_3\text{COOC}_2\text{H}_5$. A study of the interaction of ethyl benzoate with AlEt_2Cl or AlEt_3 reveals that the carbonyl groups in $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ undergo reduction [3]. The product of this reaction is unstable and its structure is unknown. AlCl_3 , as a component of the catalyst, has an unfavourable effect on the polymerization process because a co-catalyst such as AlEt_2Cl may form AlEtCl_2 , which poisons titanium catalyst activity [4]



We have embarked on an study of the reaction between AlCl_3 and ethyl benzoate. We presume that the compound which is formed between aluminium trichloride and ethyl benzoate could be used as model for the elucidation of the influence of the phenyl ring of $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ on the stereospecific propylene polymerization process.

Results and discussion

A suspension of AlCl_3 in *n*-hexane under N_2 reacts with ethyl benzoate in a 1 : 1 ratio. After 5 h, the white product can be filtered off and recrystallized from CH_2Cl_2 . Crystals for the structure determination are grown by slow diffusion of *n*-hexane into CH_2Cl_2 solution of the aluminium trichloride ethyl benzoate species.



The IR spectrum of the $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{CO}(\text{O})\text{C}_2\text{H}_5)]$ adduct shows the characteristic $\nu(\text{C}=\text{O})$ band of a coordinated carbonyl group ethyl benzoate, at 1605 cm^{-1} (vs,br). The adduct, was shown by X-ray diffraction study, to have a covalent structure. The structure of trichloro(ethyl benzoate)aluminium(III) molecule and the atom numbering scheme are shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 1. The molecule lies on the symmetry plane. Thus the phenyl ring, the carbonyl and OC_2H_5 groups, Al and Cl(1) atoms lie in one plane, with the

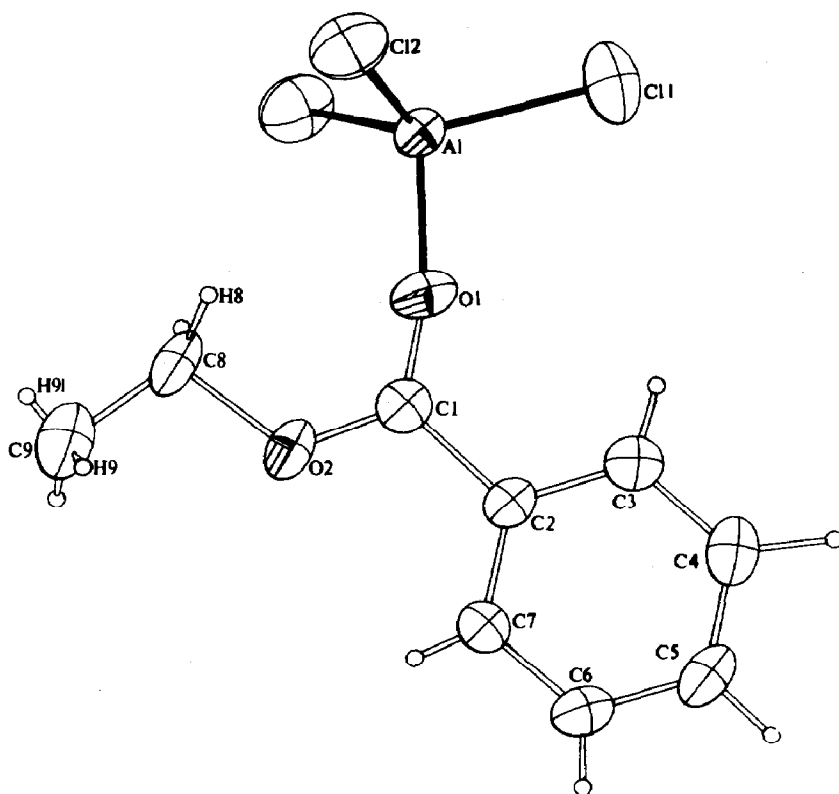


Fig. 1. The molecular structure of $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$.

Table 1

Selected bond lengths (Å) and angles (°) for $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]^a$

Al–Cl(1)	2.110(2)	Al–Cl(2)	2.102(2)
Al–O(1)	1.761(3)	O(1)–C(1)	1.230(5)
C(1)–O(2)	1.295(6)	O(2)–C(8)	1.490(6)
C(1)–C(2)	1.501(6)	C(2)–C(3)	1.382(7)
C(3)–C(4)	1.382(7)	C(4)–C(5)	1.390(7)
C(5)–C(6)	1.372(7)	C(6)–C(7)	1.370(7)
C(7)–C(2)	1.386(6)	C(8)–C(9)	1.458(8)
Cl(1)–Al–Cl(2)	112.5(1)	Cl(2)–Al–Cl(2')	112.5(1)
Cl(1)–Al–O(1)	105.2(2)	Cl(2)–Al–O(1)	106.7(2)
Al–O(1)–C(1)	168.4(3)	O(1)–C(1)–O(2)	123.1(4)
O(1)–C(1)–C(2)	122.3(4)	O(2)–C(1)–C(2)	114.6(4)
C(1)–O(2)–C(8)	120.0(3)	O(2)–C(8)–C(9)	106.1(4)
C(1)–C(2)–C(3)	118.0(4)	C(1)–C(2)–C(7)	120.6(4)
C(3)–C(2)–C(7)	121.4(4)	C(2)–C(3)–C(4)	118.8(4)
C(3)–C(4)–C(5)	120.2(4)	C(4)–C(5)–C(6)	119.8(4)
C(5)–C(6)–C(7)	121.0(4)	C(6)–C(7)–C(2)	118.9(4)

^a Symmetry code: (i) $x, 0.5 - y, z$.

