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Structure of an Erbium Complex with L-Proline

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Abstract

In the structure of *catena*-poly[{triaqua(L-proline-*O*)erbium(III)}-bis-μ-(L-proline-*O:O'*)-{triaqua-(L-proline-*O*)erbium(III)}-bis-μ-(L-proline-*O:O'*) hexaperchlorate], each Er^{3+} ion is coordinated by five carboxyl O atoms from the L-proline molecules and three water molecules. Four of the six L-proline
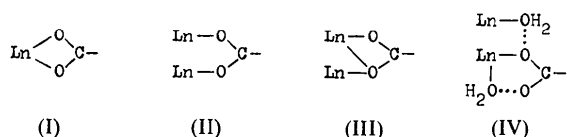
molecules act as bidentate bridging ligands to link the Er^{3+} ions through the carboxyl groups, thus producing a one-dimensional chain structure. The other two ligands coordinate unidentately to the rare-earth ions. Hydrogen bonds formed between the coordinated water molecules and between the water and unidentate proline ligand stabilize the polymeric chain.

Comment

There is an increasing interest in the stereochemistry of rare-earth ion–amino acid interactions in order to gain understanding into the biological effects of rare-earth elements. The present structure determination was undertaken as part of crystallographic studies of rare-earth (Ln^{3+}) complexes with amino acids. We reported recently the structure of a praseodymium complex with L-proline in the monoclinic form (Wang, Hu, Niu & Ni, 1993), which is isostructural with a neodymium complex previously reported by Legendziewicz, Głowiak, Huskowska & Dao (1988). The title complex crystallizes in the triclinic system and shows a different bonding mode for the amino acid to rare-earth ion bond.

In the structure, the L-proline molecule exists in its zwitterion form with the carboxyl group deprotonated and the N atom protonated. Unlike Pr^{3+}–proline (Wang *et al.*, 1993) and Nd^{3+}–proline complexes (Legendziewicz *et al.*, 1988) in which the Ln^{3+} ions are bridged alternately by four and two bidentate ligands to form a linear polymer, the title compound has two proline ligands bridging Er(1) and Er(2) by their carboxyl groups and the other two ligands bridging Er(2) and Er(1^{ii}) (*x*, *y*, *z* + 1), thus creating a one-dimensional chain in the **c** direction. The Er⋯Er separations are approximately equal [4.980 (1) and 4.951 (1) Å], differing obviously from those found in the Pr^{3+} complex [Pr⋯Pr = 4.596 (1) and 5.323 (1) Å]. The remaining two proline molecules coordinate to the rare-earth ions as unidentate ligands. Each Er^{3+} ion is also coordinated by three water molecules to complete an eight-coordination dodecahedron. The average $Er—O_{carboxyl}$ bond length is 2.32 (2) Å and the average $Er—O_{water}$ bond length is 2.41 (2) Å. The differences in $Ln—O_{carboxyl}$ distances between this structure, and those of the monoclinic Pr^{3+} [2.44 (1) Å] and Nd^{3+} [2.42 (2) Å] complexes, in which the coordination polyhedra consist of six carboxyl O atoms and two water molecules, correspond well with the reduction of ionic radius from Pr^{3+} or Nd^{3+} to Er^{3+} [ionic radii: 1.126 for Pr^{3+}, 1.109 for Nd^{3+} and 1.004 Å for Er^{3+} (Shannon, 1976)]. The differences in $Ln—O_{water}$ distances [2.58 (2) for Pr^{3+} and 2.56 (2) Å for Nd^{3+} complexes] are significantly larger than the change of ionic radii.

Although the present complex has the same type of polymeric chain as the Pr^{3+} and Nd^{3+} complexes, the bonding mode of the carboxyl groups is different. In the known Ln^{3+}-amino acid complexes, the carboxyl groups are bonded to Ln^{3+} ions in three modes: bidentate chelating (I) (Jin, Sun, Xu, Ma & Shi, 1990), bidentate bridging (II), as observed in the Pr^{3+}-proline complex, and chelating and bridging (III) (Liu, Hu, Niu & Meng, 1992). The bonding mode (IV) found here, to our knowledge, is the first observation in rare-earth ion–amino acid structures.

