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The crystal structure and properties of $[1,3,5\text{-}C_6H_3(CO_2Me)_3 \cdot 3AlCl_3]$

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Abstract

The direct reaction of $AlCl_3$ with trimethyl 1,3,5-benzenetricarboxylate in dichloromethane gives the colourless crystalline complex formulated as $[1,3,5\text{-}C_6H_3(CO_2Me)_3 \cdot 3AlCl_3]$. The crystal structure of this compound has been determined by X-ray single crystal diffraction methods. Each aluminium atom is tetrahedrally coordinated by three chlorine atoms and one carbonyl oxygen atom of the $1,3,5\text{-}C_6H_3(CO_2Me)_3$ molecule, so each ester molecule is bonded to three $AlCl_3$ moieties.

1. Introduction

The presence of esters is essential to improve the stereospecificity of high activity catalyst systems based on AlR_3 and titanium halides supported on activated $MgCl_2$ [1] and intended for olefin polymerization. Investigations of the interaction between an ester and each component of the catalytic system are therefore important.

We have studied the reaction of $AlCl_3$ with trimethyl 1,3,5-benzenetricarboxylate and here we describe the crystal structure of the title compound.

2. Experimental section

The reactions were carried out under nitrogen, using a standard Schlenk system and a vacuum line. The CH_2Cl_2 was dried before use. $1,3,5\text{-}C_6H_3(CO_2Me)_3$ was purchased from Aldrich. IR spectra were obtained on a Perkin-Elmer 180 spectrometer.

2.1. Synthesis of (trimethyl 1,3,5-benzenetricarboxylate-O,O',O")nonachlorotrialuminium (III)

$AlCl_3$ (1.11 g, 8.2 mmol) was added to $1,3,5\text{-}C_6H_3(CO_2Me)_3$ (0.7 g, 2.7 mmol) dissolved in 60 cm^3 CH_2Cl_2. Stirring and heating under reflux continued until $AlCl_3$ dissolved completely. The brown solution was filtered off and its volume reduced *in vacuo* to 30 cm^3. After 24 h at room temperature colourless crystals appeared, which were filtered off and washed with CH_2Cl_2 (2×5 cm^3). Yield 1.5 g, 82.9%. (Found: Cl, 50.3; Al, 12.0. $C_{12}H_{12}Al_3Cl_9O_6$ calc.: Cl, 48.9; Al, 12.4%). IR (Nujol): ν(C=O) 1630vs, 1650vs; other bands: 230m, 280w, 430vs, 530vs, 605s, 730vs, 850m, 910s, 990vs, 1150m, 1360s, 1375s, 1390s cm^{-1}.

2.2. Crystal data

Colourless crystals, $C_{12}H_{12}Al_3Cl_9O_6$, $M = 652.2$, monoclinic, space group $P2_1/c$, $a = 13.637(15)$, $b = 15.143(17)$, $c = 13.304(9)$ Å, $\beta = 100.91(8)°$, $U = 2698(5)$ Å^3, $Z = 4$, $D_c = 1.606(3)$ g cm^{-3}, D_m (by flotation) = 1.61 g cm^{-3}, $F(000) = 1296$ μ(Mo Kα) = 10.6 cm^{-1}, λ(Mo Kα) = 0.71069 Å.

2.3. Data collection and processing

A sample of dimensions $0.8 \times 0.9 \times 0.9$ mm was cut from a large crystal and sealed in a glass capillary. Preliminary data were recorded by photographic methods. Intensities were collected with a KM-4 diffractometer and Mo Kα radiation. 7222 ($4 < 2\theta < 56°$) reflections were measured, of which 3042 with $I > 3.0\ \sigma(I)$ were used for calculations. The structure was solved by direct methods and refined by full-matrix least-squares calculations using SHELX76 [2]. Neutral atomic scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 3. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. All hydrogen atoms were found from difference maps and refined isotropically. Absorption

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TABLE 1. Final atom parameters for [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$]

