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The crystal structure of di-μ-chlorobis[trichloro(ethyl acetate)]dizirconium(IV)

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Abstract

Crystals of di-μ-chloro-bis([trichloro(ethyl acetate)]dizirconium(IV) are monoclinic, space group $P2_1/a$, $Z = 2$, with cell dimensions a 13.756(10), b 9.331(6), c 9.270(9) Å, β 110.85(7)°. The structure was refined by full-matrix least-squares to $R = 0.040$ for 1812 non-zero reflections. In the centrosymmetric $[Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ dimer molecules, each of zirconium atoms is bonded to two bridging chlorine atoms, three terminal chlorine atoms and to one carbonyl oxygen atom of the ethyl acetate molecule in a distorted octahedral environment. The structure is isomorphous with that of di-μ-chlorobis[trichloro(ethyl acetate)di-titanium(IV).

Introduction

In the presence of $MgCl_2$ the Ziegler–Natta catalyst exhibits high activity in α-olefin polymerization [1]. The enhancement of activity and isospecifity is strongly dependent on the nature of the ester molecule (e.g. the catalyst with aromatic esters is very good for propylene polymerization), however, with ethyl acetate the catalyst is only active in ethylene polymerization [2]. To elucidate the difference in behaviour between the aromatic and the aliphatic esters the interactions between the ester molecules and each catalyst component was studied.

The formation of the titanium dimeric compound $[(L)Cl_3Ti(\mu\text{-}Cl)_2TiCl_3(L)]$ (when L = CH_3COOEt or $p\text{-}CH_3OC_6H_4COOEt$) [3,4], $\{Ti_2[\mu\text{-}m\text{-}C_6H_4(COOEt)_2]_2Cl_8\}$ [5], monomeric *cis*-$[(C_6H_5COOEt)_2TiCl_4]$ [6], $[o\text{-}C_6H_4(COOEt)_2TiCl_4]$ [7], and aluminium $[AlCl_3(C_6H_5COOEt)]$ [8], and magnesium-aluminium $[Mg(CH_3COOEt)_6][AlCl_4]_2$ [9] compounds is well documented.

In addition to the titanium catalysts, homogeneous zirconium catalysts are highly active in the polymerization process [10]. The structures of the zirconium-ester compounds are unknown.

Here we describe the crystal structure of $[Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ complex and compare its structure with that of the isomorphous titanium $[Ti_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ compound [3].

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Experimental

All reactions were carried out under N_2 in dried solvents and by use of Schlenk-tube techniques. Commercial $ZrCl_4$ was sublimed. The ethyl acetate was dried before use. The IR spectra were obtained on a Perkin–Elmer 180 spectrophotometer. The density was measured in CCl_4 and $BrCH_2CH_2Br$ mixture.

[$Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2$]. 1.53 g (6.6 mmol) $ZrCl_4$ was suspended in 75 cm^3 n-hexane and 0.65 cm^3 (6.6 mmol) of ethyl acetate was added and stirred. After 1 h the oil layer was separated off and dissolved in 40 cm^3 CH_2Cl_2, evaporated to dryness, under vacuo and washed with n-hexane (3 × 15 cm^3). Yield 2 g; 95%.

Crystals suitable for X-ray data were grown by slow diffusion of n-hexane into solution of the title compound in CH_2Cl_2 (1 g in 20 cm^3 CH_2Cl_2).

X-ray crystal structure determination

Crystal data. $C_8H_{16}Cl_8O_4Zr_2$, $M = 642.3$, a 13.756(10), b 9.331(6), c 9.270(9) Å, β 110.85(7)°, V 1112(2) $Å^3$, D_m (by flotation) 1.84 g cm^{-3}, $Z = 2$, D_c 1.92 g cm^{-3}, F(000) = 624, space group $P2_1/a$, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 18.8$ cm^{-1}, $T = 299(1)$ K.