(I)   (II)   (III)   (IV)

A proline molecule coordinates unidentately to an Er^{3+} ion through its carboxyl group while at the same time accepting two hydrogen bonds, one from the water ligand in the same coordination sphere and one from the neighbouring coordination sphere. As shown in Table 2, hydrogen bonding also occurs between the water ligands. They associate the coordination polyhedra around Er(1) and Er(2) with each other and further stabilize the polymeric chain.

The perchlorate anions fill the voids between the polymeric chains to make the compound neutral and hold the chains together by accepting hydrogen bonds from the N-atom groups and the water ligands.
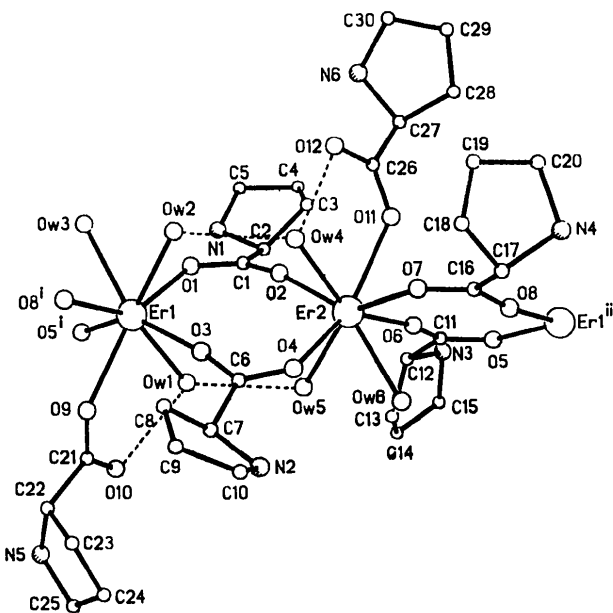
Experimental

Crystal data

$[Er_2(C_5H_9NO_2)_6(H_2O)_6]$.-6ClO$_4$
$M_r = 1730.11$
Triclinic
$P\bar{1}$
$a = 13.003 (3)$ Å
$b = 13.639 (4)$ Å
$c = 9.861 (2)$ Å
$\alpha = 110.26 (2)°$
$\beta = 100.94 (2)°$
$\gamma = 109.35 (2)°$
$V = 1453.5 (6)$ Å^3
$Z = 1$
$D_x = 1.976$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.5$- $14.2°$
$\mu = 3.36$ mm^{-1}
$T = 294$ K
Columnar
$0.61 \times 0.32 \times 0.30$ mm
Light pink
Crystal source: aqueous solution of $Er(ClO_4)_3$ and L-proline

Data collection

Nicolet $R3m/E$ diffractometer
ω scans
Absorption correction: empirical
$T_{min} = 0.888$, $T_{max} = 0.973$
4789 measured reflections
4779 independent reflections
4642 observed reflections
$[F_o > 3\sigma(F_o)]$

$R_{int} = 0.011$
$\theta_{max} = 25°$
$h = 0 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -11 \rightarrow 11$
1 standard reflection monitored every 69 reflections
intensity variation: 3.3%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.028$
$S = 1.52$
4642 reflections
766 parameters
$w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$