Cl(9), H(8) and H(9) atoms on either side of this plane. The aluminium atom is tetrahedrally coordinated by three chlorine atoms and carbonyl oxygen atom of ethyl benzoate. The complex contains an Al–O coordinate bond, of 1.761(3) Å. The C(1)–O(2) bond length is 1.295(6) Å, and the ethyl–oxygen bond O(2)–C(8) is 1.490(6) Å. The analogous oxygen–carbon bonds in the free ester are 1.36(1) and 1.43(1) Å, respectively [5]. The C(1)–O(1) distance in coordinated carbonyl group and in the free ester are equal at 1.230(5) Å. A similar effect was observed for the coordinated $\text{CH}_3\text{OC}_6\text{H}_4\text{COOC}_2\text{H}_5$ ester in $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_6(\text{CH}_3\text{OC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2]$. The average Al–Cl bond length in the cation $[\text{AlCl}_2(\text{THF})_4]^+$ [6] is 2.226(6) Å and exceeds the average Al–Cl distance of 2.105(5) Å in $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$. This difference is a distinguishing feature between bond lengths in octahedral and tetrahedral aluminium compounds. The crystal packing is shown in Fig. 2.

Elucidation of the polarization of the bonding in the ester group under effect of the Al^{3+} ions should provide an explanation as to the mechanism by which reaction between the coordinated molecules of an ester and of a co-catalyst takes place: AlEt_3 and AlEt_2Cl .

Experimental

The reactions were carried out under N_2 using standard Schlenk-tube techniques. The ethyl benzoate and CH_2Cl_2 were dried before use. Commercial AlCl_3 was sublimed. IR spectra were obtained on a Perkin–Elmer 180 spectrometer. Microanalyses were performed at the University of Wrocław.

$[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$. To a suspension of AlCl_3 (3.4 g (26 mmol)) in 100 cm^3 n-hexane was slowly added ethyl benzoate (9.7 cm^3) and stirred for 5 h. The white precipitate was filtered off and washed with n-hexane (5×10 ml), and dried under vacuo. Yield 6.1 g; 83%.

X-Ray crystal structure determination

Crystal data. $\text{C}_9\text{H}_{10}\text{O}_2\text{Cl}_3\text{Al}$, $M = 283.5$, $a = 15.016(9)$, $b = 7.166(6)$, $c = 12.009(8)$ Å, $Z = 4$, $V = 1292(2)$ Å³, D_{m} (by flotation) = 1.458 $D_{\text{c}} = 1.457(2)$ g cm^{-3} ,

Table 2

Final positional and thermal parameters with e.s.d.'s in parentheses for $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{OCOC}_2\text{H}_5)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	0.2151(1)	0.25	0.6009(2)	2.26(5)	3.07(6)	2.32(5)	0	0.29(5)	0
Cl(1)	0.1777(2)	0.25	0.4315(2)	6.45(9)	8.12(12)	2.78(6)	0	-0.90(6)	0
Cl(2)	0.1750(1)	0.4938(2)	0.6843(1)	4.38(4)	3.33(4)	5.33(5)	0.36(4)	0.90(4)	-0.76(4)
O(1)	0.3324(2)	0.25	0.6005(3)	2.08(13)	5.45(22)	3.96(17)	0	0.57(13)	0
O(2)	0.4445(3)	0.25	0.7210(3)	3.35(15)	5.27(20)	2.26(14)	0	0.88(12)	0
C(1)	0.4127(3)	0.25	0.6208(4)	2.73(19)	2.63(20)	2.76(21)	0	0.17(16)	0
C(2)	0.4817(3)	0.25	0.5305(4)	2.38(18)	2.16(18)	2.50(18)	0	0.45(15)	0
C(3)	0.4530(4)	0.25	0.4212(5)	2.69(19)	3.89(25)	3.14(22)	0	-0.02(17)	0
C(4)	0.5157(4)	0.25	0.3371(5)	4.59(27)	4.13(28)	2.44(21)	0	0.30(20)	0
C(5)	0.6060(4)	0.25	0.3628(5)	3.76(25)	4.26(28)	2.95(22)	0	1.43(19)	0
C(6)	0.6327(4)	0.25	0.4721(5)	2.26(19)	5.29(31)	3.57(23)	0	0.46(18)	0
C(7)	0.5716(3)	0.25	0.5567(4)	2.42(19)	4.20(26)	2.41(19)	0	-0.18(16)	0
C(8)	0.3829(4)	0.25	0.8183(5)	3.92(25)	6.63(37)	2.38(21)	0	1.45(19)	0
C(9)	0.4392(5)	0.25	0.9171(5)	5.37(34)	9.19(52)	2.98(26)	0	0.79(24)	0

