metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.087
Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

μ-Oxo-bis[azidobis(η^5-cyclopentadienyl)-titanium(IV)]

The title compound, [Ti$_2$(η^5-C$_5$H$_5$)$_4$(N$_3$)$_2$O], is a dinuclear oxo-bridged azido complex with two titanocene fragments connected through the oxygen bridge. The environment around each Ti atom can be considered as a distorted tetrahedron.

Comment

The title compound, (I) (Fig. 1), is the main product of the reaction of titanocene dichloride (TDC) with sodium azide in aqueous solution. It is a dinuclear oxo-bridged complex in which two titanocene units are connected *via* an oxygen bridge. The molecule has approximately C_2 symmetry and, similar to other oxo-bridged dinuclear complexes (Raptopoulou *et al.*, 1996), the Ti—O—Ti moiety is almost linear [Ti—O—Ti = 172.03 (8)°]. The coordination at each titanium(IV) center approaches tetrahedral geometry [Cg—Ti—Cg = 131.08 (4) and 131.67 (5)°, and N—Ti—O = 95.39 (7) and 95.57 (7)°; Cg is the centroid of the cyclopentadienyl ring]. The cyclopentadienyl rings have staggered conformations in both titanocene fragments with Cg—Ti bond lengths ranging from 2.0752 (11) to 2.0884 (12) Å. The Ti—N bond lengths [2.091 (2) and 2.0926 (19) Å] are slightly longer than those in the diazide titanocene complex Cp$_2$Ti(NNN)$_2$ (2.03 Å; Villa *et al.*, 1976) and comparable with those in the azide complexes [Ti(NMe$_2$)$_3$(N$_3$)(bipy)], [Ti(NMe$_2$)$_2$(N$_3$)$_2$(py)$_2$] and [Ti(NMe$_2$)$_2$(N$_3$)$_2$(bipy)] (2.07–2.15 Å; Carmalt *et al.*, 1997). In (I), the coordinated azide groups are almost linear: N1—N2—N3 = 177.1 (3)° and N4—N5—N6 = 177.6 (2)°.

(I)
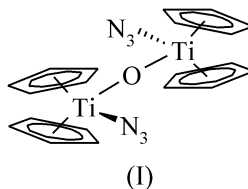
The very strong band in the IR spectrum of (I) at 724 cm^{-1} [ν_a(Ti—O)] is typical for dinuclear oxo-bridged titanocene compounds (Samuel, 1966). Furthermore, the positive-ion ESI mass spectrum shows $[M + K]^+$ (495) and $[M + Na]^+$ (479) ions, which is entirely consistent with the structure of (I).

Experimental

The title compound was prepared according to a literature procedure (Coutts & Wailes, 1966), with some modifications. (η^5-C$_5$H$_5$)$_2$TiCl$_2$ (0.5 g, 2.0 mmol) was dissolved in boiling water (30 ml). To this solution, sodium azide (0.3 g, 4.6 mmol) was added and the mixture was cooled rapidly to room temperature. The orange precipitate was
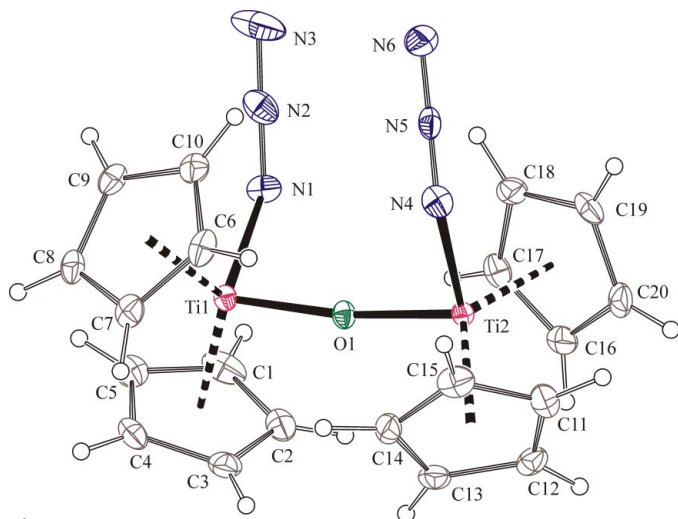
Figure 1
The molecular structure of (I), showing 30% displacement ellipsoids.

