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### Structure of Di- $\mu$ -chloro-bis[(allyl acetate-*O*)]trichlorotitanium(IV) at 80 K

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## Abstract

In the centrosymmetric dimer molecules each of the Ti atoms is bonded to two bridging Cl atoms, three terminal Cl atoms and one carbonyl O atom of the allyl acetate molecule in a distorted octahedral environment with a Ti···Ti distance of 3.851 (4) Å. The title crystals are isostructural with those of di- $\mu$ -chloro-bis[(ethyl acetate)trichlorotitanium(IV)] and di- $\mu$ -chloro-bis[(ethyl acetate)trichlorozirconium(IV)].

## Comment

The presence of ester as both an internal and an external donor is essential to improve the stereospecificity of high-activity systems for olefin polymerization based on  $AlR_3$  and titanium halides supported on activated  $MgCl_2$  (Giannini, Giunchi, Albizzati & Barbé, 1987). The formation of dimeric compounds of the formula  $M_2(\mu-Cl)_2Cl_6(CH_3COOEt)_2$  ( $M = Ti, Zr$ ) from titanium (Brun, 1966) and zirconium (Sobota, Mustafa & Lis, 1989) tetrachlorides and ethyl acetate is well documented. To discover whether the preference of the coordination centre on the catalyst metal site was for the carbonyl O atom or the C=C double bond, the reaction of  $TiCl_4$  with allyl acetate ( $CH_3CO_2CH_2CH=CH_2$ ) was studied.

In the crystalline adduct (1:1) of titanium tetrachloride and allyl acetate the Ti atoms are surrounded by three terminal Cl atoms, two bridging Cl atoms and one carbonyl O atom of the allyl acetate ligand forming an edge-sharing

di-octahedron. The allyl acetate molecules are coordinated via carbonyl O atoms with the O(1) atom situated *cis* to the bridging Cl(1) and Cl(1') atoms. The Ti atom is 0.15 (1) Å out of the plane formed by the four Cl atoms, Cl(1), Cl(1'), Cl(2) and Cl(3), towards the O(1) atom. The torsion angle Ti—O(1)—C(2)—C(1) is  $-8.7(7)^\circ$  and the Ti—O(1)—C(2) bond angle is  $153.2(2)^\circ$ . In the ligand molecule, the planes through O(1), C(2), C(1), O(2) and C(3), C(4), C(5) are tilted by  $133.7(8)^\circ$  to each other. The C(4)—C(5) bond distance of 1.308 (4) Å is typical of a C=C bond length. The methyl group C(1) is *trans* to the C(3) atom and the C(5) atom is antiperiplanar to the O(2) atom. All Ti—ligand and Ti···Ti' distances are similar to those reported for  $Ti_2(\mu-Cl)_2Cl_6(CH_3COOEt)_2$  (Brun, 1966). However, the C(2)···Cl(4') intramolecular distance in the allyl acetate complex, 3.268(4) Å, is shorter than the respective C(9)···Cl(5') intramolecular distance of 3.41 (1) Å in the ethyl acetate complex.

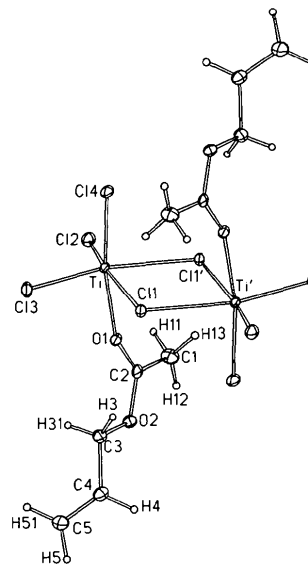


Fig. 1. The molecular structure of the di- $\mu$ -chlorobis[(allyl acetate-*O*)]trichlorotitanium(IV) molecule.

