Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.090$
$S = 1.706$
1883 reflections
203 parameters
H atoms not refined
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983)
Flack parameter = 1.01 (2)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
Cu	0.62611 (3)	0.17195 (2)	0.72711	0.0334 (2)
O1	1/2	0.2471 (4)	0.6000 (5)	0.070 (4)
O2	1/2	0.1123 (3)	0.7453 (3)	0.044 (2)
N1	0.6759 (3)	0.0924 (2)	0.6293 (3)	0.042 (2)
C2	0.7598 (4)	0.1224 (3)	0.5688 (4)	0.049 (3)
C3	0.7673 (4)	0.2084 (3)	0.5808 (4)	0.052 (3)
N4	0.7582 (3)	0.2310 (2)	0.6846 (3)	0.040 (2)
C4	0.7524 (5)	0.3153 (3)	0.6939 (5)	0.065 (3)
C5	0.8473 (3)	0.2024 (3)	0.7432 (4)	0.048 (3)
C6	0.8152 (4)	0.1680 (3)	0.8379 (4)	0.053 (3)
N7	0.7361 (3)	0.1083 (2)	0.8260 (3)	0.044 (2)
C7	0.6894 (5)	0.0877 (4)	0.9179 (4)	0.068 (4)
C8	0.7715 (4)	0.0406 (3)	0.7698 (5)	0.056 (3)
C9	0.7015 (4)	0.0226 (3)	0.6856 (4)	0.051 (3)
C10	1/2	0.2820 (4)	0.8365 (5)	0.045 (4)
O10	0.5856 (2)	0.2550 (2)	0.8155 (3)	0.051 (2)
C11	1/2	0.3552 (6)	0.8939 (8)	0.076 (6)
Cl1	1/2	0.46626 (10)	0.5763 (2)	0.0544 (10)
O11	1/2	0.5402 (3)	0.6208 (5)	0.072 (4)
O12	1/2	0.4097 (6)	0.6448 (11)	0.204 (14)
O13	0.4119 (7)	0.4555 (5)	0.5300 (9)	0.197 (9)
Cl2	1/2	0.8869 (1)	−0.1040 (1)	0.055 (1)
O21	1/2	0.9230 (8)	−0.1888 (8)	0.158 (11)
O22†	1/2	0.9365 (4)	−0.0196 (5)	0.080 (4)
O23†	0.4196 (11)	0.8390 (9)	−0.0955 (8)	0.252 (13)
O22′‡	0.599 (3)	0.895 (2)	−0.151 (3)	0.047 (8)
O21′‡	1/2	0.809 (2)	−0.096 (3)	0.022 (7)

† Site occupancy = 0.9. ‡ Site occupancy = 0.1.

Table 2. *Selected geometric parameters (Å, °)*

Cu—O1	2.737 (5)	Cu—N7	2.269 (4)
Cu—O2	1.963 (2)	Cu—O10	1.960 (4)
Cu—N1	2.037 (4)	Cu···Cu^{i}	3.2975 (8)
Cu—N4	2.092 (4)		
Cu—O1—Cu^{i}	74.07 (16)	Cu—O2—Cu^{i}	114.3 (2)

Symmetry code: (i) $1 - x, y, z$.

H atoms on N and methylene C atoms were placed in calculated positions with a C(N)—H distance of 0.95 Å. H atoms on methyl C atoms were placed on peaks in the difference map. The hydroxy H atom was placed on a likely peak in the difference map, but the water H atoms could not be located and were not included in the refinement; U_{iso}(H) was fixed at 0.07 Å^2 and coordinates were refined in intermediate cycles but not in the final cycle of refinement. The perchlorate ion (Cl2) is disordered. The disorder was modelled by including two orientations of the tetrahedra having Cl2 and O22 in common. Atoms Cl2, O21, O22 and O23 were refined with anisotropic displacement parameters and fixed occupancies for O21 and O23 of 0.9; atoms O21′ and O22′ were refined with isotropic displacement parameters and fixed occupancies of 0.1. The displacement ellipsoid of O23 is elongated and is an indication of the limitations of the modelling of the disorder. The reported coordinates are for a crystal with the opposite hand to that used in the experiment. *Xtal*3.4 software (Hall *et al.*, 1995) was used throughout the analysis (structure solution and refinement, molecular graphics and preparation of material for publication).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.4.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1241). Services for accessing these data are described at the back of the journal.

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$[Ti_2(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2(O^iPr)_4(\mu\text{-}O^iPr)_2]$

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Abstract

The title titanium(IV) alkoxide dimer, bis(μ-isopropoxido-*O*:*O*)bis[triisopropoxido(2,4,6-trimethylphenoxido)titanium(IV)], $[Ti_2(C_3H_7O)_6(C_9H_{11}O)_2]$, has been prepared and characterized by X-ray crystallography.