filtered off, washed with water and vacuum dried (0.40 g, yield 78%). Yellow crystals suitable for X-ray analysis were obtained by careful layering of a CH_2Cl_2 solution with a double volume of hexane. ^{1}H NMR (CDCl$_3$, p.p.m.): 6.37 (s, Cp). ^{13}C NMR (CDCl$_3$, p.p.m.): 117.0 (s, Cp). Positive-ion MS (ESI): m/z 551 [M + Na + methanol]$^+$, 495 [M + K]$^+$, 479 [M + Na]$^+$, 414 [$M − N_3$]$^+$ (100%), 220 [Cp$_2$TiN$_3$]$^+$, 195 [Cp$_2$TiOH]$^+$. Positive-ion MS/MS of 479: m/z 414 [M + Na − Cp]$^+$, 391 [M − Cp]$^+$ (100%), 339, 316, 293. IR (KBr pellet, cm^{-1}): 3118 (m, ν_aC−H, Cp), 3091 (sh, ν_sC−H, Cp), 2074 (vs, ν_aN−N), 1986 (m, ν_sN−N), 1448 (m, ν_aC−C, Cp), 1346 (s, ν_aC−C, Cp), 1262 (m, δ C−H, Cp), 1022 (s, δ C−H), 822 (vs, γC−H), 724 (vs, ν_aTi−O) 598 (s), 408 (s). Raman (quartz capillary, cm^{-1}): 3112 (4) (ν_aC−H, Cp), 3096 (sh, ν_sC−H, Cp), 2096 (<1), 2066 (1) (ν_sN−N), 1443 (1) (ν_aC−C), 1366 (1), 1349 (2) (ν_aC−C, Cp), 1131 (10) (ν_sC−C), 1082 (<1), 1071 (<1), 1020 (<1), 945 (<1), 866 (<1), 843 (<1), 423 (1), 406 (1), 343 (6), 267 (9), 240 (7), 185 (7), 104 (6).

Crystal data

[Ti$_2$(C$_5$H$_5$)$_4$(N$_3$)$_2$O]
$M_r = 456.22$
Monoclinic, $P2_1/c$
$a = 15.2860 (4)$ Å
$b = 8.3620 (2)$ Å
$c = 15.6900 (4)$ Å
$\beta = 101.0860 (16)°$
$V = 1968.10 (9)$ Å^3
$Z = 4$

$D_x = 1.540$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4685 reflections
$\theta = 1–27.5°$
$\mu = 0.84$ mm^{-1}
$T = 150 (2)$ K
Block, yellow
$0.30 \times 0.27 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
28 006 measured reflections
4508 independent reflections
3429 reflections with $I > 2\sigma(I)$

$R_{int} = 0.047$
$\theta_{max} = 27.5°$
$h = -19 \rightarrow 19$
$k = -10 \rightarrow 10$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 1.03$
4508 reflections
262 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.7094P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å,°).

Cg_1−Ti1	2.0884 (12)	Ti1−O1	1.8310 (14)
Cg_2−Ti1	2.0752 (11)	Ti2−O1	1.8311 (14)
Cg_3−Ti2	2.0890 (11)	Ti1−N1	2.0926 (19)
Cg_4−Ti2	2.0850 (10)	Ti2−N4	2.091 (2)
Cg_1−Ti1−Cg_2	131.08 (4)	O1−Ti1−N1	95.39 (7)
Cg_3−Ti2−Cg_4	131.67 (5)	O1−Ti2−N4	95.57 (7)
N1−N2	1.171 (3)	Ti1−N1−N2	129.60 (16)
N2−N3	1.160 (3)	Ti2−N4−N5	129.81 (17)
N4−N5	1.138 (3)	N1−N2−N3	177.1 (3)
N5−N6	1.187 (3)	N4−N5−N6	177.6 (2)

Notes: Cg_1 = centroid of atoms C1–C5, Cg_2 = centroid of atoms C6–C10, Cg_3 = centroid of atoms C11–C15 and Cg_4 = centroid of atoms C16–C20.

All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C−H = 0.93 Å and U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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