$(\Delta/\sigma)_{max} = 0.31$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Fig. 1. Perspective view of the polymeric chain structure of the title complex. Broken lines denote hydrogen bonds.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Er(1)	0.0	0.0	0.0	0.0227 (1)
Er(2)	0.04310 (3)	−0.00607 (3)	0.50939 (3)	0.0231 (1)
O(1)	−0.1569 (4)	−0.1223 (4)	0.0342 (5)	0.033 (2)
O(2)	−0.0940 (4)	−0.1003 (4)	0.2728 (5)	0.036 (2)
N(1)	−0.3807 (6)	−0.2391 (6)	−0.0166 (7)	0.051 (3)
C(1)	−0.1715 (5)	−0.1328 (5)	0.1517 (7)	0.021 (3)
C(2)	−0.2954 (6)	−0.1846 (6)	0.1466 (7)	0.033 (3)
C(3)	−0.3262 (9)	−0.2805 (8)	0.199 (1)	0.047 (5)
C(4)	−0.4548 (8)	−0.3456 (7)	0.117 (1)	0.062 (5)
C(5)	−0.4801 (9)	−0.346 (1)	−0.039 (1)	0.084 (6)
O(3)	0.1280 (4)	0.0851 (4)	0.2385 (5)	0.041 (2)
O(4)	0.2044 (4)	0.1241 (4)	0.4838 (5)	0.032 (2)
N(2)	0.3890 (6)	0.3217 (6)	0.5503 (7)	0.056 (3)
C(6)	0.2053 (6)	0.1466 (5)	0.3735 (7)	0.030 (3)
C(7)	0.3068 (7)	0.2482 (6)	0.3874 (8)	0.037 (4)
C(8)	0.382 (1)	0.218 (1)	0.293 (1)	0.075 (6)
C(9)	0.504 (1)	0.300 (1)	0.393 (1)	0.102 (8)
C(10)	0.5013 (8)	0.341 (1)	0.546 (1)	0.090 (7)
O(5)	−0.1468 (6)	0.0095 (6)	0.8369 (7)	0.030 (3)

