Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

μ-Oxido-bis[dichlorido(diethylamido-κN)(diethylamine-κN)titanium(IV)]

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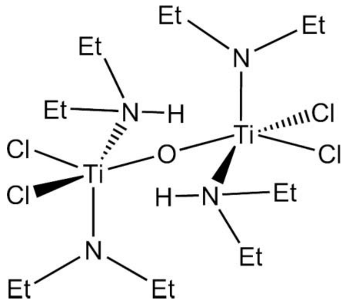
Received 9 September 2007; accepted 13 September 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.058; wR factor = 0.153; data-to-parameter ratio = 18.9.

In the title compound, $[Ti_2(C_4H_{10}N)_2Cl_4O(C_4H_{11}N)_2]$, the bridging O atom resides on an inversion center, resulting in a 180° Ti—O—Ti bond angle.

Related literature

For related literature, see: Addison *et al.* (1984); Honzíček *et al.* (2004); Krug & Müller (1990); Levason *et al.* (2003); Mahrwald *et al.* (2001); Schormann (2003); Thewalt & Schomburg (1977).



Experimental

Crystal data

$[Ti_2(C_4H_{10}N)_2Cl_4O(C_4H_{11}N)_2]$
M_r = 544.14
Monoclinic, $I2/a$
a = 13.204 (3) Å
b = 10.131 (2) Å
c = 20.795 (5) Å
β = 99.973 (3)°
V = 2739.7 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.99 mm^{-1}
T = 298 (2) K
0.40 × 0.35 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003*a*)
T_{min} = 0.693, T_{max} = 0.827
10591 measured reflections
2421 independent reflections
1446 reflections with $I > 2\sigma(I)$
R_{int} = 0.093

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.153
S = 0.93
2421 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2003*b*); software used to prepare material for publication: *SHELXTL*.

We would like to express our gratitude to the US National Science Foundation for their contribution toward the purchase of the single-crystal instrumentation used in this study through Award #CHE-9808440.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2295).

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doi:10.1107/S1600536807044832

supplementary materials

Acta Cryst. (2007). E**63**, m2563 [**doi:10.1107/S1600536807044832**]

μ-Oxido-bis[dichlorido(diethylamido-*κN*)(diethylamine-*κN*)titanium(IV)]

N. A. Straessler, M. T. Caudle and T. L. Groy

Comment

The structure of **I** was determined as part of an investigation into the effects of water on the synthesis of Ti(IV) complexes derived from secondary amines. Because the two titanium atoms in **I** are related by an inversion center on the bridging oxygen atom, the Ti—O—Ti bond angle is 180° indicating complete *sp* hybridization of the oxygen atom. This arises from dπpπ bonding through overlap of the p_x and p_y orbitals on oxygen with titanium d_{xy} and d_{yz} orbitals. Perfectly linear Ti—O—Ti complexes with oxygen as an inversion center have been reported (Krug & Müller, 1990; Thewalt & Schomburg, 1977). However, μ-oxo homodinuclear titanium species with Ti—O—Ti bond angles slightly less than 180° appear to be more common. (Honzíček *et al.*, 2004; Levason *et al.*, 2003; Mahrwald *et al.*, 2001; Schormann, 2003)

In addition to the bridging oxygen in **I**, there is one diethylamido (N2) and one diethylamino (N1) group, as well as two chlorides (Cl1 and Cl2) coordinated to the titanium. Each titanium atom is best viewed as having distorted square pyramidal coordination geometry as judged by the τ-descriptor (Addison *et al.*, 1984) which is 0.13 for this molecule. The amido group occupies the axial position, and Cl1, Cl2, N1 and O1 create the equatorial pseudo-square base. One chloride (Cl2) is *trans* to the bridging oxygen and the other chloride (Cl1) is *trans* to the amino group.

The diethylamido N atoms are nearly planar (N2 deviates from the Ti–C21–C23 plane by 0.077 (6) Å) as a result of strong pi interactions with the d^0 Ti^{4+}. Three of the four bond angles making up the base of the square pyramid in **I** are smaller than the ideal 90° (O1—Ti1—N1 = 82.49 (10)°, N1—Ti1—Cl2 = 83.20 (11)°, Cl2—Ti1—Cl1 = 89.73 (7)°). The four bond angles from the respective equatorial positions to the axial nitrogen are all larger than the ideal 90° and range from 102.09 (17)° to 108.65 (11)°. Deviation from ideal square pyramidal geometry can be attributed to electrostatic repulsions, particularly from the diethylamido nitrogen, and significant steric crowding around the Ti^{4+} centers.