Atom	x	y	z	U_{eq} / U_{iso}
Cl(1)	0.09799(9)	0.17332(8)	0.45168(9)	0.0667(5)
Cl(2)	0.19413(11)	0.30333(11)	0.27690(9)	0.0973(8)
Cl(3)	0.01301(10)	0.39178(9)	0.40413(10)	0.0865(7)
Cl(4)	−0.23501(11)	0.27234(10)	0.75277(11)	0.0962(7)
Cl(5)	−0.09070(11)	0.22973(9)	0.57479(13)	0.1054(8)
Cl(6)	−0.24838(11)	0.41433(11)	0.54776(13)	0.1181(9)
Cl(7)	0.53517(11)	0.73324(10)	0.76299(12)	0.1024(8)
Cl(8)	0.63165(10)	0.61878(10)	0.99030(11)	0.1011(7)
Cl(9)	0.57742(10)	0.50389(10)	0.76029(12)	0.0929(7)
Al(1)	0.13049(11)	0.30191(9)	0.40872(10)	0.0526(6)
Al(2)	−0.15765(9)	0.32807(9)	0.64674(10)	0.0480(5)
Al(3)	0.54287(10)	0.61398(10)	0.84332(11)	0.0579(6)
O(11)	0.22344(22)	0.33959(19)	0.51325(21)	0.0621(13)
O(12)	0.36681(22)	0.40669(20)	0.57442(21)	0.0562(13)
O(31)	−0.05680(20)	0.39445(20)	0.71119(22)	0.0602(13)
O(32)	−0.02799(19)	0.49513(19)	0.83439(22)	0.0521(12)
O(51)	0.42022(20)	0.59765(20)	0.86624(21)	0.0589(13)
O(52)	0.30051(19)	0.61255(18)	0.95564(20)	0.0481(11)
C(1)	0.23644(29)	0.43025(25)	0.66199(28)	0.0386(15)
C(2)	0.13917(31)	0.41756(27)	0.67478(31)	0.0426(16)
C(3)	0.10432(28)	0.46066(25)	0.75223(28)	0.0366(15)
C(4)	0.16728(31)	0.51456(28)	0.81865(32)	0.0382(16)
C(5)	0.26479(28)	0.52566(24)	0.80857(28)	0.0364(14)
C(6)	0.29889(30)	0.48437(27)	0.72966(31)	0.0403(16)
C(11)	0.27523(33)	0.38822(27)	0.57648(31)	0.0467(17)
C(12)	0.41150(58)	0.37328(53)	0.48996(53)	0.0787(31)
C(31)	−0.00114(32)	0.44705(28)	0.76433(32)	0.0461(17)
C(32)	−0.12960(42)	0.48472(46)	0.85567(56)	0.0778(28)
C(51)	0.33423(30)	0.58138(26)	0.87883(29)	0.0417(16)
C(52)	0.36411(45)	0.67013(46)	1.03033(46)	0.0684(24)
H(11)	0.385(4)	0.395(4)	0.427(4)	0.089(21)
H(12)	0.408(4)	0.314(4)	0.494(4)	0.097(23)
H(13)	0.486(5)	0.381(4)	0.510(5)	0.140(27)
H(31)	−0.128(4)	0.535(4)	0.900(4)	0.103(21)
H(32)	−0.128(4)	0.423(3)	0.882(4)	0.088(20)
H(33)	−0.186(5)	0.488(4)	0.778(5)	0.171(29)
H(51)	0.382(4)	0.725(4)	0.992(4)	0.120(25)
H(52)	0.326(4)	0.697(4)	1.075(4)	0.103(21)
H(53)	0.426(4)	0.643(3)	1.059(4)	0.087(19)
H(2)	0.101(3)	0.381(2)	0.635(3)	0.022(10)
H(4)	0.147(3)	0.541(3)	0.860(3)	0.020(11)
H(6)	0.364(3)	0.488(3)	0.725(3)	0.056(14)

corrections following the DIFABS procedure [4] were applied, minimum and maximum absorption corrections were 0.825 and 1.078. The final R and R_w values were 0.0404 and 0.0291 for the observed reflections. For the last cycle of the refinement the maximal value of the Δ/σ ratio was 0.05 and the final difference map showed a general background within −0.31 and 0.36 e Å^{-3}.

The final atomic parameters are summarized in Table 1.

3. Results and discussion

The addition of trimethyl 1,3,5-benzenetricarboxylate to $AlCl_3$ in dichloromethane, in 1:3 molar ratio, leads to air-sensitive colourless crystals of composition [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$], which can be stored under nitrogen. The IR spectrum shows a stretching ν(C=O) mode at 1630 and 1650vs and a phenyl ring at 1600s cm^{-1}.

$$3AlCl_3 + 1,3,5\text{-}C_6H_3(CO_2Me)_3 \xrightarrow{CH_2Cl_2} [1,3,5\text{-}C_6H_3(CO_2Me)_3 \cdot 3AlCl_3] \quad (1)$$

