

Tetrakis(*N,N*-diethylcarbamato)-titanium(IV)

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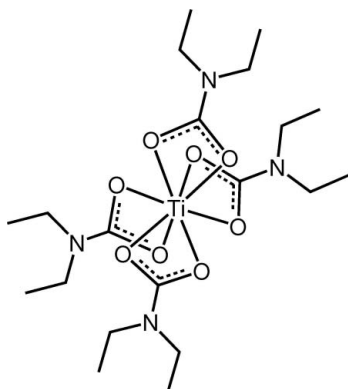
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Key indicators: single-crystal X-ray study; $T = 263$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; disorder in main residue; R factor = 0.044; wR factor = 0.114; data-to-parameter ratio = 15.2.

The mononuclear title compound, $[\text{Ti}(\text{C}_5\text{H}_{10}\text{NO}_2)_4]$, is a rare example of an eight-coordinate Ti^{IV} compound in which all donor atoms are O atoms. The coordination geometry around Ti^{IV} is pseudo-dodecahedral and the O—C—O angles of the carbamate ligands are slightly compressed [range 115.3 (2)–116.7 (2)°], apparently on account of the high coordination number. One ethyl group is disordered over two positions; the site occupancy factors are 0.64 and 0.36.

Related literature

The *pseudo*-dodecahedral description of the coordination geometry is discussed in: Dell'Amico *et al.* (2000). For related structures, see: Chisholm & Extine (1977*b*); Dell'Amico *et al.* (2003); McCowan *et al.* (2004). Related synthesis details are given in: Calderazzo *et al.* (1991); Chisholm & Extine (1977*a*).



Experimental

Crystal data

| | |
|---|-----------------------------------|
| $[\text{Ti}(\text{C}_5\text{H}_{10}\text{NO}_2)_4]$ | $V = 2688.4$ (3) Å ³ |
| $M_r = 512.46$ | $Z = 4$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 13.9906$ (9) Å | $\mu = 0.37$ mm ⁻¹ |
| $b = 11.7183$ (8) Å | $T = 263$ (2) K |
| $c = 17.7483$ (12) Å | $0.23 \times 0.18 \times 0.14$ mm |
| $\beta = 112.494$ (1)° | |

Data collection

| | |
|--|--|
| Bruker SMART APEX CCD diffractometer | 21432 measured reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | 4751 independent reflections |
| $T_{\min} = 0.922$, $T_{\max} = 0.950$ | 3280 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.052$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | 4 restraints |
| $wR(F^2) = 0.114$ | H-atom parameters constrained |
| $S = 0.94$ | $\Delta\rho_{\text{max}} = 0.21$ e Å ⁻³ |
| 4751 reflections | $\Delta\rho_{\text{min}} = -0.25$ e Å ⁻³ |
| 313 parameters | |

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: B12252).

References

- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SADABS* (Version 2.03), *SAINT* (Version 6.28A) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
- Calderazzo, F., Ianelli, S., Pampaloni, G., Pelizzi, G. & Sperrle, M. (1991). *J. Chem. Soc. Dalton Trans.* pp. 693–698.
- Chisholm, M. H. & Extine, M. W. (1977*a*). *J. Am. Chem. Soc.* **99**, 782–792.
- Chisholm, M. H. & Extine, M. W. (1977*b*). *J. Am. Chem. Soc.* **99**, 792–802.
- Dell'Amico, D. B., Calderazzo, F., Ianelli, S., Labella, L., Marchetti, F. & Pelizzi, G. (2000). *J. Chem. Soc. Dalton Trans.* pp. 4339–4342.
- Dell'Amico, D. B., Calderazzo, F., Labella, L., Marchetti, F. & Pampaloni, G. (2003). *Chem. Rev.* **103**, 3857–3897.
- McCowan, C. S., Buss, C. E., Young, V. G. Jr, McDonnell, R. L. & Caudle, M. T. (2004). *Acta Cryst.* **E60**, m285–m287.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

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Tetrakis(*N,N*-diethylcarbamato)titanium(IV)

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Comment

Preparation of the title compound has been previously reported *via* direct reaction of $\text{Ti}(\text{NEt}_2)_4$ with CO_2 (Chisholm & Extine, 1977*a*), and by a one-pot approach similar to that described herein but using a different solvent system (Calderazzo *et al.*, 1991). In neither case was the compound structurally established by X-ray crystallography, although it was suggested to be mononuclear.