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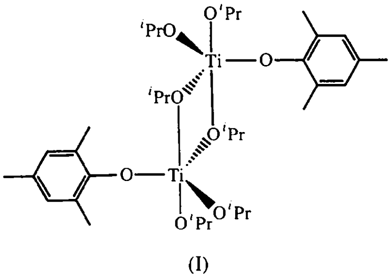
Comment

Titanium alkoxides are important as catalysts in organic reactions and as precursors to mixed-metal oxide electroceramic and ferroelectric materials, for example, $BaTiO_3$ or $PbBiTiSbO_7$.

Titanium(IV) alkoxides are most commonly observed with the titanium centre in a six-coordinate octahedral environment which is generally achieved either by dimerization/oligomerization or coordination of ancillary ligands such as tetrahydrofuran. In situations where particularly bulky substituents are involved, monomeric four-coordinate species have been reported.

In comparison, only a few five-coordinate species have been structurally characterized, almost all existing as dimers. These include bis{(μ_2-isopropoxo)(isopropoxy)[2,2′-thiobis(4-methyl-6-*tert*-butylphenoxy)]titanium} (Capelli *et al.*, 1996), bis[pentacarbonyl(μ_2-*n*-butylcarbenyloxy)(μ_2-isopropoxo)diisopropoxychromium(0)-titanium(IV)] (Finn *et al.*, 1992) and bis[(μ_2-2,6-difluorophenoxo)bis(2,6-difluorophenoxy)(isopropoxy)]-dititanium(IV) (Bott *et al.*, 1994), with titanium in a square-based pyramidal geometry, and bis[(μ_2-isopropoxo)bis(1,1,1,3,3,3-hexafluoro-2-propoxy)titanium] (Fisher *et al.*, 1993) and bis(μ_2-2,2′,4,4′-tetrachloro-3,3′,5,5′-tetramethylbiphenolato-*O*,*O*)tetrakis(isopropoxy)dititanium(IV) dichloromethane solvate (Corey *et al.*, 1994), with titanium in a trigonal-bipyramidal geometry.

This paper describes a further example, (I), of a dititanium(IV) mixed alkoxide in which each titanium is bonded to two terminal O^{i}Pr and one terminal O-2,4,6-$Me_3C_6H_2$ groups, with two further O^{i}Pr groups acting as μ_2-bridging ligands.



(I)

Each titanium in (I) resides in a slightly distorted trigonal-bipyramidal geometry, with one μ_2-O^{i}Pr group in an axial and one in an equatorial site. The O-2,4,6-$Me_3C_6H_2$ groups occupy terminal equatorial sites on the titanium and are arranged *trans* to each other such that the molecule has crystallographic C_i symmetry.

The bridges are asymmetric, with the axial bond being longer [2.117 (2) Å] and the equatorial bond [1.938 (2) Å] being shorter. The Ti—O bond lengths are 1.784 (2) and 1.793 (2) Å for the titanium–isopropoxide bonds, and 1.812 (2) Å for the titanium–trimethylphenoxide bond. The bond angles at titanium are distorted from ideal values towards tetrahedral [ignoring O4^i; symmetry code: (i) $1-x$, $1-y$, $1-z$]. Thus, the longer axial Ti—μ_2-O distance (Ti—O4^i) shows O_{ax}—Ti—O_{eq} angles of less than 90°, whilst the other axial bond (Ti—O3) has angles greater than 90°. Other bond lengths and angles in this structure are similar to those observed for the analogous structures listed above.

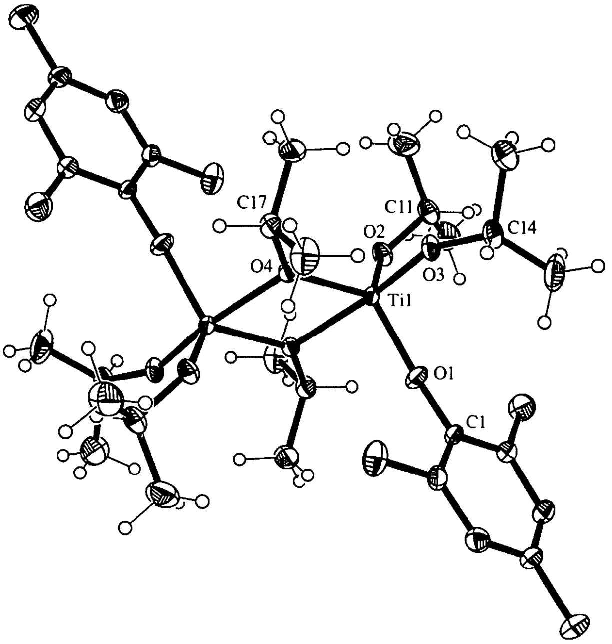


Fig. 1. The structure of $[Ti_2(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2(O^iPr)_4(\mu\text{-}O^iPr)_2]$ with displacement ellipsoids drawn at the 30% probability level. Only unique atoms are labelled.