Experimental

While stirring under a nitrogen atmosphere, 2 ml (18.24 mmol) of $TiCl_4$ were added to approximately 60 ml of n-hexane in a Schlenk flask. Next, 0.16 ml (8.90 mmol) of distilled water mixed with 7.54 ml (72.90 mmol) of diethylamine was added dropwise to the solution. After 16 h of stirring, solid white diethylammonium chloride was removed by no-air filtration. The orange filtrate was evaporated to a minimal volume over a period of two days with a slow stream of nitrogen yielding X-ray quality crystals of **I**.

Refinement

Hydrogen atoms were positioned geometrically and allowed to ride on their bonding partners with C—H distances = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl H atoms, C—H distances = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the methylene H atoms, and N—H distance = 0.91 Å and $U_{iso}(H) = 1.2U_{eq}(N)$ for the amino hydrogen.

Figures

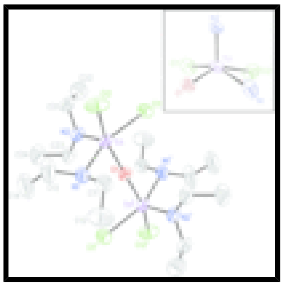


Fig. 1. Thermal ellipsoid plot of **I** shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Square pyramidal coordination geometry around the titanium atoms shown inset. [Symmetry operation (i): $-x + 1/2$, $-y + 1/2$, $-z + 1/2$].

μ-Oxo-bis[dichlorido(diethylamido-κ*N*)(diethylamine-κ*N*)titanium(IV)]

Crystal data

$[Ti_2(C_4H_{10}N)_2Cl_4O(C_4H_{11}N)_2]$

$M_r = 544.14$

Monoclinic, *I*2/*a*

Hall symbol: -I 2ya

$a = 13.204$ (3) Å

$b = 10.131$ (2) Å

$c = 20.795$ (5) Å

$\beta = 99.973$ (3)°

$V = 2739.7$ (10) Å^3

$Z = 4$

$F_{000} = 1144$

$D_x = 1.319$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 3400 reflections

θ = 4.5–49.2°

μ = 0.99 mm^{-1}

$T = 298$ (2) K

Block, orange

0.40 × 0.35 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298(2)$ K

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003a)

$T_{min} = 0.693$, $T_{max} = 0.827$

10591 measured reflections

2421 independent reflections

1446 reflections with $I > 2\sigma(I)$

$R_{int} = 0.093$

$\theta_{max} = 25.0$°

$\theta_{min} = 2.0$°

$h = -15\rightarrow15$

$k = -12\rightarrow12$

$l = -24\rightarrow24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.058$

$wR(F^2) = 0.153$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0883P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} = 0.004$
2421 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
128 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ti1	0.21205 (5)	0.21280 (9)	0.32732 (4)	0.0574 (3)
Cl1	0.12134 (10)	0.02633 (18)	0.28158 (7)	0.0953 (6)
Cl2	0.09047 (11)	0.24341 (17)	0.39498 (9)	0.1030 (6)
O1	0.2500	0.2500	0.2500	0.0595 (11)
N1	0.2372 (3)	0.4269 (4)	0.34308 (18)	0.0729 (12)
H1A	0.2879	0.4479	0.3202	0.087*
C11	0.1437 (4)	0.4984 (6)	0.3087 (3)	0.0835 (16)
H11A	0.1142	0.4468	0.2707	0.100*
H11B	0.0935	0.5004	0.3377	0.100*
C12	0.1579 (6)	0.6342 (7)	0.2870 (4)	0.128 (3)
H12A	0.1932	0.6850	0.3230	0.192*
H12B	0.0920	0.6732	0.2713	0.192*
H12C	0.1978	0.6330	0.2526	0.192*
C13	0.2737 (5)	0.4784 (10)	0.4096 (3)	0.144 (3)
H13A	0.2316	0.5544	0.4155	0.173*
H13B	0.2593	0.4115	0.4401	0.173*
N2	0.3284 (2)	0.1426 (4)	0.37576 (16)	0.0595 (10)
C21	0.3131 (4)	0.0542 (6)	0.4290 (2)	0.0805 (17)
H21A	0.2433	0.0646	0.4369	0.097*
H21B	0.3592	0.0806	0.4684	0.097*
C22	0.3315 (5)	−0.0908 (7)	0.4159 (3)	0.111 (2)
H22A	0.2891	−0.1168	0.3757	0.166*
H22B	0.3145	−0.1433	0.4510	0.166*
H22C	0.4025	−0.1039	0.4129	0.166*
C23	0.4344 (3)	0.1478 (7)	0.3616 (2)	0.0812 (16)
H23A	0.4377	0.2151	0.3289	0.097*