The coordination environment around the Ti^{IV} atom in the title compound consists of eight O atoms derived from the four bidentate carbamate ligands. The Ti—O bond distances are all similar, ranging between 2.0530 (15) and 2.1087 (16) Å, while the O—C—O angles of the carbamate ligands range from 115.3 (2) to 116.7 (2)°. These angles are considerably smaller than O—C—O angles in complexes having terminal η^1 or $\mu_{1,3}$ -bridging carbamate ligands, which tend to be greater than 120°, and they are small even when compared to other bidentate carbamate ligands (Dell'Amico *et al.*, 2003; McCowan *et al.*, 2004). The compressed O—C—O angles in the title compound are attributed in part to the high coordination number about the Ti^{IV} center, which has the effect of forcing the O atoms closer to one another.

Eight-coordinate Ti^{IV} compounds are rare, particularly in an environment consisting solely of O donor ligands (Dell'Amico *et al.*, 2000). The title compound has a similar core structure to tetrakis(*N,N*-diisopropylcarbamato)titanium(IV) (Dell'Amico *et al.*, 2000), which together with the six-coordinate distorted octahedral compound bis(dimethylamido)bis(*N,N*-dimethylcarbamato)titanium(IV) (Chisholm & Extine, 1977*b*) are the only other crystallographically characterized mononuclear carbamate complexes of Ti^{IV} .

Experimental

While stirring under an atmosphere of N_2 , 1.00 ml (9.12 mmol) of TiCl_4 was added to approximately 70 ml of anhydrous THF in a Schlenk flask. A yellow solid formed that dissolved within several minutes. To the resulting bright yellow solution was added 7.50 ml (72.50 mmol) of anhydrous diethylamine. The mixture turned dark blue, almost black, in color. After ten minutes the flask was evacuated of all N_2 and charged with 1 atm of anhydrous CO_2 gas which caused the reaction mixture to turn yellow/orange and precipitate solid. After stirring overnight, solid white diethylammonium chloride was removed by filtration under N_2 . Approximately 30 ml freshly distilled *n*-hexane was added to the clear light yellow filtrate and the volume was reduced by slow evaporation under a stream of N_2 . This gave 2.85 g (61%) of pale yellow crystals suitable for X-ray analysis.

Refinement

H atoms were positioned geometrically and allowed to ride with C—H = 0.96 Å, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl groups and C—H = 0.97 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the methylene groups. One ethyl group on the diethylcarbamate ligand

supplementary materials

containing N1A is disordered. Atoms C1D–C1E represent the majority component (site occupancy factor 0.639 (4)) and C1D'–C1E' represent the minority component (site occupancy factor 0.361 (4)). The components were refined with N–C and C–C bond lengths restrained to 1.46 (1) and 1.48 (1) Å, respectively, and with anisotropic displacement parameters constrained to be identical for the atom pairs C1D/C1D' and C1E/C1E'. Data were collected at 263 K because the crystals undergo what is believed to be a destructive phase transformation somewhere in the range 173–243 K.

Figures

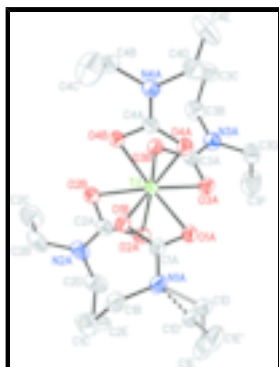


Fig. 1. Molecular structure of the title compound with displacement ellipsoids shown at the 25% probability level. H atoms are omitted. Disorder of one ethyl group bonded to N1A is shown using C1D–C1E as the major component and C1D'–C1E' as the minor component.

Tetrakis(*N,N*-diethylcarbamato)titanium(IV)

Crystal data

[Ti(C₅H₁₀NO₂)₄]

M_r = 512.46

Monoclinic, *P*2₁/*n*

Hall symbol: -*P* 2₁ *n*

a = 13.9906 (9) Å

b = 11.7183 (8) Å

c = 17.7483 (12) Å

β = 112.494 (1)°

V = 2688.4 (3) Å³

Z = 4

*F*₀₀₀ = 1096

D_x = 1.266 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 7268 reflections

θ = 2.4–25.3°

μ = 0.37 mm⁻¹

T = 263 (2) K

Block, light-yellow

0.23 × 0.18 × 0.14 mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 263(2) K

ω scan

Absorption correction: multi-scan
(SADABS; Bruker, 2001)