O(6)	−0.0793 (4)	−0.0041 (4)	0.6439 (5)	0.035 (2)
N(3)	−0.3470 (5)	0.0031 (5)	0.6882 (7)	0.037 (3)
C(11)	−0.1514 (5)	0.0082 (5)	0.7069 (7)	0.022 (3)
C(12)	−0.2454 (6)	0.0347 (6)	0.6270 (8)	0.034 (3)
C(13)	−0.2110 (8)	0.1548 (9)	0.658 (1)	0.063 (6)
C(14)	−0.315 (1)	0.176 (1)	0.666 (2)	0.105 (9)
C(15)	−0.3759 (9)	0.1034 (8)	0.729 (1)	0.060 (5)
O(7)	0.1746 (7)	−0.0256 (6)	0.6759 (7)	0.038 (3)
O(8)	0.1393 (4)	−0.0006 (4)	0.8922 (5)	0.034 (2)
N(4)	0.2720 (6)	−0.1097 (5)	0.9526 (6)	0.036 (3)
C(16)	0.1972 (6)	−0.0215 (6)	0.8060 (7)	0.031 (3)
C(17)	0.3046 (6)	−0.0331 (6)	0.8688 (7)	0.027 (3)
C(18)	0.3407 (7)	−0.1027 (8)	0.7487 (9)	0.044 (4)
C(19)	0.266 (1)	−0.2238 (8)	0.701 (1)	0.071 (6)
C(20)	0.223 (1)	−0.2355 (7)	0.830 (1)	0.066 (5)
O(9)	0.0878 (4)	0.1910 (4)	0.0164 (5)	0.031 (2)
O(10)	−0.0106 (5)	0.2900 (5)	0.0979 (7)	0.057 (3)
N(5)	0.0970 (8)	0.4652 (6)	0.0403 (9)	0.060 (5)
C(21)	0.0677 (7)	0.2785 (6)	0.0509 (8)	0.036 (3)
C(22)	0.1493 (8)	0.3815 (6)	0.037 (1)	0.048 (4)
C(23)	0.2629 (9)	0.452 (1)	0.166 (2)	0.14 (1)
C(24)	0.246 (1)	0.547 (1)	0.276 (1)	0.119 (8)
C(25)	0.161 (1)	0.5669 (9)	0.186 (2)	0.094 (7)
O(11)	−0.0577 (4)	−0.2006 (4)	0.4906 (5)	0.037 (2)
O(12)	−0.0183 (5)	−0.3183 (4)	0.3053 (7)	0.054 (3)
N(6)	−0.2095 (7)	−0.5043 (6)	0.2303 (8)	0.051 (4)
C(26)	−0.0753 (7)	−0.2999 (6)	0.3934 (8)	0.036 (4)
C(27)	−0.1700 (7)	−0.4051 (6)	0.3858 (8)	0.038 (4)
C(28)	−0.123 (1)	−0.4487 (7)	0.496 (1)	0.090 (7)
C(29)	−0.169 (1)	−0.5752 (9)	0.407 (1)	0.095 (7)
C(30)	−0.202 (1)	−0.6032 (7)	0.250 (1)	0.067 (5)
O(W1)	−0.0762 (4)	0.1132 (4)	0.1630 (5)	0.032 (2)
O(W2)	0.0661 (4)	−0.1389 (4)	0.0485 (5)	0.032 (2)
O(W3)	−0.0896 (4)	−0.1828 (4)	−0.2282 (5)	0.036 (2)
O(W4)	0.1189 (4)	−0.1187 (4)	0.3455 (5)	0.031 (2)
O(W5)	−0.0191 (5)	0.1264 (4)	0.4616 (5)	0.035 (2)
O(W6)	0.1385 (4)	0.1712 (4)	0.7392 (5)	0.036 (2)
Cl(1)	0.4646 (2)	0.3123 (2)	0.9355 (2)	0.052 (1)
O(13)	0.394 (1)	0.3506 (8)	0.862 (1)	0.088 (5)
O(14)†	0.384 (1)	0.221 (1)	0.954 (2)	0.090 (4)
O(15)†	0.534 (1)	0.399 (1)	1.090 (1)	0.085 (3)
O(16)†	0.541 (2)	0.292 (2)	0.864 (2)	0.160 (7)
O(14′)†	0.433 (2)	0.314 (3)	1.061 (2)	0.18 (1)
O(15′)†	0.584 (1)	0.383 (2)	0.950 (2)	0.104 (8)
O(16′)†	0.441 (2)	0.203 (1)	0.809 (2)	0.080 (6)
Cl(2)	−0.4252 (2)	−0.3290 (2)	−0.4117 (3)	0.069 (1)
O(17)	−0.3338 (8)	−0.3306 (8)	−0.3051 (9)	0.078 (5)
O(18)†	−0.512 (1)	−0.434 (1)	−0.520 (2)	0.109 (6)
O(19)†	−0.458 (1)	−0.244 (1)	−0.317 (1)	0.051 (3)
O(20)†	−0.362 (2)	−0.255 (2)	−0.483 (3)	0.129 (9)
O(18′)†	−0.527 (1)	−0.430 (1)	−0.426 (2)	0.074 (4)
O(19′)†	−0.448 (2)	−0.234 (1)	−0.376 (2)	0.123 (7)
O(20′)†	−0.434 (2)	−0.383 (2)	−0.571 (2)	0.109 (6)
Cl(3)	0.1568 (2)	0.4442 (2)	0.6657 (3)	0.064 (1)
O(21)	0.2242 (8)	0.5253 (6)	0.8225 (8)	0.100 (5)
O(22)	0.0510 (7)	0.3653 (6)	0.667 (1)	0.092 (5)
O(23)	0.206 (1)	0.3731 (9)	0.602 (1)	0.148 (8)
O(24)	0.1269 (9)	0.5024 (7)	0.586 (1)	0.111 (6)
Cl(4)	−0.1446 (2)	−0.4641 (2)	−0.1068 (2)	0.047 (1)
O(25)	−0.1308 (6)	−0.5348 (5)	−0.0314 (7)	0.062 (3)
O(26)	−0.2174 (7)	−0.5325 (7)	−0.2571 (8)	0.088 (4)
O(27)	−0.198 (1)	−0.3973 (9)	−0.030 (1)	0.110 (7)
O(28)	−0.0340 (7)	−0.3911 (6)	−0.0940 (9)	0.098 (5)
Cl(5)	−0.3812 (2)	0.0488 (2)	0.1177 (2)	0.045 (1)
O(29)	−0.3039 (7)	0.0831 (8)	0.2657 (7)	0.094 (5)
O(30)	−0.4740 (6)	−0.0616 (6)	0.0695 (8)	0.076 (4)
O(31)	−0.4282 (7)	0.1238 (7)	0.101 (1)	0.121 (6)
O(32)	−0.3175 (6)	0.0322 (7)	0.0182 (8)	0.084 (5)
Cl(6)	0.3928 (2)	−0.1193 (3)	0.3171 (3)	0.058 (1)
O(33)	0.5026 (7)	−0.1115 (8)	0.3715 (8)	0.102 (5)
O(34)	0.3357 (7)	−0.2055 (7)	0.1642 (7)	0.095 (5)
O(35)	0.395 (1)	−0.017 (1)	0.317 (1)	0.156 (9)
O(36)	0.3275 (9)	−0.155 (1)	0.406 (1)	0.121 (7)

† Disordered O atoms, refined isotropically with occupancy factors of 0.65 for O(14)-O(16), 0.35 for O(14′)-O(16′) and 0.5 for O(18)-O(20′).