The pentacoordinate  $[TiCl_4(CH_3CO_2CH_2CH=CH_2)]$  complex is probably intermediate in the formation of dimeric di- $\mu$ -chloro-bis[(allyl acetate-*O*)]trichlorotitanium(IV). The dimerization of the pentacoordinate species occurs through chlorine bridges to compensate for the lack of electron density on the Ti atom even in the presence of allyl acetate. It follows that the titanium metal site prefers Cl and carbonyl O atoms to C=C double bonds. Similar behaviour was observed in the  $TiCl_4$  complex with acrylate (Poll, Metter & Helmchen, 1985) in which the Ti atom forms a seven-membered ring with the ester molecule through the two carbonyl O atoms of the ligand, leaving the C=C double bond uncoordinated.

In the following experimental details, crystal data collected at 300 K are given in brackets.

## Experimental

Crystal data (at 300 K in square brackets)

[TiCl<sub>4</sub>(C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub>]<sub>2</sub>  
*M<sub>r</sub>* = 579.7  
 Monoclinic  
*P*2<sub>1</sub>/*a*  
*a* = 13.381 (12)  
 [13.588 (9)] Å  
*b* = 8.910 (9) [9.141 (7)] Å  
*c* = 9.178 (9) [9.364 (9)] Å  
 $\beta$  = 101.27 (9) [102.55 (7)]°  
*V* = 1073.1 (19)  
 [1135.3 (17)] Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.794 (4)  
 [1.696 (3)] Mg m<sup>-3</sup>

*D<sub>m</sub>* = [1.69] Mg m<sup>-3</sup>  
 Density measured by flotation in CCl<sub>4</sub>-C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>  
 Mo *K*α radiation  
 $\lambda$  = 0.7093 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 10–12°  
 $\mu$  = 1.73 [1.64] mm<sup>-1</sup>  
*T* = 80 (1) [300 (2)] K  
 Columnar habit  
 0.5 × 0.4 × 0.4 mm  
 Yellow

## Data collection

Kuma KM4 automated four-circle  $\kappa$ -axis diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical (DIFABS; Walker & Stuart, 1983)  
*T<sub>min</sub>* = 0.927, *T<sub>max</sub>* = 1.114  
 2515 measured reflections  
 2412 independent reflections

2258 observed reflections  
 $[F > 6.0\sigma(F)]$   
*R<sub>int</sub>* = 0.017  
 $\theta_{\max}$  = 28°  
*h* = 0 → 14  
*k* = 0 → 11  
*l* = -12 → 11  
 3 standard reflections monitored every 100 reflections  
 intensity variation: -5%

## Refinement

Refinement on *F*  
*R* = 0.0258  
*wR* = 0.0280  
 2168 reflections  
 141 parameters  
 All H-atom parameters refined  
 Calculated weights  
 $w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} = 0.09$   
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{Å}^{-3}$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Ti	0.02786 (4)	0.19276 (5)	0.09401 (5)	0.0091 (2)
Cl(1)	-0.11888 (5)	0.03580 (7)	-0.03146 (7)	0.0101 (2)
Cl(2)	0.17560 (5)	0.31044 (7)	0.16395 (7)	0.0141 (2)
Cl(3)	-0.07986 (6)	0.37790 (7)	0.10842 (7)	0.0140 (2)
Cl(4)	0.02141 (6)	0.08821 (7)	0.31313 (7)	0.0137 (2)
O(1)	0.02809 (15)	0.2461 (2)	-0.12001 (18)	0.0110 (6)
O(2)	0.01256 (15)	0.2936 (2)	-0.35898 (19)	0.0122 (6)
C(1)	0.1727 (3)	0.2076 (4)	-0.2341 (3)	0.0167 (10)
C(2)	0.0670 (2)	0.2499 (3)	-0.2323 (3)	0.0118 (9)
C(3)	-0.0945 (2)	0.3278 (3)	-0.3594 (3)	0.0134 (9)
C(4)	-0.1461 (2)	0.3568 (3)	-0.5151 (3)	0.0147 (9)
C(5)	-0.2061 (3)	0.4717 (4)	-0.5547 (3)	0.0202 (10)

Table 2. Geometric parameters (Å, °)