*T*_{min} = 0.922, *T*_{max} = 0.950

4751 independent reflections

3280 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.052

θ_{max} = 25.0°

θ_{min} = 2.1°

h = -16→16

k = -13→13

21432 measured reflections

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.044$

H-atom parameters constrained

$wR(F^2) = 0.114$

$$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 0.94$

$(\Delta/\sigma)_{\max} = 0.001$

4751 reflections

$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$

313 parameters

$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

4 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|-------------|--------------|----------------------------------|-----------|
| Ti1 | 0.53057 (3) | 0.40515 (3) | 0.75825 (2) | 0.04645 (15) | |
| C1A | 0.70112 (19) | 0.4099 (2) | 0.75016 (15) | 0.0550 (6) | |
| C1B | 0.8487 (2) | 0.5285 (2) | 0.7645 (2) | 0.0790 (9) | |
| H1B1 | 0.7999 | 0.5833 | 0.7294 | 0.095* | |
| H1B2 | 0.9061 | 0.5228 | 0.7468 | 0.095* | |
| C1C | 0.8880 (2) | 0.5717 (3) | 0.8500 (2) | 0.0964 (11) | |
| H1C1 | 0.8315 | 0.5789 | 0.8677 | 0.145* | |
| H1C2 | 0.9198 | 0.6450 | 0.8524 | 0.145* | |
| H1C3 | 0.9381 | 0.5192 | 0.8849 | 0.145* | |
| C1D | 0.8506 (4) | 0.3100 (4) | 0.7419 (3) | 0.0744 (17) | 0.639 (4) |
| H1D1 | 0.8011 | 0.2484 | 0.7214 | 0.089* | 0.639 (4) |
| H1D2 | 0.8828 | 0.3242 | 0.7031 | 0.089* | 0.639 (4) |
| C1E | 0.9301 (5) | 0.2802 (5) | 0.8232 (4) | 0.130 (2) | 0.639 (4) |
| H1E1 | 0.9822 | 0.3386 | 0.8402 | 0.195* | 0.639 (4) |
| H1E2 | 0.9615 | 0.2086 | 0.8197 | 0.195* | 0.639 (4) |
| H1E3 | 0.8980 | 0.2742 | 0.8621 | 0.195* | 0.639 (4) |