A crystal of approximate size 0.5 × 0.9 × 0.5 mm was selected for data collection. The Weissenberg photographs show that the space group $P2_1/a$ and unit cell data are similar to those found for the crystals of $(TiCl_4CH_3COOC_2H_5)_2$ [3]. The intensity data were recorded on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo-K_α radiation. Intensities were collected by 2θ–ω scan technique up to 2θ 55°. The intensities of two standard reflections, measured after every 50 scan intensities showed ±4% variation. 2150 reflections were collected of which 1812 with $I > 3\sigma(I)$ were used for structure analysis; $R_{merg} = 0.0339$. Final coordinates of $(TiCl_4CH_3COOC_2H_5)_2$ [3] were used as the starting parameters of Zr, Cl, O and C atoms for refinement. The H atoms were located from a difference-Fourier synthesis. An absorption correction was by the DIFABS procedure [13]; minimum and maximum absorption corrections were 0.882 and 1.128, respectively. Full-matrix least-squares refinement, based on F values, was performed with SHELX 76 [11] on the positional and anisotropic (isotropic for H) parameters. The H atoms were refined with the constraint that d(C–H) 1.08 Å. The isotropic extinction correction in the form of $1 - xF_c^2/\sin\theta$ was applied and the final x parameter was $35.8(15) \times 10^{-8}$. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(I_o)$.

Final R and R_w were 0.0391 and 0.0401, respectively. The maximal Δ/σ ratio in the final cycle of refinement was 0.4. The maximal and minimal residual electron densities in the difference Fourier map were to be found within −1.20 and 0.48 e $Å^{-3}$. Neutral atom scattering factors were taken from ref. 12. Real and imaginary components of anomalous dispersion were included for all the non-H atoms. Final atom parameters are listed in Table 1.

Results and Discussion

The addition of ethyl acetate to $ZrCl_4$ in n-hexane, gives a colourless air-sensitive compound formulated as [$Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2$].

$$2\,ZrCl_4 + 2\,CH_3COOEt \rightarrow \left[(CH_3COOEt)Cl_3Zr(\mu\text{-}Cl)_2ZrCl_3(CH_3COOEt)\right]$$

Table 1

Table 1

Final atomic parameters with esd's in parentheses for di-μ-chlorobis[trichloro(ethyl acetate)]dizirconium(IV)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	0.03225(6)	0.19379(8)	0.10181(8)	0.0556(5)	0.0316(4)	0.0331(4)	−0.0011(3)	0.0164(3)	−0.0002(3)
Cl(1)	−0.1264(2)	0.0329(3)	−0.0495(3)	0.048(1)	0.036(1)	0.050(2)	−0.0021(8)	0.0126(8)	0.0033(8)
Cl(2)	0.1927(2)	0.3168(3)	0.1965(3)	0.065(2)	0.058(2)	0.071(2)	−0.008(2)	0.018(2)	−0.011(2)
Cl(3)	−0.0816(2)	0.3834(3)	0.1013(3)	0.075(2)	0.043(2)	0.072(2)	−0.008(2)	0.033(2)	0.006(2)
Cl(4)	0.0393(3)	0.0869(3)	0.3384(3)	0.100(2)	0.068(2)	0.036(2)	0.005(2)	0.027(2)	−0.007(2)
O(1)	0.0195(5)	0.2438(7)	−0.1285(6)	0.075(4)	0.044(4)	0.037(3)	0.009(3)	0.025(3)	0.001(3)
O(2)	−0.0099(5)	0.3090(8)	−0.3687(7)	0.064(4)	0.078(5)	0.041(4)	0.011(4)	0.020(3)	0.000(4)
C(1)	0.1569(8)	0.2147(13)	−0.2288(13)	0.058(6)	0.079(8)	0.068(7)	0.010(6)	0.024(5)	0.005(6)
C(2)	0.0515(7)	0.2553(9)	−0.2370(9)	0.061(5)	0.035(4)	0.042(5)	−0.001(4)	0.020(4)	−0.007(4)
C(3)	−0.1165(8)	0.3543(13)	−0.3846(12)	0.055(6)	0.089(8)	0.066(7)	0.016(6)	0.024(5)	0.008(6)
C(4)	−0.1509(9)	0.4601(13)	−0.5122(13)	0.074(7)	0.085(9)	0.062(7)	0.019(6)	0.013(5)	0.010(7)

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(11)	0.217(9)	0.248(12)	−0.123(8)	0.25(9)	H(42)	−0.227(3)	0.492(7)	−0.517(8)	0.06(3)
H(12)	0.188(11)	0.241(13)	−0.318(13)	0.55(10)	H(43)	−0.159(6)	0.448(8)	−0.631(4)	0.12(5)
H(13)	0.162(9)	0.098(2)	−0.223(13)	0.13(5)	H(3)	−0.1681	0.2629	−0.4116	0.12(5)
H(41)	−0.104(4)	0.555(5)	−0.474(8)	0.05(3)	H(31)	−0.1160	0.4029	−0.2786	0.17(7)