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
H(3)	0.397(3)	0.25	0.399(4)	3.1(11)	H(4)	0.507(4)	0.25	0.248(5)	5.5(15)
H(5)	0.649(4)	0.25	0.308(5)	5.1(14)	H(6)	0.688(4)	0.25	0.474(5)	6.1(16)
H(7)	0.594(3)	0.25	0.617(4)	1.6(9)	H(8)	0.345(3)	0.375(6)	0.800(4)	5.9(11)
H(9)	0.470(3)	0.372(8)	0.914(4)	10.0(16)	H(91)	0.407(6)	0.25	0.949(9)	17.3(39)

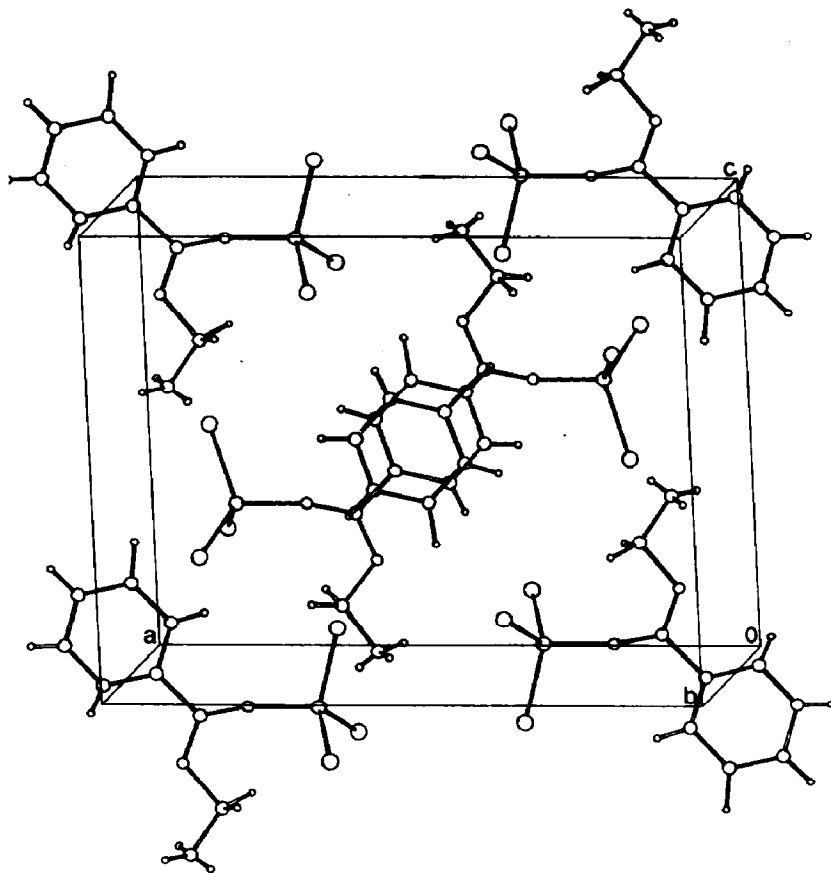


Fig. 2. View of the crystal packing for $[\text{AlCl}_3(\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$.

$F(000) = 576$, space group $Pnma$, Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu = 7.53 \text{ cm}^{-1}$, $T = 298(1) \text{ K}$.

A sample of $0.7 \times 0.9 \times 0.5 \text{ mm}$ was cut from a large crystal and sealed in a capillary. Preliminary examination by Weissenberg photography showed the space group to be $Pnma$ or $Pn2_1a$. The intensity data were measured on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo- K_α radiation. Intensities were collected by 2θ - ω scan technique up to $2\theta = 60^\circ$. The intensities of two standard reflections, measured after every 50 scan intensities showed a $\pm 2.5\%$ variation. Of the 2106 reflections collected, the 1293 with $I > 3\sigma(I)$ were used for the structure determination. The structure was solved by direct methods on the assumption of the centrosymmetric $Pnma$ space group. The H atoms were located from difference Fourier synthesis. An absorption correction carried out by use of DIFABS [7], was applied to isotropically refined data. Block-diagonal least-squares refinement based on F values was performed with BLOCK program [8] on positional and anisotropic (isotropic for H) thermal parameters. The function minimized was $\sum w[(F_o) - (F_c)]^2$, where $w = 1/\sigma^2(F_o)$.

Final R and R_w values were 0.049 and 0.055, respectively. The maximal Δ/σ in the final cycle of refinement was 0.05. The maximal and minimal residual electron densities in the difference Fourier map were found to lie between -0.36 and 0.32

$\text{e}\text{\AA}^3$. Neutral atom scattering factors were taken from ref. 9. Real and imaginary components of anomalous dispersion were included for all the non-H atoms. Final atom parameters are given in Table 2.

Supplementary material. A table of the anisotropic thermal parameters and a listing of observed and calculated structure factors for compound $[\text{AlCl}_3\text{-(C}_6\text{H}_5\text{COOC}_2\text{H}_5)]$ (8 pages) are available from the authors.

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