supplementary materials

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|------|--------------|--------------|--------------|-------------|-----------|
| C1D' | 0.8672 (7) | 0.3171 (8) | 0.7944 (6) | 0.0744 (17) | 0.361 (4) |
| H1DA | 0.9128 | 0.3364 | 0.8496 | 0.089* | 0.361 (4) |
| H1DB | 0.8264 | 0.2510 | 0.7961 | 0.089* | 0.361 (4) |
| C1E' | 0.9272 (10) | 0.2938 (9) | 0.7440 (7) | 0.130 (2) | 0.361 (4) |
| H1EA | 0.9733 | 0.2310 | 0.7669 | 0.195* | 0.361 (4) |
| H1EB | 0.9665 | 0.3602 | 0.7425 | 0.195* | 0.361 (4) |
| H1EC | 0.8809 | 0.2748 | 0.6896 | 0.195* | 0.361 (4) |
| N1A | 0.79773 (16) | 0.41651 (17) | 0.75455 (16) | 0.0756 (7) | |
| O1A | 0.65588 (12) | 0.31632 (13) | 0.75096 (10) | 0.0585 (4) | |
| O1B | 0.64677 (11) | 0.50028 (13) | 0.74517 (10) | 0.0549 (4) | |
| C2A | 0.5985 (2) | 0.4936 (2) | 0.89342 (16) | 0.0617 (7) | |
| C2B | 0.6239 (3) | 0.6631 (3) | 0.97834 (19) | 0.0927 (10) | |
| H2B1 | 0.6057 | 0.7042 | 0.9273 | 0.111* | |
| H2B2 | 0.6853 | 0.6981 | 1.0181 | 0.111* | |
| C2C | 0.5377 (3) | 0.6704 (3) | 1.0072 (2) | 0.1165 (13) | |
| H2C1 | 0.4762 | 0.6390 | 0.9666 | 0.175* | |
| H2C2 | 0.5259 | 0.7489 | 1.0166 | 0.175* | |
| H2C3 | 0.5553 | 0.6282 | 1.0570 | 0.175* | |
| C2D | 0.7143 (3) | 0.4758 (3) | 1.03593 (18) | 0.1000 (11) | |
| H2D1 | 0.6949 | 0.3960 | 1.0270 | 0.120* | |
| H2D2 | 0.7048 | 0.5002 | 1.0848 | 0.120* | |
| C2E | 0.8246 (3) | 0.4874 (5) | 1.0491 (3) | 0.171 (2) | |
| H2E1 | 0.8347 | 0.4634 | 1.0009 | 0.257* | |
| H2E2 | 0.8656 | 0.4407 | 1.0943 | 0.257* | |
| H2E3 | 0.8453 | 0.5658 | 1.0605 | 0.257* | |
| N2A | 0.64547 (18) | 0.5425 (2) | 0.96643 (13) | 0.0782 (7) | |
| O2A | 0.61867 (13) | 0.39039 (15) | 0.88078 (10) | 0.0660 (5) | |
| O2B | 0.53366 (13) | 0.54604 (14) | 0.83306 (10) | 0.0587 (4) | |
| C3A | 0.4128 (2) | 0.2649 (2) | 0.77832 (14) | 0.0554 (6) | |
| C3B | 0.2466 (2) | 0.2274 (3) | 0.78633 (19) | 0.0814 (9) | |
| H3B1 | 0.2532 | 0.3053 | 0.8062 | 0.098* | |
| H3B2 | 0.2271 | 0.1799 | 0.8229 | 0.098* | |
| C3C | 0.1656 (3) | 0.2221 (3) | 0.7042 (2) | 0.1197 (13) | |
| H3C1 | 0.1867 | 0.2653 | 0.6673 | 0.180* | |
| H3C2 | 0.1026 | 0.2533 | 0.7050 | 0.180* | |
| H3C3 | 0.1545 | 0.1440 | 0.6865 | 0.180* | |
| C3D | 0.3691 (2) | 0.0673 (2) | 0.79305 (19) | 0.0792 (9) | |
| H3D1 | 0.4157 | 0.0511 | 0.7656 | 0.095* | |
| H3D2 | 0.3056 | 0.0252 | 0.7652 | 0.095* | |
| C3F | 0.4174 (3) | 0.0266 (3) | 0.8796 (2) | 0.1360 (16) | |
| H3F1 | 0.4800 | 0.0684 | 0.9077 | 0.204* | |
| H3F2 | 0.4330 | -0.0532 | 0.8803 | 0.204* | |
| H3F3 | 0.3701 | 0.0386 | 0.9063 | 0.204* | |
| N3A | 0.34594 (17) | 0.18900 (18) | 0.78668 (13) | 0.0661 (6) | |
| O3A | 0.49815 (13) | 0.23417 (13) | 0.77522 (10) | 0.0591 (4) | |
| O3B | 0.39348 (12) | 0.37213 (14) | 0.77267 (10) | 0.0561 (4) | |
| C4A | 0.42082 (17) | 0.4551 (2) | 0.61816 (14) | 0.0500 (6) | |
| C4B | 0.3207 (2) | 0.5963 (2) | 0.51902 (16) | 0.0681 (7) | |
| H4B1 | 0.3264 | 0.6367 | 0.5682 | 0.082* | |

