ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.064$, $T_{max} = 0.131$
18 940 measured reflections
12 806 independent reflections

$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 16$
$k = -16 \rightarrow 17$
$l = 0 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.107$
$S = 1.038$
12 806 reflections
622 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0410P)^2 + 8.4051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.346$ e Å^{-3}
$\Delta\rho_{min} = -2.128$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

W1—Se4	2.263 (1)	Ag1—Se1	2.640 (1)
W1—Se1	2.370 (1)	Ag1—Br1	2.901 (1)
W1—Se3	2.382 (1)	Ag2—Se3	2.658 (1)
W1—Se2	2.383 (1)	Ag2—Se1	2.679 (1)
W1—Ag3	3.001 (1)	Ag2—Br1	2.979 (1)
W1—Ag1	3.007 (1)	Ag3—Se3	2.638 (1)
W1—Ag2	3.033 (1)	Ag3—Se2	2.647 (1)
Ag1—Se2	2.625 (1)	Ag3—Br1	2.963 (1)
Se4—W1—Se1	107.20 (3)	Se2—Ag1—Br1	101.59 (3)
Se4—W1—Se3	106.95 (3)	Se1—Ag1—Br1	103.34 (3)
Se1—W1—Se3	111.66 (2)	Se3—Ag2—Br1	102.80 (3)
Se4—W1—Se2	107.70 (3)	Se1—Ag2—Br1	100.38 (3)
Se1—W1—Se2	111.20 (2)	Se3—Ag3—Br1	103.72 (3)
Se3—W1—Se2	111.84 (2)	Se2—Ag3—Br1	99.49 (3)

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set was over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analyzing the duplicate reflections; it was found to be negligible.

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SAINT* (Siemens, 1996*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Dichloro{2-[(η^5-cyclopentadienyl)phenylmethyl]phenolato-*O*}titanium

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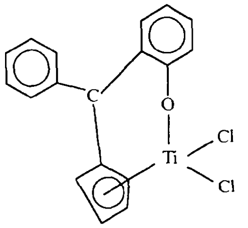
Abstract

The title compound, [$TiCl_2(C_{18}H_{14}O)$], with a chiral C atom, crystallizes as a racemate. The Ti—O bond length is 1.794 (3) Å. The plane of the cyclopentadienyl ring forms dihedral angles of 68.8 (7) and 79.2 (6)° with the two phenyl rings.

Comment

Group IV metallocene complexes are becoming increasingly important as 'single-site' catalysts for the polymerization of α-olefins (Bochmann, 1996) and the number of industrial processes based on cyclopentadienyl (Cp) complexes is growing rapidly (Thayer, 1995). Consequently, a large number of complexes with different metals are now available (Plenio & Burth, 1995, 1996). Metallocenes that carry two different substituents on one or both of their Cp rings exhibit 'planar chirality' (Vemura, 1994). There is a specific interest in this type of *ansa*-metallocene, owing to their use as catalyst precursors for the homogeneous polymerization of ethylene and the stereo-regular polymerization of propylene (Mohring & Coville, 1994). A second way to produce chiral metallocenes is to connect each Cp ring to the metal centre with a chelating chain, producing a helical structure (du Plooy *et al.*, 1995). In the latter case, breaking the metal–chelate bonds in the complex destroys the chirality of the system.



(I)

We describe here a titanocene, (I), which has a chiral C atom whose presence may be expected to exert an influence at the metal centre. A view of the asymmetric unit with the atomic numbering scheme is shown in Fig. 1. The title compound crystallizes in the centrosymmetric $P\overline{1}$ space group and thus the crystal is racemic with equal numbers of molecules of each chirality. The Ti—C distances range from 2.315 (5) to 2.337 (6) Å, with a mean value of 2.330 (8) Å. A large difference between the mean Ti—Cl [2.250 (7) Å] and Ti—*Cp* (where *Cp* is the Cp ring centroid) distances [2.000 (5) Å] is observed compared with those in similar titanocenes, *e.g.* [*rac*-BpTiCl$_2$] (Chacon *et al.*, 1995) [where Bp represents (η^5-C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)SiMe$_2$] and [Ti{(C$_5$H$_3$Bu)$_2$}$_2$Cl$_2$] (Hughes *et al.*, 1996). This difference may result from intramolecular steric repulsion in the title compound. The conformation of the title compound is defined by the interplanar angles which the aromatic rings make with the Cp ring plane; these values are 79.2 (6)° for the dihedral angle between C13–C18 and C7–C12/C18 and 68.8 (7)° for the dihedral angle between C13–C18 and C1–C6/C18.

There are no unusual intermolecular contacts and the molecules are separated by normal van der Waals distances. A view of the crystal packing has been deposited with the supplementary material.

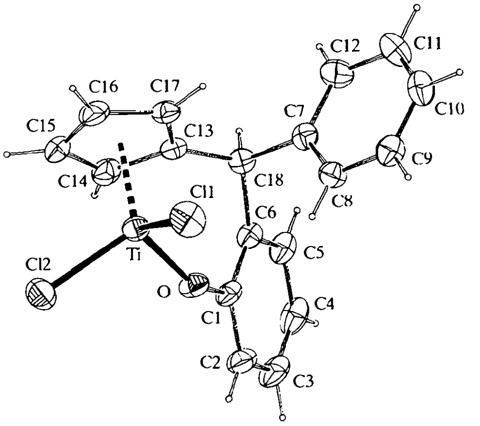


Fig. 1. A view of the molecular structure of (I) showing 30% probability displacement ellipsoids.