H23B	0.4505	0.0637	0.3435	0.097*
C24	0.5138 (4)	0.1774 (8)	0.4206 (3)	0.116 (2)
H24A	0.4975	0.2594	0.4395	0.175*
H24B	0.5802	0.1839	0.4080	0.175*
H24C	0.5146	0.1077	0.4520	0.175*
C14	0.3706 (6)	0.5140 (10)	0.4276 (4)	0.163 (4)
H14A	0.4143	0.4526	0.4103	0.244*
H14B	0.3876	0.5145	0.4744	0.244*
H14C	0.3804	0.6008	0.4112	0.244*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti1	0.0338 (4)	0.0910 (7)	0.0502 (5)	0.0052 (4)	0.0148 (3)	0.0161 (4)
Cl1	0.0633 (8)	0.1336 (14)	0.0909 (10)	−0.0350 (8)	0.0190 (7)	0.0076 (9)
Cl2	0.0806 (10)	0.1190 (13)	0.1287 (12)	0.0258 (8)	0.0724 (9)	0.0354 (10)
O1	0.054 (2)	0.078 (3)	0.048 (2)	0.004 (2)	0.0136 (19)	0.009 (2)
N1	0.052 (2)	0.111 (4)	0.059 (2)	−0.017 (2)	0.0183 (18)	−0.014 (2)
C11	0.072 (4)	0.083 (4)	0.094 (4)	−0.006 (3)	0.009 (3)	0.001 (3)
C12	0.137 (6)	0.090 (6)	0.169 (7)	0.000 (5)	0.060 (5)	0.008 (5)
C13	0.084 (4)	0.261 (10)	0.092 (5)	−0.041 (6)	0.023 (4)	−0.076 (6)
N2	0.0385 (18)	0.096 (3)	0.045 (2)	0.0096 (19)	0.0109 (15)	0.0081 (19)
C21	0.064 (3)	0.116 (5)	0.061 (3)	0.015 (3)	0.010 (2)	0.020 (3)
C22	0.102 (5)	0.101 (5)	0.123 (5)	0.019 (4)	0.002 (4)	0.022 (4)
C23	0.038 (2)	0.143 (5)	0.064 (3)	0.009 (3)	0.011 (2)	0.001 (3)
C24	0.051 (3)	0.188 (8)	0.105 (5)	−0.003 (4)	−0.002 (3)	0.001 (5)
C14	0.127 (7)	0.205 (10)	0.140 (7)	−0.053 (7)	−0.024 (6)	−0.050 (6)

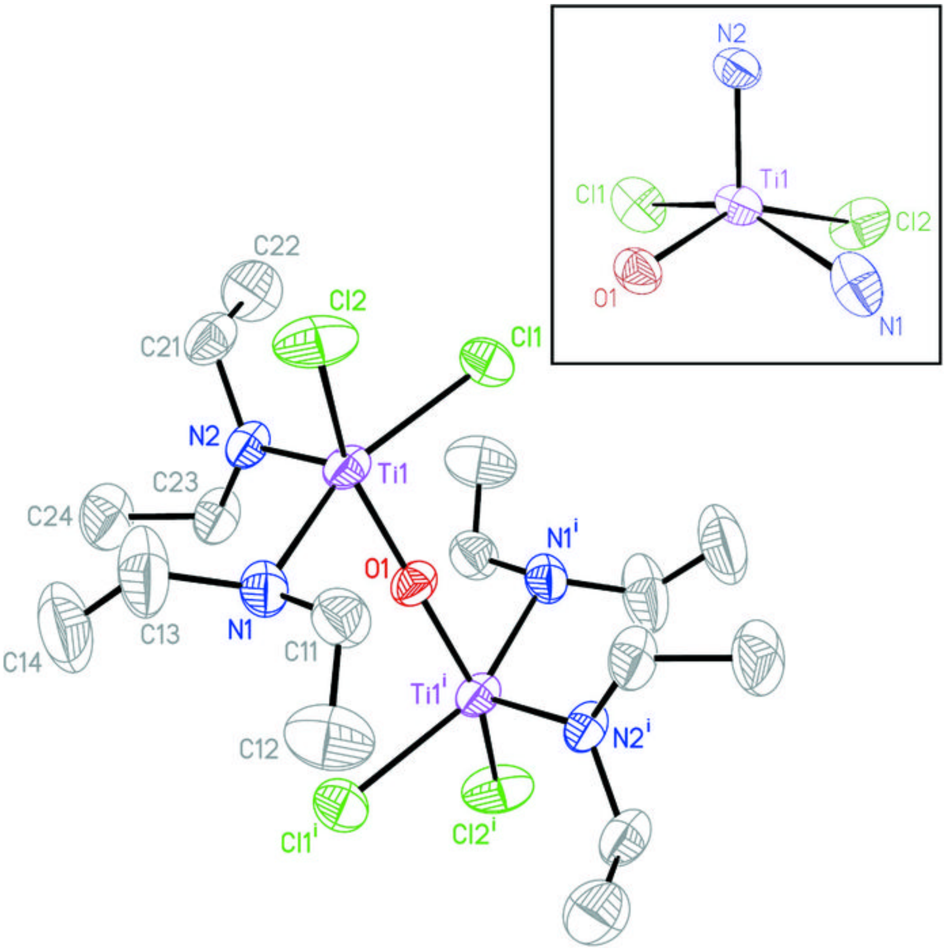
Geometric parameters (Å, °)