The structure of [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$] is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. There are three crystallographically different Al atoms in the complex molecule. Three chlorine atoms and one carbonyl oxygen atom from trimethyl 1,3,5-benzenetricarboxylate form a distorted tetrahedron around each aluminium atom. The atoms Al(1), Al(2), Al(3) are placed 1.789(3), 1.786(3), 1.773(3) Å from the O(11), O(31) and O(51) carbonyl oxygens, respectively. The Al–Cl bond lengths range from 2.073(2) to 2.102(2) Å. The Al(3)–O(51)–C(51) angle of 176.0(3)° is larger than the Al(1)–O(11)–C(11) and Al(2)–O(31)–C(31) angles of 161.8(3) and 167.8(3)°, respectively. It was found [5] that in the trichloro(ethyl benzoate)aluminium(III) molecule the Al–O–C bond angle is obtuse to 168.4(3)°. In the Et_2Al(OAryl)-methyl

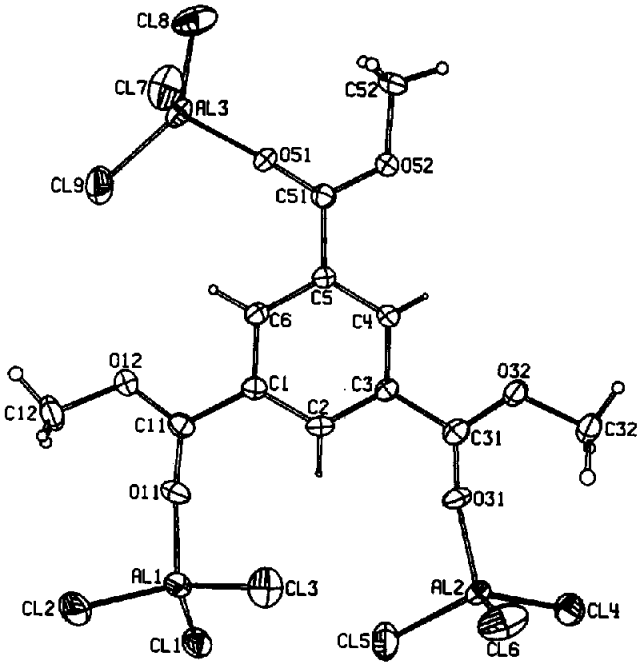

Fig. 1. View of the [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$] molecule perpendicular to the benzene ring.

TABLE 2. Principal interatomic distances (Å) and bond angles (°) for [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$]

Al(1)–Cl(1)	2.100(2)	O(11)–C(11)	1.234(5)
Al(1)–Cl(2)	2.099(2)	O(12)–C(11)	1.285(5)
Al(1)–Cl(3)	2.094(2)	O(12)–C(12)	1.466(8)
Al(1)–O(11)	1.789(3)	C(11)–C(1)	1.486(6)
Al(2)–Cl(4)	2.092(2)	O(31)–C(31)	1.228(5)
Al(2)–Cl(5)	2.073(2)	O(32)–C(31)	1.289(5)
Al(2)–Cl(6)	2.087(2)	O(32)–C(32)	1.474(7)
Al(2)–O(31)	1.786(3)	C(31)–C(3)	1.491(6)
Al(3)–Cl(7)	2.091(2)	O(51)–C(51)	1.240(5)
Al(3)–Cl(8)	2.097(2)	O(52)–C(51)	1.287(5)
Al(3)–Cl(9)	2.102(2)	O(52)–C(52)	1.474(7)
Al(3)–O(51)	1.773(3)	C(51)–C(5)	1.465(5)
C(1)–C(2)	1.382(6)	C(5)–C(6)	1.376(6)
C(2)–C(3)	1.378(6)	C(6)–C(1)	1.385(6)
C(3)–C(4)	1.377(6)	C(4)–C(5)	1.372(6)
Cl(1)–Al(1)–Cl(2)	112.3(1)	Cl(5)–Al(2)–Cl(6)	114.7(1)
Cl(1)–Al(1)–Cl(3)	114.3(1)	Cl(6)–Al(2)–Cl(4)	111.3(1)
Cl(2)–Al(1)–Cl(3)	113.8(1)	Cl(4)–Al(2)–Cl(5)	110.1(1)
Cl(2)–Al(1)–O(11)	107.6(2)	Cl(5)–Al(2)–O(31)	105.0(2)
Cl(3)–Al(1)–O(11)	103.9(2)	Cl(4)–Al(2)–O(31)	110.1(2)
Cl(1)–Al(1)–O(11)	103.8(2)	Cl(6)–Al(2)–O(31)	105.1(2)
Al(1)–O(11)–C(11)	161.8(3)	Al(2)–O(31)–C(31)	167.8(4)
Cl(7)–Al(3)–Cl(8)	114.3(1)	C(11)–O(12)–C(12)	119.2(5)
Cl(7)–Al(3)–Cl(9)	114.3(1)	C(31)–O(32)–C(32)	119.0(4)
Cl(8)–Al(3)–Cl(9)	111.7(1)	C(51)–O(52)–C(52)	119.9(4)
Cl(7)–Al(3)–O(51)	104.5(2)	Cl(9)–Al(3)–O(51)	107.0(1)
Cl(8)–Al(3)–O(51)	104.0(2)	Al(3)–O(51)–C(51)	176.0(3)

