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Enantiomeric disorder in racemic *cis*-dichlorobis(pentane-2,4-dionato)-titanium(IV)

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The title compound, $[Ti(C_5H_7O_2)_2Cl_2]$, adopts the *cis* configuration. The racemic compound crystallizes in space group $P\overline{1}$ and each molecular site has 0.50 occupancy by each of the two enantiomorphs. The enantiomeric disorder is correlated in two dimensions.

Comment

Pentane-2,4-dione ($CH_3COCH_2COCH_3$, Hacac) reacts with both titanium(IV) chloride and titanium(IV) alkoxides to yield neutral products $[Ti(acac)_2X_2]$, where X = Cl (Dilthey, 1904) or X = O*R* (Yamamoto & Kambara, 1957). NMR studies suggest that, in solution, these products and the analogous complexes derived from other 1,3-diketones are all octahedral, containing bidentate *O*,*O*′-chelating diketonate ligands with a *cis* arrangement of the two ligands X (Fay & Lowry, 1967; Serpone & Fay, 1967; Bradley & Holloway, 1969). We have recently reported the structure of dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV), $[(Me_3CCOCHCOCMe_3)_2TiCl_2]$ (Glidewell *et al.*, 1996), where the molecules adopt the *cis* configuration with equal numbers of Λ and Δ enantiomers present in space group $P2_1/c$. However, apart from this, the only analogous structure recorded in the Cambridge Structural Database (Allen & Kennard, 1993) is that of $[(PhCOCHCOPh)_2TiCl_2]$ (TOPZUT; Matilainen *et al.*, 1996); here, the molecules were again shown to adopt the *cis* configuration, but the final *R* value was 0.089 for a data-to-parameter ratio of only 7.6. It is striking that the structure of the simplest member of this series $[(CH_3COCHCOCH_3)_2TiCl_2]$, (I), has not yet been reported; an attempted structure analysis of $[Ti(acac)_2Cl_2]$ was thwarted by hydrolysis, and the compound actually studied was $[\{Ti(acac)_2Cl\}_2O]$ (Watenpaugh & Caughlin, 1967), where the chloride and bridging oxide ligands occupy *cis* sites. We report here the structure of (I) which shows an uncommon form of disorder, which itself may have hampered earlier attempts at structure analysis.

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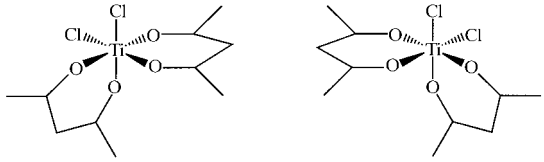
Compound (I) crystallizes in the triclinic space group $P\overline{1}$ with Z = 2. The molecules have the *cis* configuration (Fig. 1) and the centrosymmetric space group accommodates equal numbers of Λ and Δ enantiomers. However, each molecular site is occupied with equal probability by the two enantiomers:



Λ-(I) Δ-(I)

only the Ti and one of the Cl have sites common to both enantiomers, and several pairs of corresponding atoms in the two enantiomers occupy closely similar positions (Fig. 2). Because of this, a number of restraints were necessary in the refinement but, subject to these, the mean values of the leading geometric parameters are: Ti—Cl = 2.282 (4) Å; Ti—O(*trans* to Cl) = 1.973 (7) Å; Ti—O(*trans* to O) = 1.930 (7) Å; C—O = 1.266 (13) Å; C—C(ring) = 1.374 (9) Å; C—C(methyl) = 1.480 (10) Å. The facial arrangement of the Cl sites (Fig. 2) precludes the presence of any *trans* isomer.

The nature of the disorder (Fig. 2) necessarily raises the question (Marsh, 1999), *P*1 or $P\overline{1}$? Using coordinates derived from the disordered $P\overline{1}$ refinement, a refinement in *P*1 with one Λ and one Δ enantiomorph in the unit cell led to *R* values above 0.10 accompanied by wholly unreasonable anisotropic displacement parameters and unsatisfactory intermolecular contacts; the ordered *P*1 model was therefore decisively rejected.