| | | | | |
|------|--------------|--------------|--------------|-------------|
| H4B2 | 0.2478 | 0.5909 | 0.4846 | 0.082* |
| C4D | 0.3324 (3) | 0.3942 (3) | 0.47780 (17) | 0.0915 (10) |
| H4D1 | 0.3785 | 0.3293 | 0.4966 | 0.110* |
| H4D2 | 0.3398 | 0.4244 | 0.4294 | 0.110* |
| C4C | 0.3734 (3) | 0.6632 (3) | 0.4759 (2) | 0.1295 (15) |
| H4C1 | 0.4431 | 0.6791 | 0.5124 | 0.194* |
| H4C2 | 0.3371 | 0.7337 | 0.4572 | 0.194* |
| H4C3 | 0.3744 | 0.6204 | 0.4301 | 0.194* |
| C4E | 0.2238 (3) | 0.3556 (4) | 0.4564 (3) | 0.1613 (19) |
| H4E1 | 0.2174 | 0.3206 | 0.5032 | 0.242* |
| H4E2 | 0.2058 | 0.3013 | 0.4127 | 0.242* |
| H4E3 | 0.1781 | 0.4200 | 0.4397 | 0.242* |
| N4A | 0.36206 (16) | 0.48149 (18) | 0.54101 (12) | 0.0624 (6) |
| O4A | 0.46113 (12) | 0.35681 (14) | 0.63830 (9) | 0.0567 (4) |
| O4B | 0.43958 (11) | 0.52675 (12) | 0.67580 (9) | 0.0499 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-------------|-------------|-------------|--------------|--------------|---------------|
| Ti1 | 0.0451 (3) | 0.0418 (3) | 0.0482 (3) | 0.00093 (18) | 0.01313 (19) | -0.00154 (18) |
| C1A | 0.0531 (15) | 0.0437 (14) | 0.0666 (17) | 0.0018 (12) | 0.0210 (12) | 0.0013 (12) |
| C1B | 0.0607 (18) | 0.0499 (17) | 0.129 (3) | -0.0032 (13) | 0.0386 (18) | 0.0121 (17) |
| C1C | 0.079 (2) | 0.062 (2) | 0.132 (3) | -0.0101 (16) | 0.022 (2) | 0.0070 (19) |
| C1D | 0.049 (2) | 0.055 (2) | 0.110 (5) | 0.0029 (18) | 0.022 (3) | -0.003 (3) |
| C1E | 0.131 (4) | 0.075 (3) | 0.150 (5) | 0.044 (3) | 0.015 (5) | -0.008 (4) |
| C1D' | 0.049 (2) | 0.055 (2) | 0.110 (5) | 0.0029 (18) | 0.022 (3) | -0.003 (3) |
| C1E' | 0.131 (4) | 0.075 (3) | 0.150 (5) | 0.044 (3) | 0.015 (5) | -0.008 (4) |
| N1A | 0.0499 (13) | 0.0448 (13) | 0.136 (2) | 0.0011 (10) | 0.0398 (14) | 0.0025 (12) |
| O1A | 0.0495 (10) | 0.0411 (10) | 0.0844 (13) | 0.0000 (7) | 0.0250 (9) | -0.0010 (8) |
| O1B | 0.0487 (9) | 0.0408 (9) | 0.0736 (11) | 0.0040 (7) | 0.0217 (8) | 0.0026 (8) |
| C2A | 0.0604 (16) | 0.0686 (18) | 0.0503 (16) | -0.0084 (14) | 0.0147 (13) | -0.0044 (14) |
| C2B | 0.104 (3) | 0.110 (3) | 0.060 (2) | -0.039 (2) | 0.0262 (18) | -0.0267 (18) |
| C2C | 0.123 (3) | 0.140 (4) | 0.094 (3) | -0.022 (3) | 0.049 (2) | -0.028 (2) |
| C2D | 0.096 (3) | 0.128 (3) | 0.0536 (19) | -0.020 (2) | 0.0041 (17) | 0.0037 (18) |
| C2E | 0.080 (3) | 0.257 (6) | 0.140 (4) | -0.016 (3) | 0.001 (3) | 0.071 (4) |
| N2A | 0.0854 (17) | 0.0863 (18) | 0.0474 (14) | -0.0137 (14) | 0.0083 (12) | -0.0113 (12) |
| O2A | 0.0680 (12) | 0.0646 (12) | 0.0520 (10) | 0.0045 (9) | 0.0080 (8) | 0.0042 (9) |
| O2B | 0.0616 (11) | 0.0568 (10) | 0.0489 (10) | 0.0036 (8) | 0.0112 (8) | -0.0082 (8) |
| C3A | 0.0567 (16) | 0.0596 (17) | 0.0489 (15) | -0.0058 (13) | 0.0192 (12) | 0.0004 (12) |
| C3B | 0.079 (2) | 0.087 (2) | 0.091 (2) | -0.0163 (17) | 0.0456 (18) | -0.0010 (17) |
| C3C | 0.073 (2) | 0.146 (4) | 0.128 (3) | -0.014 (2) | 0.025 (2) | -0.020 (3) |
| C3D | 0.088 (2) | 0.0605 (19) | 0.097 (2) | -0.0171 (15) | 0.0442 (19) | -0.0013 (16) |
| C3F | 0.199 (5) | 0.084 (3) | 0.110 (3) | 0.016 (3) | 0.043 (3) | 0.022 (2) |
| N3A | 0.0642 (14) | 0.0626 (14) | 0.0794 (16) | -0.0077 (11) | 0.0361 (12) | 0.0024 (11) |
| O3A | 0.0544 (11) | 0.0472 (10) | 0.0761 (12) | 0.0012 (8) | 0.0255 (9) | 0.0055 (8) |
| O3B | 0.0538 (10) | 0.0522 (10) | 0.0634 (11) | 0.0003 (8) | 0.0235 (8) | -0.0006 (8) |
| C4A | 0.0468 (14) | 0.0538 (15) | 0.0485 (15) | -0.0024 (11) | 0.0173 (11) | -0.0055 (12) |
| C4B | 0.0665 (17) | 0.0782 (19) | 0.0540 (16) | 0.0120 (14) | 0.0167 (13) | 0.0083 (14) |