p-toluate complex [6] (Aryl = 2,6-^{t}Bu$_2$-4-Me-C_6H_2) the Al–O–C bond angle is 143.0(6)°. Therefore, in the investigated complex the Al(3)–O(51)–C(51) angle is much larger than similar angles in other known compounds, in which the aluminium atom is coordinated to carbonyl group. The C=O bond lengths in the carbonyl groups O(11)–C(11) [1.234(5) Å], O(31)–C(31) [1.228(5) Å] and O(51)–C(51) [1.240(5) Å] are comparable to the C=O bond length of 1.230(5) Å, found [5] in [$AlCl_3(C_6H_5CO_2Et)$]. In the examined compound the phenyl ring is not strictly planar. The C(2) and C(5) atoms are located under the plane formed by the C(1), C(6), C(4) and C(3) atoms, so the angle between two planes formed by the C(5), C(6), C(1), C(2) atoms and the C(5), C(4), C(3), C(2) atoms is 178.2(8)°. The similar angles in [{μ-1,3,5-$C_6H_3(CO_2Me)_3$}$_2Cl_8Ti_2$] · $2CH_2Cl_2$ [7] and [{μ-m-$C_6H_4(CO_2Et)_2$}$_2Cl_8Ti_2$] [8] are 178.2(8)° and 177.6(8)°, respectively. On the contrary, in the polymeric [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3TiCl_4$] compound [7] and dimeric [{μ-m-$C_6H_4(CO_2CH_2CH_2Ph)_2$}Cl_8Ti_2] · $2CH_2Cl_2$ complex [9] the phenyl rings of the ester molecules are strictly planar. In both these compounds there are large distances between the phenyl rings. Furthermore, there are rather short intermolecular contacts in the crystal of [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$]. The C(3) atom is 3.354(4) and 3.259(4) Å from the Cl ($1^{x,0.5-y,0.5+z}$) and Cl($3^{-x,1-y,1-z}$) atoms, respectively. These distances are shorter than the sum of the van der Waals radii.

The available data indicate that $AlCl_3$ in ethyl acetate and tetrahydrofuran forms ionic salts [10,11]. With aromatic esters the molecular compounds [$AlCl_3(C_6H_5CO_2Et)$] and [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$] are obtained instead. This observation could be important in the explanation of the different behaviours in olefin polymerization processes displayed by the complexes formed in CH_3CO_2Et, THF and aromatic esters.

Supplementary material available

Tables of observed and calculated structure factors for [1,3,5-$C_6H_3(CO_2Me)_3 \cdot 3AlCl_3$] are available from the authors.

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References

1 V. Giannini, G. Giunchi and E. Albizzati, *Recent Adv. Mech. Synth. Aspects Polym. (Eng.)*, (1987) 473; P. Sobota, *Polyhedron, 11* (1992) 715.
2 G. M. Sheldrick, *SHELX76, Program for Structure Determination*, University of Cambridge, 1976.
3 *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.
4 N. Walker and D. Stuart, *Acta Crystallogr.*, Sect. A, 39 (1983) 158.
5 P. Sobota, M. O. Mustafa, J. Utko and T. Lis, *J. Organomet. Chem., 368* (1989) 257.
6 A. P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins and S. D. Ittel, *Organometallics, 7* (1988) 409.
7 P. Sobota, J. Utko and T. Lis, *J. Organomet. Chem.*, in press.
8 J. Utko, P. Sobota and T. Lis, *J. Organomet. Chem., 373* (1989) 63.
9 P. Sobota, J. Utko and T. Lis, *J. Organomet. Chem., 417* (1991) 389.
10 P. Sobota, M. O. Mustafa, J. Utko and T. Lis, *J. Chem. Soc., Dalton Trans.*, (1990) 1809.
11 N. C. Means, C. M. Means. S. G. Bott and J. L. Atwood, *Inorg. Chem., 26* (1987) 1466.