Ti1—O1	1.8048 (8)	N2—C21	1.465 (6)
Ti1—N2	1.828 (3)	N2—C23	1.480 (5)
Ti1—N1	2.210 (5)	C21—C22	1.521 (8)
Ti1—Cl2	2.3314 (14)	C21—H21A	0.9700
Ti1—Cl1	2.3480 (18)	C21—H21B	0.9700
O1—Ti1$^{\mathrm{i}}$	1.8049 (8)	C22—H22A	0.9600
N1—C13	1.479 (7)	C22—H22B	0.9600
N1—C11	1.502 (6)	C22—H22C	0.9600
N1—H1A	0.9100	C23—C24	1.499 (7)
C11—C12	1.470 (9)	C23—H23A	0.9700
C11—H11A	0.9700	C23—H23B	0.9700
C11—H11B	0.9700	C24—H24A	0.9600
C12—H12A	0.9600	C24—H24B	0.9600
C12—H12B	0.9600	C24—H24C	0.9600
C12—H12C	0.9600	C14—H14A	0.9600
C13—C14	1.320 (9)	C14—H14B	0.9600
C13—H13A	0.9700	C14—H14C	0.9600
C13—H13B	0.9700		

O1—Ti1—N2	103.63 (10)	H13A—C13—H13B	106.9
O1—Ti1—N1	82.49 (10)	C21—N2—C23	115.5 (4)
N2—Ti1—N1	102.09 (17)	C21—N2—Ti1	116.2 (3)
O1—Ti1—Cl2	146.75 (6)	C23—N2—Ti1	127.6 (3)
N2—Ti1—Cl2	108.65 (11)	N2—C21—C22	114.1 (4)
N1—Ti1—Cl2	83.20 (11)	N2—C21—H21A	108.7
O1—Ti1—Cl1	90.46 (5)	C22—C21—H21A	108.7
N2—Ti1—Cl1	103.37 (14)	N2—C21—H21B	108.7
N1—Ti1—Cl1	154.52 (11)	C22—C21—H21B	108.7
Cl2—Ti1—Cl1	89.73 (7)	H21A—C21—H21B	107.6
Ti1—O1—Ti1^{i}	180.00	C21—C22—H22A	109.5
C13—N1—C11	112.5 (5)	C21—C22—H22B	109.5
C13—N1—Ti1	120.1 (5)	H22A—C22—H22B	109.5
C11—N1—Ti1	108.2 (3)	C21—C22—H22C	109.5
C13—N1—H1A	104.9	H22A—C22—H22C	109.5
C11—N1—H1A	104.9	H22B—C22—H22C	109.5
Ti1—N1—H1A	104.9	N2—C23—C24	113.4 (4)
C12—C11—N1	117.3 (5)	N2—C23—H23A	108.9
C12—C11—H11A	108.0	C24—C23—H23A	108.9
N1—C11—H11A	108.0	N2—C23—H23B	108.9
C12—C11—H11B	108.0	C24—C23—H23B	108.9
N1—C11—H11B	108.0	H23A—C23—H23B	107.7
H11A—C11—H11B	107.2	C23—C24—H24A	109.5
C11—C12—H12A	109.5	C23—C24—H24B	109.5
C11—C12—H12B	109.5	H24A—C24—H24B	109.5
H12A—C12—H12B	109.5	C23—C24—H24C	109.5
C11—C12—H12C	109.5	H24A—C24—H24C	109.5
H12A—C12—H12C	109.5	H24B—C24—H24C	109.5
H12B—C12—H12C	109.5	C13—C14—H14A	109.5
C14—C13—N1	120.3 (6)	C13—C14—H14B	109.5
C14—C13—H13A	107.3	H14A—C14—H14B	109.5
N1—C13—H13A	107.3	C13—C14—H14C	109.5
C14—C13—H13B	107.3	H14A—C14—H14C	109.5
N1—C13—H13B	107.3	H14B—C14—H14C	109.5

Symmetry codes: (i) $-x+1/2$, $-y+1/2$, $-z+1/2$.

Fig. 1


N2
Ti1
Cl1
Cl2
O1
N1
C22
Cl2
Cl1
C21
N2
Ti1
C23
C24
O1
N1^i
C13
N1
C11
C14
Ti1^i
N2^i
C12
Cl1^i
Cl2^i