supplementary materials

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|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| C4D | 0.109 (3) | 0.091 (2) | 0.0515 (18) | 0.0121 (19) | 0.0055 (16) | -0.0182 (16) |
| C4C | 0.171 (4) | 0.113 (3) | 0.138 (4) | 0.013 (3) | 0.097 (3) | 0.040 (3) |
| C4E | 0.160 (4) | 0.156 (4) | 0.139 (4) | -0.081 (4) | 0.024 (3) | -0.062 (3) |
| N4A | 0.0682 (14) | 0.0642 (14) | 0.0449 (12) | 0.0067 (11) | 0.0104 (10) | -0.0070 (10) |
| O4A | 0.0646 (11) | 0.0486 (10) | 0.0516 (10) | 0.0069 (8) | 0.0162 (8) | -0.0081 (8) |
| O4B | 0.0540 (10) | 0.0455 (9) | 0.0456 (9) | 0.0024 (7) | 0.0139 (7) | -0.0044 (7) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|----------|-----------|
| Ti1—O4A | 2.0530 (15) | C2D—N2A | 1.467 (3) |
| Ti1—O2A | 2.0561 (16) | C2D—C2E | 1.477 (4) |
| Ti1—O1B | 2.0562 (15) | C2D—H2D1 | 0.970 |
| Ti1—O3B | 2.0663 (16) | C2D—H2D2 | 0.970 |
| Ti1—O1A | 2.0851 (16) | C2E—H2E1 | 0.960 |
| Ti1—O4B | 2.0897 (15) | C2E—H2E2 | 0.960 |
| Ti1—O3A | 2.1013 (16) | C2E—H2E3 | 0.960 |
| Ti1—O2B | 2.1087 (16) | C3A—O3A | 1.269 (3) |
| C1A—O1A | 1.269 (3) | C3A—O3B | 1.281 (3) |
| C1A—O1B | 1.287 (3) | C3A—N3A | 1.339 (3) |
| C1A—N1A | 1.326 (3) | C3B—N3A | 1.458 (3) |
| C1B—N1A | 1.471 (3) | C3B—C3C | 1.466 (4) |
| C1B—C1C | 1.491 (4) | C3B—H3B1 | 0.970 |
| C1B—H1B1 | 0.970 | C3B—H3B2 | 0.970 |
| C1B—H1B2 | 0.970 | C3C—H3C1 | 0.960 |
| C1C—H1C1 | 0.960 | C3C—H3C2 | 0.960 |
| C1C—H1C2 | 0.960 | C3C—H3C3 | 0.960 |
| C1C—H1C3 | 0.960 | C3D—N3A | 1.457 (3) |
| C1D—C1E | 1.487 (7) | C3D—C3F | 1.501 (4) |
| C1D—N1A | 1.511 (5) | C3D—H3D1 | 0.970 |
| C1D—H1D1 | 0.970 | C3D—H3D2 | 0.970 |
| C1D—H1D2 | 0.970 | C3F—H3F1 | 0.960 |
| C1E—H1E1 | 0.960 | C3F—H3F2 | 0.960 |
| C1E—H1E2 | 0.960 | C3F—H3F3 | 0.960 |
| C1E—H1E3 | 0.960 | C4A—O4B | 1.271 (3) |
| C1D'—C1E' | 1.468 (9) | C4A—O4A | 1.272 (3) |
| C1D'—N1A | 1.508 (8) | C4A—N4A | 1.336 (3) |
| C1D'—H1DA | 0.970 | C4B—N4A | 1.458 (3) |
| C1D'—H1DB | 0.970 | C4B—C4C | 1.475 (4) |
| C1E'—H1EA | 0.960 | C4B—H4B1 | 0.970 |
| C1E'—H1EB | 0.960 | C4B—H4B2 | 0.970 |
| C1E'—H1EC | 0.960 | C4D—N4A | 1.457 (3) |
| C2A—O2B | 1.267 (3) | C4D—C4E | 1.488 (5) |
| C2A—O2A | 1.281 (3) | C4D—H4D1 | 0.970 |
| C2A—N2A | 1.337 (3) | C4D—H4D2 | 0.970 |
| C2B—N2A | 1.477 (4) | C4C—H4C1 | 0.960 |
| C2B—C2C | 1.481 (4) | C4C—H4C2 | 0.960 |
| C2B—H2B1 | 0.970 | C4C—H4C3 | 0.960 |
| C2B—H2B2 | 0.970 | C4E—H4E1 | 0.960 |
| C2C—H2C1 | 0.960 | C4E—H4E2 | 0.960 |