Ti...Ti <sup>1</sup>	3.851 (4)	O(1)—C(2)	1.243 (3)
Ti—Cl(1)	2.501 (2)	C(1)—C(2)	1.467 (5)
Ti—Cl(1 <sup>1</sup> )	2.497 (2)	O(2)—C(2)	1.305 (3)
Ti—Cl(2)	2.219 (2)	O(2)—C(3)	1.464 (4)

Ti—Cl(3)	2.212 (2)	C(3)—C(4)	1.483 (4)
Ti—Cl(4)	2.233 (2)	C(4)—C(5)	1.308 (4)
Ti—O(1)	2.022 (2)		
Cl(1)—Ti—Cl(1 <sup>1</sup> )	79.2 (1)	O(1)—Ti—Cl(2)	90.0 (1)
Cl(1)—Ti—Cl(2)	166.5 (1)	O(1)—Ti—Cl(3)	90.4 (1)
Cl(1)—Ti—Cl(3)	89.0 (1)	O(1)—Ti—Cl(4)	168.7 (1)
Cl(1)—Ti—Cl(4)	90.9 (1)	Ti <sup>1</sup> —Cl(1)—Ti	100.8 (1)
Cl(1 <sup>1</sup> )—Ti—Cl(2)	90.3 (1)	Ti—O(1)—C(2)	153.2 (2)
Cl(1 <sup>1</sup> )—Ti—Cl(3)	167.2 (1)	O(1)—C(2)—O(2)	119.7 (3)
Cl(1 <sup>1</sup> )—Ti—Cl(4)	88.5 (1)	O(1)—C(2)—C(1)	124.3 (3)
Cl(2)—Ti—Cl(3)	100.6 (1)	O(2)—C(2)—C(1)	116.0 (3)
Cl(2)—Ti—Cl(4)	97.2 (1)	C(2)—O(2)—C(3)	116.1 (3)
Cl(3)—Ti—Cl(4)	96.7 (1)	O(2)—C(3)—C(4)	108.0 (3)
O(1)—Ti—Cl(1)	80.5 (1)	C(3)—C(4)—C(5)	123.3 (3)
O(1)—Ti—Cl(1 <sup>1</sup> )	82.8 (1)		
Ti—O(1)—C(2)—C(1)	-8.7 (7)	C(2)—O(2)—C(3)—C(4)	-173.2 (5)
Ti—O(1)—C(2)—O(2)	171.2 (5)	O(2)—C(3)—C(4)—C(5)	-132.9 (6)
O(1)—C(2)—O(2)—C(3)	-3.2 (5)	C(1)—C(2)—O(2)—C(3)	176.7 (4)

Symmetry code: (i) -x, -y, -z.

4 g (40 mmol) of allyl acetate was added dropwise to a solution of 7.6 g (40 mmol) of TiCl<sub>4</sub> in 50 cm<sup>3</sup> dichloromethane and stirred. After 1 h the solution was evaporated under vacuum to 20 cm<sup>3</sup> and left at 273 K. After one week yellow columnar crystals appeared. Oscillation and Weissenberg photographs as well as preliminary diffractometer data collection suggested that the title compound was isostructural with di- $\mu$ -chlorobis[trichloro(ethyl acetate)zirconium(IV)] crystals (Sobota, Mustafa & Lis, 1989).

A crystal was sealed in a glass capillary and diffractometer data were collected at 300 (2) K. Two standard reflections decreased approximately 60% over the period of data collection and the data were rescaled using the intensities of the standards.

The refinement was started by using the published coordinates for the heavy atoms of the Zr<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>Cl<sub>6</sub>(CH<sub>3</sub>COOEt)<sub>2</sub> crystal. Most of the final thermal parameters for the ester atoms were very high and the bond lengths were rather unrealistic. We decided, therefore, to obtain new diffractometer data at 80 K. Three standard reflections dropped to 95% of their initial values. Data were corrected for crystal decay. The refinement was started using the coordinates for heavy atoms of the room-temperature data.