Experimental

Addition of dried 2,4,6-trimethylphenol (0.550 g) in tetrahydrofuran (2 ml) to $Ti(O^iPr)_4$ (0.180 g) in tetrahydrofuran (2 ml) at 273 K, under an atmosphere of dry nitrogen, and subsequent stirring at room temperature for 30 min gave an orange–red solution. On removal of some of the solvent and layering with hexane, orange block-like crystals were grown overnight at 240 K. Crystals were mounted in silicone grease, under an atmosphere of argon, in oil.

Crystal data

$[Ti_2(C_3H_7O)_6(C_9H_{11}O)_2]$
$M_r = 720.67$
Orthorhombic
Pbcn
$a = 22.036\ (4)$ Å
$b = 9.243\ (2)$ Å
$c = 19.816\ (3)$ Å
$V = 4036.0\ (13)$ Å^3
$Z = 4$
$D_x = 1.186$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 159 reflections
$\theta = 5\text{–}50°$
$\mu = 0.439$ mm^{-1}
$T = 173\ (2)$ K
Block
0.5 × 0.4 × 0.4 mm
Orange

Data collection

Siemens CCD area-detector diffractometer
ω rotation scans with narrow frame
Absorption correction: *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.515$, $T_{\max} = 0.839$
23 897 measured reflections
4627 independent reflections
2884 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.075$
$\theta_{\max} = 27.53°$
$h = -28 \rightarrow 28$
$k = -12 \rightarrow 11$
$l = -25 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.056$
$wR(F^2) = 0.150$
$S = 1.088$
4627 reflections
208 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 1.048$ e Å^{-3}
$\Delta\rho_{\min} = -0.418$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ti1—O3	1.784 (2)	Ti1—O4	1.938 (2)
Ti1—O2	1.793 (2)	Ti1—O4'	2.117 (2)
Ti1—O1	1.812 (2)		
O3—Ti1—O2	99.59 (10)	O1—Ti1—O4	126.35 (10)
O3—Ti1—O1	97.58 (10)	O3—Ti1—O4'	168.38 (9)
O2—Ti1—O1	111.85 (11)	O2—Ti1—O4'	88.26 (9)
O3—Ti1—O4	96.72 (9)	O1—Ti1—O4'	87.29 (9)
O2—Ti1—O4	116.18 (9)	O4—Ti1—O4'	72.01 (8)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 10 s exposure. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 90 and 180°, with the area detector held at $2\theta = -29°$. The crystal-to-detector distance was 4.974 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed. H atoms were included in the model in idealized sp^2 or sp^3 geometries, riding on their attached C atom.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1214). Services for accessing these data are described at the back of the journal.

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[*N*,*N*'-Ethylenebis(3-*tert*-butyl-5-methylsalicylideneaminato)]oxovanadium(IV)†

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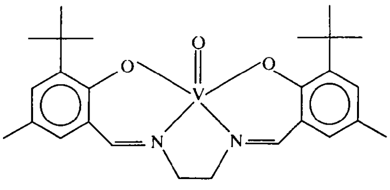
Abstract

$[\mathrm{VO}(\mathrm{C}_{26}\mathrm{H}_{34}\mathrm{N}_2\mathrm{O}_2)]$ was synthesized in order to study its reactivity in the oxygen-transfer catalysis of alkyl hydroperoxides to a wide array of substituted olefins. The geometry about the V center is nearly square pyramidal, with an axial oxo ligand and a four-coordinate substituted Schiff base ligand. The axial V—O bond distance of 1.592 (3) Å is indicative of double-bond character.

Comment

The crystal structure of the title compound, (I), is formed by essentially discrete molecules with only one intermolecular interaction between any two molecules.



(I)

The unique molecule contains a central V atom, which exhibits square-pyramidal coordination where the phenolate O atoms and the imino N atoms are *cis* due to geometrical constraints of the backbone ligand (Fig. 1). The axial V═O bond is essentially perpendicu-

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† Alternative name: {6,6'-di-*tert*-butyl-2,2'-[1,2-ethanediylbis(nitrilomethylidyne-*N*)]-4,4'-dimethyldiphenolato-*O*,*O*'}oxovanadium(IV).