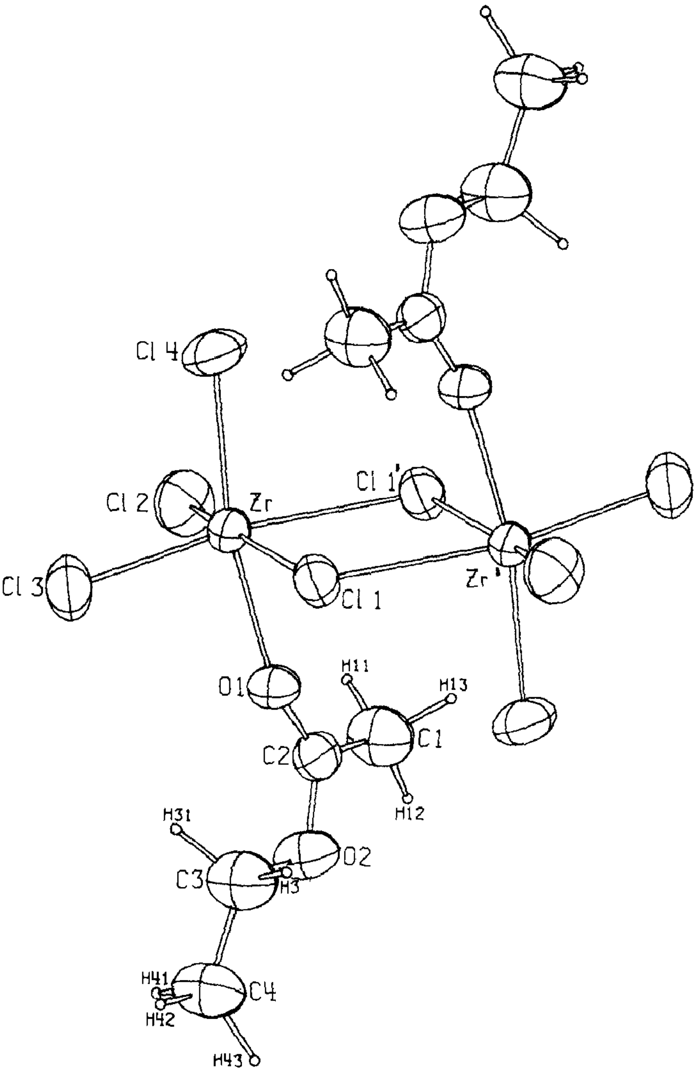

Fig. 1. The structure of $[Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$.

The new species is diamagnetic. The IR spectrum shows the stretching $\nu(C=O)$ mode at 1595 cm^{-1} (s,br), 1650 cm^{-1} (sh) and $\nu(C-O)$ at 1340 cm^{-1} (m). The crystal contains a centrosymmetric dimer. The overall view of $[Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ molecule and the numbering scheme are shown in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 2. The zirconium atoms are surrounded by two bridging and three terminal chlorine atoms, and by ethyl acetate molecules. The ethyl acetate molecules are coordinated by carbonyl oxygen atoms.

The Zr–Cl(terminal) bond lengths range from 2.362(3) to 2.379(3) Å, whereas the average Zr–Cl(bridge) distance is 2.611(3) Å. The Zr–Cl distances are similar to those found in $[Zr_2(\mu\text{-}Cl)_2Cl_6(SOCl_2)_2]$ [13]. In the isomorphous titanium $[Ti_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ compound the average Ti–Cl(terminal) bond length is

Table 2

Principal interatomic distances (Å), bond angles (°) and torsion angles (°) in di-μ-chlorobis[trichloro(ethyl acetate)]dizirconium(IV) [a]