The H atoms were found from a difference map and refined isotropically. Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Data collection: *Kuma KM4 Software* (Kuma Diffraction, 1989).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71407 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1046]

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**Structure of *cyclo*-Hexakis[*bis*- $\mu$ -(methoxycarbonylmethylthiolato)-palladium(II)], [Pd(SCH<sub>2</sub>COOCH<sub>3</sub>)<sub>2</sub>]<sub>6</sub>**

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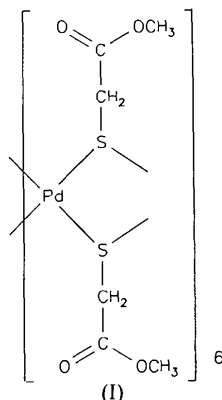
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**Abstract**

The title compound, [Pd(C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>S)<sub>2</sub>]<sub>6</sub>, results from the reaction of PdCl<sub>4</sub><sup>2-</sup> and thioglycolic acid in CH<sub>3</sub>OH. It forms a centrosymmetric hexameric structure of a cyclic ribbon in which the square-planar-coordinated Pd<sup>2+</sup> ions are bridged by the S atoms of the deprotonated thioglycolic acid methyl esters. The Pd—S distances are in the range 2.309 (1)–2.324 (1) Å.

**Comment**

In connection with our attempts to use thioglycolic acid as a ligand in metal complexes we investigated the reaction of thioglycolic acid with PdCl<sub>4</sub><sup>2-</sup> and obtained the new hexameric complex (I).



In the hexanuclear complex (I), the Pd<sup>II</sup> centres are bridged by the S atoms of the deprotonated thiolate group of the thioglycolic acid methyl ester ligand, SCH<sub>2</sub>COOCH<sub>3</sub><sup>-</sup>, forming a centrosymmetric cyclic ribbon of PdS<sub>4</sub> groups (Fig. 1). The coordination of the Pd<sup>2+</sup> ions is approximately square planar with a maximum deviation from the best planes through the PdS<sub>4</sub> groups of 0.169 (1) Å (S2 in the coordination plane of Pd2) and bond angles S—Pd—S between 81.74 (5) and 98.56 (5)° (Table 2). The Pd—S distances within the symmetrical Pd—S—Pd bridges are in the narrow range 2.309 (1)–2.324 (1) Å and correspond to covalent single bonds. The PdS<sub>4</sub> coordination planes forming the cyclic ribbon are inclined to each other by 113.47 (3)–124.36 (4)°, resulting in Pd...Pd distances of 3.0495 (6)–3.1439 (6) Å. Hexa-

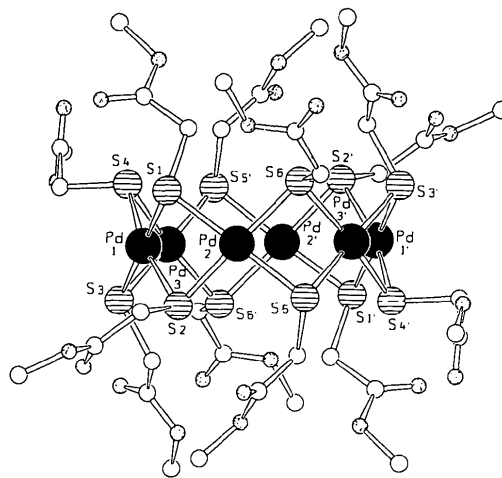


Fig. 1. A perspective view of [Pd(SCH<sub>2</sub>COOCH<sub>3</sub>)<sub>2</sub>]<sub>6</sub> with atomic numbering.

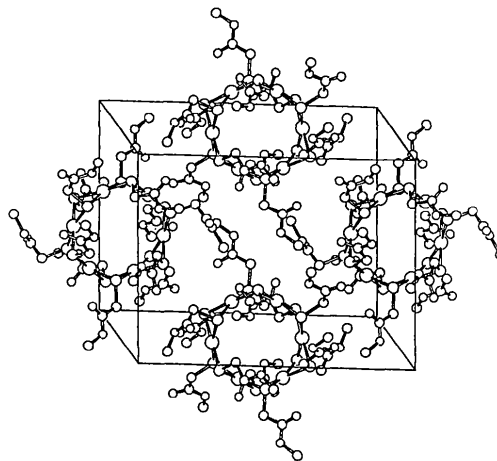


Fig. 2. Packing diagram.