Experimental

TiCl$_4$ was added to a solution of the 2-[(η^5-cyclopentadienyl)phenylmethyl]phenol ligand in hexane and the reaction mixture heated under reflux for 3h. Yellow crystals formed and were isolated by crystallization from toluene/hexane.

Crystal data

[TiCl$_2$(C$_{18}$H$_{14}$O)]
M_r = 365.09
Triclinic
$P\overline{1}$
a = 7.1325 (6) Å
b = 9.7959 (8) Å
c = 12.3235 (8) Å
α = 74.082 (6)°
β = 81.086 (6)°
γ = 86.242 (7)°
V = 817.78 (11) Å^3
Z = 2
D_x = 1.483 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 44 reflections
θ = 4.78–12.41°
μ = 0.847 mm^{-1}
T = 293 (2) K
Plate
0.6 × 0.5 × 0.1 mm
Yellow

Data collection

Siemens *P*4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (*XSCANS*; Siemens, 1994*a*)
$T_{\min}$ = 0.710, $T_{\max}$ = 0.936
6553 measured reflections
3555 independent reflections

2069 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026
$\theta_{\max}$ = 27°
$h = -1 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 12.02%

Refinement

Refinement on F^2
$R(F)$ = 0.042
$wR(F^2)$ = 0.062
S = 1.189

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.356 e Å^{-3}
$\Delta\rho_{\min}$ = −0.244 e Å^{-3}
Extinction correction: none

3553 reflections
199 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.7230P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cp is the centroid of the C13–C17 ring.

Ti—O	1.794 (3)	Ti—C15	2.337 (6)
Ti—Cl2	2.243 (2)	Ti—*Cp*	2.000
Ti—Cl1	2.256 (2)	O—C1	1.378 (5)
Ti—C14	2.315 (5)	C6—C18	1.518 (6)
Ti—C13	2.331 (4)	C7—C18	1.518 (6)
Ti—C17	2.331 (5)	C13—C18	1.518 (6)
Ti—C16	2.336 (5)		
O—Ti—Cl2	104.84 (11)	Cl2—Ti—*Cp*	116.9
O—Ti—Cl1	103.45 (12)	O—Ti—*Cp*	110.7
Cl2—Ti—Cl1	103.28 (6)	C1—O—Ti	143.6 (3)
O—Ti—C14	89.8 (2)	O—C1—C2	118.0 (4)
Cl2—Ti—C14	103.30 (14)	O—C1—C6	121.0 (4)
Cl1—Ti—C14	145.97 (13)	C6—C18—C13	112.8 (4)
O—Ti—C13	81.56 (14)	C6—C18—C7	112.9 (4)
Cl1—Ti—*Cp*	116.2	C13—C18—C7	112.2 (3)

The title compound crystallized in the triclinic system. The space group $P\overline{1}$ was assumed and confirmed by analysis. H atoms were treated as riding atoms (C—H 0.93 and 0.98 Å).

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1495). Services for accessing these data are described at the back of the journal.

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A copper(II) dimer: aqua(μ-2,2′-bipyrimidine-*N*,*N*′)(perchlorato)bis{[2,6-bis(2-pyridyl)pyridine-*N*,*N*′,*N*″]copper(II)} triperchlorate†

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Abstract

The title compound, $[Cu_2(ClO_4)(C_8H_6N_4)(C_{15}H_{11}N_3)_2(H_2O)](ClO_4)_3$, consists of a dinuclear copper(II) unit, the bridge being the bipyrimidine (bipym) ligand, which contains a twofold rotation axis. The Cu atoms are six-coordinated by five N atoms from the bipym and terpyridine (terpy) molecules, and by an O atom that belongs either to a water molecule or a perchlorate anion, presenting a distorted octahedral geometry. The equatorial Cu—N distances range between 1.943 (3) and 2.056 (3) Å. One apical position is occupied by a bipym N atom at a distance of 2.328 (3) Å, while the other apex of the octahedron is occupied alternatively by the O atom of the water molecule or an O atom of the perchlorate, with Cu—O distances of 2.445 (11) and 2.721 (11) Å, respectively. Most of the remaining perchlorate O atoms are disordered.

Comment

2,2′-Bipyrimidine (bipym) is known to be a versatile ligand able to coordinate transition metals in a bidentate or in a bis-bidentate bridging mode, leading to mono- or polynuclear complexes (De Munno & Julve, 1996). Several examples of dimers containing copper(II) and bipym are present in the literature (De Munno *et al.*, 1993, 1995; Castro *et al.*, 1994), together with their crystal structures and their magnetic properties. The exchange coupling between the magnetic centers can be modified by copper(II) distortions such as elongation or compression (De Munno *et al.*, 1995). The present work represents a new bipyrimidine dimer, (I), with two copper(II) ions coordinated by two 2,6-bis(2-pyridyl)-

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† Systematic name: aqua-1κO-μ-(2,2′-bipyrimidine)-1$\kappa^2 N^1,N^{1'}$:2$\kappa^2 N^3,N^{3'}$-perchlorato-2κO-bis(2,2′:6′,2″-terpyridine)-1$\kappa^3 N$,2$\kappa^3 N$-dicopper(II) triperchlorate.

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