Zr···Zr	4.030(4)	Zr–Cl(1)	2.608(3)
Zr–Cl(1^{i})	2.614(3)	Zr–Cl(2)	2.362(3)
Zr–Cl(3)	2.362(3)	Zr–Cl(4)	2.379(3)
Zr–O(1)	2.131(5)	O(1)–C(2)	1.238(10)
O(2)–C(2)	1.312(10)	O(2)–C(3)	1.482(12)
C(1)–C(2)	1.474(14)	C(3)–C(4)	1.483(16)
Cl(1)–Zr–Cl(1^{i})	79.0(1)	Cl(1)–Zr–Cl(2)	166.3(1)
Cl(1)–Zr–Cl(3)	90.2(1)	Cl(1)–Zr–Cl(4)	90.4(1)
Cl(1^{i})–Zr–Cl(2)	90.2(1)	Cl(1^{i})–Zr–Cl(3)	167.9(1)
Cl(1^{i})–Zr–Cl(4)	88.3(1)	Cl(2)–Zr–Cl(3)	99.7(1)
Cl(2)–Zr–Cl(4)	97.7(1)	Cl(3)–Zr–Cl(4)	97.2(1)
O(1)–Zr–Cl(1)	80.3(2)	O(1)–Zr–Cl(1^{i})	82.0(2)
O(1)–Zr–Cl(2)	89.9(2)	O(1)–Zr–Cl(3)	90.9(2)
O(1)–Zr–Cl(4)	167.7(2)	Zr–Cl(1)–Zr^{i}	101.0(1)
Zr–O(1)–C(2)	155.1(6)	C(2)–O(2)–C(3)	119.2(7)
O(1)–C(2)–O(2)	119.5(8)	O(1)–C(2)–C(1)	124.3(8)
O(2)–C(2)–C(1)	116.2(8)	O(2)–C(3)–C(4)	107.0(9)
C(4)–C(3)–O(2)–C(2)	157.4(12)	C(3)–O(2)–C(2)–C(1)	−179.1(9)
C(3)–O(2)–C(2)–O(1)	−0.2(11)	O(2)–C(2)–O(1)–Zr	−176.5(13)

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

2.225(5) Å and the average length of the Ti–Cl(bridge) bonds is 2.498(2) Å. The Zr–Cl bonds in our structure are 0.11–0.15 Å longer than the Ti–Cl bonds and this difference is similar to the difference in the octahedral radii of the Zr (1.48 Å) and of the Ti (1.36 Å) atoms [16]. The zirconium atom is 0.16(1) Å out of the plane formed by the four chlorine atoms Cl(1), Cl(1^{i}), Cl(2) and Cl(3), in the direction of the Cl(4) atom. The Cl(4)–Zr–Cl(2,3) angles are greater than 90°.

The ester group C(1), C(2), O(1), O(2) of the coordinated ethyl acetate molecule, is planar. The C(3) carbon atom is located in this plane. The methyl group C(1) is *trans* to the C(3) atom, and the C(2) is anti-clinal to the C(4) atom (see torsion angles in Table 2). All bond lengths and angles in the coordinated ethyl acetate molecule (see Table 2) are similar to those found in $[Ti_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ [3], $[(CH_3COOEt)_4Mg(\mu\text{-}Cl)_2TiCl_4]$ [15] and in $[Mg(CH_3COOEt)_6]^{2+}$ [8].

In $[M_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ (M = Zr, Ti) are found short intramolecular contacts between Cl(4) and C($2^{-x,-y,-z}$) atoms. In these dimeric complexes the titanium–titanium and zirconium–zirconium distances are 3.85(2) Å and 4.03(1) Å, respectively. However, the contacts between Cl(4) and C($2^{-x,-y,-z}$) atoms [3.41(1) Å and 3.436(9) Å for titanium and zirconium compounds, respectively] are similar. In the zirconium compound the M–M and M–Cl(1) distances exceed those in the titanium compound and for that reason the M–Cl(1)–M^{i} angles are the same. However, the change of the M–O(1) bond length is accompanied by a change in the M–O(1)–C(2) angle from 155.1(6)° in the Zr to 152.1(3)° in the Ti compound. This suggests the considerable effect of the intramolecular interactions on the structure of $[M_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ compounds.

In contrast to the intramolecular interactions between the chlorine and carbon atoms of the compounds described, intermolecular interactions between the chlorine and carbon atoms of the coordinated carbonyl group in crystalline $\{Cl_4Ti[\mu$-*m*-

$C_6H_4(COOEt)_2]_2TiCl_4\}$ have been observed [5]. Such interactions could be a reason for the stereospecific propylene polymerization process. This conclusion, however, requires further experimental confirmation.

Supplementary material available. A table of observed and calculated structure factors for $[Zr_2(\mu\text{-}Cl)_2Cl_6(CH_3COOEt)_2]$ (11 pages) is available from the authors.

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