| | | | |
|---------------|------------|---------------|------------|
| C2C—H2C2 | 0.960 | C4E—H4E3 | 0.960 |
| C2C—H2C3 | 0.960 | | |
| O4A—Ti1—O2A | 158.13 (7) | H2C2—C2C—H2C3 | 109.5 |
| O4A—Ti1—O1B | 96.51 (7) | N2A—C2D—C2E | 113.2 (3) |
| O2A—Ti1—O1B | 89.14 (7) | N2A—C2D—H2D1 | 108.9 |
| O4A—Ti1—O3B | 89.05 (7) | C2E—C2D—H2D1 | 108.9 |
| O2A—Ti1—O3B | 93.58 (7) | N2A—C2D—H2D2 | 108.9 |
| O1B—Ti1—O3B | 157.96 (7) | C2E—C2D—H2D2 | 108.9 |
| O4A—Ti1—O1A | 82.73 (6) | H2D1—C2D—H2D2 | 107.8 |
| O2A—Ti1—O1A | 81.12 (7) | C2D—C2E—H2E1 | 109.5 |
| O1B—Ti1—O1A | 62.86 (6) | C2D—C2E—H2E2 | 109.5 |
| O3B—Ti1—O1A | 139.16 (7) | H2E1—C2E—H2E2 | 109.5 |
| O4A—Ti1—O4B | 62.75 (6) | C2D—C2E—H2E3 | 109.5 |
| O2A—Ti1—O4B | 139.12 (7) | H2E1—C2E—H2E3 | 109.5 |
| O1B—Ti1—O4B | 81.22 (6) | H2E2—C2E—H2E3 | 109.5 |
| O3B—Ti1—O4B | 82.46 (6) | C2A—N2A—C2D | 120.5 (3) |
| O1A—Ti1—O4B | 126.75 (6) | C2A—N2A—C2B | 119.8 (2) |
| O4A—Ti1—O3A | 80.97 (7) | C2D—N2A—C2B | 119.6 (2) |
| O2A—Ti1—O3A | 80.98 (7) | C2A—O2A—Ti1 | 91.30 (14) |
| O1B—Ti1—O3A | 139.15 (7) | C2A—O2B—Ti1 | 89.34 (15) |
| O3B—Ti1—O3A | 62.76 (6) | O3A—C3A—O3B | 116.7 (2) |
| O1A—Ti1—O3A | 76.44 (6) | O3A—C3A—N3A | 121.7 (2) |
| O4B—Ti1—O3A | 130.05 (6) | O3B—C3A—N3A | 121.6 (2) |
| O4A—Ti1—O2B | 139.16 (7) | N3A—C3B—C3C | 111.3 (3) |
| O2A—Ti1—O2B | 62.63 (7) | N3A—C3B—H3B1 | 109.4 |
| O1B—Ti1—O2B | 79.62 (6) | C3C—C3B—H3B1 | 109.4 |
| O3B—Ti1—O2B | 82.25 (7) | N3A—C3B—H3B2 | 109.4 |
| O1A—Ti1—O2B | 127.93 (6) | C3C—C3B—H3B2 | 109.4 |
| O4B—Ti1—O2B | 76.54 (6) | H3B1—C3B—H3B2 | 108.0 |
| O3A—Ti1—O2B | 127.58 (7) | C3B—C3C—H3C1 | 109.5 |
| O1A—C1A—O1B | 115.3 (2) | C3B—C3C—H3C2 | 109.5 |
| O1A—C1A—N1A | 123.5 (2) | H3C1—C3C—H3C2 | 109.5 |
| O1B—C1A—N1A | 121.2 (2) | C3B—C3C—H3C3 | 109.5 |
| N1A—C1B—C1C | 113.5 (2) | H3C1—C3C—H3C3 | 109.5 |
| N1A—C1B—H1B1 | 108.9 | H3C2—C3C—H3C3 | 109.5 |
| C1C—C1B—H1B1 | 108.9 | N3A—C3D—C3F | 113.0 (3) |
| N1A—C1B—H1B2 | 108.9 | N3A—C3D—H3D1 | 109.0 |
| C1C—C1B—H1B2 | 108.9 | C3F—C3D—H3D1 | 109.0 |
| H1B1—C1B—H1B2 | 107.7 | N3A—C3D—H3D2 | 109.0 |
| C1B—C1C—H1C1 | 109.5 | C3F—C3D—H3D2 | 109.0 |
| C1B—C1C—H1C2 | 109.5 | H3D1—C3D—H3D2 | 107.8 |
| H1C1—C1C—H1C2 | 109.5 | C3D—C3F—H3F1 | 109.5 |
| C1B—C1C—H1C3 | 109.5 | C3D—C3F—H3F2 | 109.5 |
| H1C1—C1C—H1C3 | 109.5 | H3F1—C3F—H3F2 | 109.5 |
| H1C2—C1C—H1C3 | 109.5 | C3D—C3F—H3F3 | 109.5 |
| C1E—C1D—N1A | 106.1 (4) | H3F1—C3F—H3F3 | 109.5 |
| C1E—C1D—H1D1 | 110.5 | H3F2—C3F—H3F3 | 109.5 |
| N1A—C1D—H1D1 | 110.5 | C3A—N3A—C3D | 120.9 (2) |
| C1E—C1D—H1D2 | 110.5 | C3A—N3A—C3B | 119.9 (2) |