Table 2. Geometric parameters (Å, °)

Er(1)—O(1)	2.335 (5)	Er(2)—O(2)	2.258 (4)
Er(1)—O(3)	2.235 (4)	Er(2)—O(4)	2.378 (5)
Er(1)—O(5^i)	2.322 (8)	Er(2)—O(6)	2.257 (6)
Er(1)—O(8^i)	2.269 (6)	Er(2)—O(7)	2.287 (9)
Er(1)—O(9)	2.405 (5)	Er(2)—O(11)	2.460 (5)
Er(1)—O(W1)	2.419 (6)	Er(2)—O(W4)	2.414 (6)
Er(1)—O(W2)	2.471 (6)	Er(2)—O(W5)	2.356 (6)
Er(1)—O(W3)	2.415 (4)	Er(2)—O(W6)	2.382 (4)
O(1)—Er(1)—O(3)	98.9 (2)	O(2)—Er(2)—O(4)	104.3 (2)
O(1)—Er(1)—O(5^i)	82.3 (2)	O(2)—Er(2)—O(6)	96.7 (2)
O(1)—Er(1)—O(8^i)	142.2 (2)	O(2)—Er(2)—O(7)	143.3 (2)
O(1)—Er(1)—O(9)	142.4 (2)	O(2)—Er(2)—O(11)	77.7 (2)
O(1)—Er(1)—O(W1)	70.1 (2)	O(2)—Er(2)—O(W4)	74.8 (2)
O(1)—Er(1)—O(W2)	76.1 (2)	O(2)—Er(2)—O(W5)	71.6 (2)
O(1)—Er(1)—O(W3)	73.1 (2)	O(2)—Er(2)—O(W6)	144.4 (2)
O(3)—Er(1)—O(5^i)	144.9 (2)	O(4)—Er(2)—O(6)	140.2 (2)
O(3)—Er(1)—O(8^i)	92.6 (2)	O(4)—Er(2)—O(7)	87.1 (2)
O(3)—Er(1)—O(9)	82.7 (2)	O(4)—Er(2)—O(11)	146.9 (2)
O(3)—Er(1)—O(W1)	74.1 (2)	O(4)—Er(2)—O(W4)	71.9 (2)
O(3)—Er(1)—O(W2)	70.0 (2)	O(4)—Er(2)—O(W5)	75.0 (2)
O(3)—Er(1)—O(W3)	186 (2)	O(4)—Er(2)—O(W6)	70.5 (2)
O(5^i)—Er(1)—O(8^i)	107.9 (2)	O(6)—Er(2)—O(7)	95.9 (3)
O(5^i)—Er(1)—O(9)	76.0 (2)	O(6)—Er(2)—O(11)	70.3 (2)
O(5^i)—Er(1)—O(W1)	73.5 (2)	O(6)—Er(2)—O(W4)	147.3 (2)
O(5^i)—Er(1)—O(W2)	142.2 (2)	O(6)—Er(2)—O(W5)	80.2 (2)
O(5^i)—Er(1)—O(W3)	74.1 (2)	O(6)—Er(2)—O(W6)	72.7 (2)
O(8^i)—Er(1)—O(9)	74.6 (2)	O(7)—Er(2)—O(11)	74.4 (2)
O(8^i)—Er(1)—O(W1)	147.5 (2)	O(7)—Er(2)—O(W4)	76.0 (2)
O(8^i)—Er(1)—O(W2)	74.3 (2)	O(7)—Er(2)—O(W5)	144.7 (2)
O(8^i)—Er(1)—O(W3)	75.1 (2)	O(7)—Er(2)—O(W6)	72.4 (2)
O(9)—Er(1)—O(W1)	74.4 (2)	O(11)—Er(2)—O(W4)	77.0 (2)
O(9)—Er(1)—O(W2)	137.2 (2)	O(11)—Er(2)—O(W5)	134.1 (2)
O(9)—Er(1)—O(W3)	127.6 (2)	O(11)—Er(2)—O(W6)	126.4 (2)
O(W1)—Er(1)—O(W2)	125.2 (2)	O(W4)—Er(2)—O(W5)	124.3 (2)
O(W1)—Er(1)—O(W3)	133.4 (2)	O(W4)—Er(2)—O(W6)	131.3 (2)
O(W2)—Er(1)—O(W3)	70.1 (2)	O(W5)—Er(2)—O(W6)	73.0 (2)