Equal occupancy by the two enantiomers of the average molecular site may be a reflection of spacial or temporal disorder, or of a combination of these. In compound (I), spacial disorder cannot however be merely a random distribution of the two enantiomers amongst all the molecular sites. The short intermolecular contacts C3···C3^{i} [symmetry code: (i) $1 + x, y, z$] and C23···C33^{ii} [symmetry code: (ii) $x, -1 + y, z$] of 1.94 (2) and 2.15 (2) Å, respectively, preclude the presence of the same enantiomer at adjacent sites in both the [100] and [010] directions; hence, in the *ab* plane, the Λ and Δ enantiomers must alternate in checkerboard fashion. There

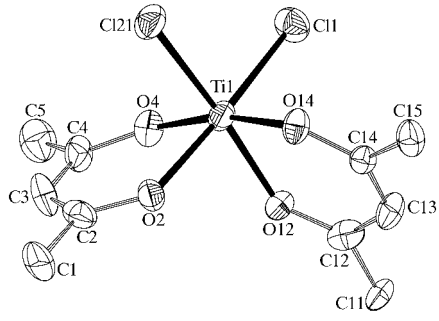


Figure 1
The Δ enantiomer of compound (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for the sake of clarity.

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are no prohibitively short contacts in the [001] direction and hence there is no correlation of the arrangements in neighbouring (001) planes; thus, the structure is correctly described in terms of the present unit cell with $Z = 2$, rather than of a larger cell having $Z = 8$.

Solution studies using NMR have indicated that the intramolecular Λ/Δ isomerization in (I) has a low activation barrier and hence is rapid at ambient temperature (Bradley & Holloway, 1969). It is possible that the disordered model derived from the X-ray diffraction data may also reflect, at least in part, rapid intramolecular exchange; again, because of the short intermolecular contacts, exchange events at adjacent sites in the *ab* plane would necessarily be correlated.

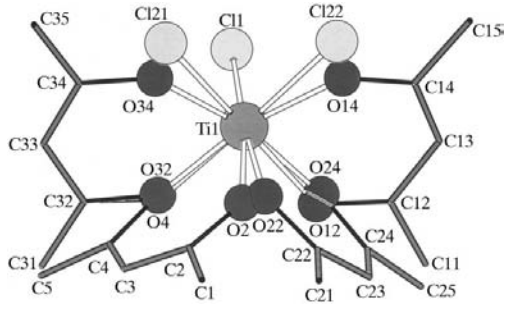

Figure 2
The contents of a single molecular site in (I) showing the relative orientations of the two enantiomers. All sites except Ti1 and Cl1 have occupancy 0.50. Atoms are depicted as spheres whose radii are ranked thus: Ti > Cl > O > C. H atoms have been omitted for the sake of clarity.

Experimental

Compound (I) was prepared by slow addition, under N_2, of titanium(IV) chloride to a threefold molar excess of pentane-2,4-dione in sodium-dried toluene, followed by heating under reflux for 20 min. After removal of the solvent under reduced pressure, crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in toluene.

Crystal data

$[Ti(C_5H_7O_2)_2Cl_2]$
$M_r = 317.01$
Triclinic, $P\overline{1}$
$a = 7.764\ (3)$ Å
$b = 7.8810\ (15)$ Å
$c = 13.0470\ (15)$ Å
$\alpha = 79.507\ (6)^\circ$
$\beta = 78.790\ (11)^\circ$
$\gamma = 63.308\ (11)^\circ$
$V = 695.5\ (3)$ Å^3
$Z = 2$
$D_x = 1.514$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15.80$–27.72°
$\mu = 0.998$ mm^{-1}
$T = 293\ (2)$ K
Block, orange
0.40 × 0.20 × 0.20 mm

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*ABSCOR* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.691$, $T_{max} = 0.825$
3012 measured reflections
3012 independent reflections
1283 reflections with $I > 2\sigma(I)$
$\theta_{max} = 26.97^\circ$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity variation: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.171$
$S = 0.942$
3012 reflections
277 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0894P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Compound (I) crystallized in the triclinic system; space group $P\overline{1}$ was assumed and confirmed by the analysis. It was apparent at the structure-solution stage that there was significant disorder in the structure and the density maps could only be interpreted in terms of two (Λ and Δ) enantiomers occupying the same site with one Ti (Ti1) and one Cl (Cl1) in common. Careful selection of peaks from electron-density maps allowed all sites for all the non-H atoms to be determined. Because of the disorder, we imposed several restraints and refined as free variables the distances Csp^3-Csp^2, Csp^2-Csp^2, Csp^2-O, Ti—O(*trans* to O), Ti—O(*trans* to Cl) and Ti—Cl. H atoms were positioned on geometrical grounds and treated as riding atoms, with C—H distances of 0.93 (ring H) and 0.96 Å (methyl H). The methyl groups were each modelled using six H-atom sites, each with occupancy 0.50, mutually offset by 60°. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*; data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1440). Services for accessing these data are described at the back of the journal.

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