supplementary materials

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|----------------|------------|---------------|------------|
| N1A—C1D—H1D2 | 110.5 | C3D—N3A—C3B | 119.1 (2) |
| H1D1—C1D—H1D2 | 108.7 | C3A—O3A—Ti1 | 89.66 (14) |
| C1E'—C1D'—N1A | 105.9 (7) | C3A—O3B—Ti1 | 90.89 (14) |
| C1E'—C1D'—H1DA | 110.6 | O4B—C4A—O4A | 116.1 (2) |
| N1A—C1D'—H1DA | 110.6 | O4B—C4A—N4A | 121.9 (2) |
| C1E'—C1D'—H1DB | 110.5 | O4A—C4A—N4A | 122.0 (2) |
| N1A—C1D'—H1DB | 110.6 | N4A—C4B—C4C | 113.8 (2) |
| H1DA—C1D'—H1DB | 108.7 | N4A—C4B—H4B1 | 108.8 |
| C1D'—C1E'—H1EA | 109.5 | C4C—C4B—H4B1 | 108.8 |
| C1D'—C1E'—H1EB | 109.5 | N4A—C4B—H4B2 | 108.8 |
| H1EA—C1E'—H1EB | 109.5 | C4C—C4B—H4B2 | 108.8 |
| C1D'—C1E'—H1EC | 109.5 | H4B1—C4B—H4B2 | 107.7 |
| H1EA—C1E'—H1EC | 109.5 | N4A—C4D—C4E | 111.9 (3) |
| H1EB—C1E'—H1EC | 109.5 | N4A—C4D—H4D1 | 109.2 |
| C1A—N1A—C1B | 119.7 (2) | C4E—C4D—H4D1 | 109.2 |
| C1A—N1A—C1D' | 116.2 (4) | N4A—C4D—H4D2 | 109.2 |
| C1B—N1A—C1D' | 115.9 (5) | C4E—C4D—H4D2 | 109.2 |
| C1A—N1A—C1D | 119.3 (3) | H4D1—C4D—H4D2 | 107.9 |
| C1B—N1A—C1D | 120.8 (3) | C4B—C4C—H4C1 | 109.5 |
| C1A—O1A—Ti1 | 90.24 (14) | C4B—C4C—H4C2 | 109.5 |
| C1A—O1B—Ti1 | 91.02 (14) | H4C1—C4C—H4C2 | 109.5 |
| O2B—C2A—O2A | 116.4 (2) | C4B—C4C—H4C3 | 109.5 |
| O2B—C2A—N2A | 122.6 (3) | H4C1—C4C—H4C3 | 109.5 |
| O2A—C2A—N2A | 121.0 (3) | H4C2—C4C—H4C3 | 109.5 |
| N2A—C2B—C2C | 110.1 (3) | C4D—C4E—H4E1 | 109.5 |
| N2A—C2B—H2B1 | 109.6 | C4D—C4E—H4E2 | 109.5 |
| C2C—C2B—H2B1 | 109.6 | H4E1—C4E—H4E2 | 109.5 |
| N2A—C2B—H2B2 | 109.6 | C4D—C4E—H4E3 | 109.5 |
| C2C—C2B—H2B2 | 109.6 | H4E1—C4E—H4E3 | 109.5 |
| H2B1—C2B—H2B2 | 108.2 | H4E2—C4E—H4E3 | 109.5 |
| C2B—C2C—H2C1 | 109.5 | C4A—N4A—C4D | 120.6 (2) |
| C2B—C2C—H2C2 | 109.5 | C4A—N4A—C4B | 120.9 (2) |
| H2C1—C2C—H2C2 | 109.5 | C4D—N4A—C4B | 118.4 (2) |
| C2B—C2C—H2C3 | 109.5 | C4A—O4A—Ti1 | 91.41 (13) |
| H2C1—C2C—H2C3 | 109.5 | C4A—O4B—Ti1 | 89.78 (13) |

Fig. 1