D	A	$D \cdots A$	$H \cdots A$	$D—H \cdots A$
O(W1)	O(10)	2.621 (9)	1.66	165
O(W2)	O(W4)	2.771 (8)	1.75	173
O(W3)	O(11^i)	2.821 (9)	1.93	160
O(W4)	O(12)	2.552 (9)	1.62	162
O(W5)	O(W1)	2.823 (8)	1.84	176
O(W6)	O(9^{ii})	2.875 (9)	1.98	164

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, z + 1$.

The structure was solved by heavy-atom methods and refined by block-diagonal least squares. Two perchlorate groups were found to be disordered in the mode of rotation around either the Cl(1)—O(13) or the Cl(2)—O(17) bond. The occupancy factors for the disordered atoms, each in two positions, were estimated on the basis of their electron densities. The disordered atoms were refined isotropically and the remaining non-H atoms anisotropically. The H atoms were added to the structure in calculated positions, except for those attached to water molecules, which were located from difference Fourier maps. All H atoms were fixed in the final cycles of refinement with isotropic thermal parameters ($U = 0.06$ Å^2). The absolute configuration was assigned to agree with the known chirality of L-proline. All calculations were performed using the SHELXTL program system (Sheldrick, 1983).

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Structure of Di-μ-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-μ-chloro-bis[(ethyl acetate)trichlorotitanium(IV)] and di-μ-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(μ-Cl)$_2$Cl$_6$(CH$_3$COOEt)$_2$ (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

dioctahedron. 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^i) atoms. The Ti atom is 0.15 (1) Å out of the plane formed by the four Cl atoms, Cl(1), Cl(1^i), Cl(2) and Cl(3), towards the O(1) atom. The torsion angle Ti—O(1)—C(2)—C(1) is −8.7 (7)° and the Ti—O(1)—C(2) bond angle is 153.2 (2)°. 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)° 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 anticlinal to the O(2) atom. All Ti–ligand and Ti···Ti^i distances are similar to those reported for Ti$_2$(μ-Cl)$_2$Cl$_6$(CH$_3$COOEt)$_2$ (Brun, 1966). However, the C(2)···Cl(4^i) intramolecular distance in the allyl acetate complex, 3.268(4) Å, is shorter than the respective C(9)···Cl(5^i) intramolecular distance of 3.41 (1) Å in the ethyl acetate complex.
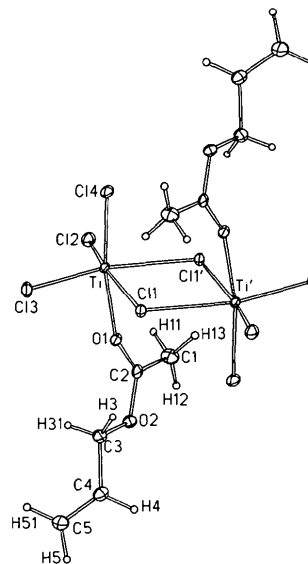

Fig. 1. The molecular structure of the di-μ-chlorobis[(allyl acetate-*O*)-trichlorotitanium(IV)] molecule.

The pentacoordinate [TiCl$_4$(CH$_3$CO$_2$CH$_2$CH=CH$_2$)] complex is probably intermediate in the formation of dimeric di-μ-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.