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# Decaaqua-1$\kappa^5O$,4$\kappa^5O$-bis($\mu$-nitrilotriacetato)-1:2$\kappa^5O$:$N$,$O'$,$O''$,$O'''$;3:4$\kappa^5N$,$O$,$O'$,$O''$:$O'''$-$\mu$-oxido-2:3$\kappa^2O$:$O$-diperoxido-2$\kappa^2O$,$O'$;3$\kappa^2O$,$O'$-1,4-dicopper(II)-2,3-dititanium(IV) heptahydrate

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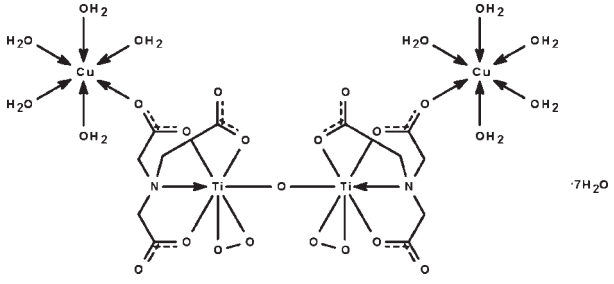
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.026; $wR$ factor = 0.075; data-to-parameter ratio = 16.5.

The tetranuclear title compound, $[Cu_2Ti_2(C_6H_6NO_6)_2O(O_2)_2(H_2O)_{10}]\cdot 7H_2O$, lies about a twofold rotation axis that passes through the bridging oxide atom. The titanium atom is $N$,$O$,$O'$,$O''$-chelated by the nitrilotriacetate and $O$,$O'$-chelated by the peroidxo group and is coordinated to the bridging O atom in an overall pentagonal-bipyramidal geometry. The O atom of one of the carboxylate –$CO_2$ groups binds to the water-coordinated Cu atom, whose coordination polyhedron is an elongated octahedron. Adjacent tetranuclear molecules are linked through the coordinated and uncoordinated water molecules by O—H···O hydrogen bonds into a three-dimensional network.

## Related literature

For the hydrated sodium and ammonium salts of oxobis(nitrilotriacetatoperoxotitanates), see: Schwarzenbach & Girgis (1975); Zhou *et al.* (2004).



## Experimental

### Crystal data

$[Cu_2Ti_2(C_6H_6NO_6)_2O(O_2)_2(H_2O)_{10}]\cdot 7H_2O$
$M_r$ = 985.39
Monoclinic, $C2/c$
$a$ = 14.9312 (10) Å
$b$ = 13.2892 (9) Å
$c$ = 17.4449 (10) Å
$\beta$ = 100.825 (2)°
$V$ = 3399.9 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.81 mm$^{-1}$
$T$ = 293 K
0.30 × 0.20 × 0.20 mm

### Data collection

Rigaku R-AXIS Spider IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.694, $T_{max}$ = 1.000
16221 measured reflections
3894 independent reflections
3408 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.075
$S$ = 1.08
3894 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$w$—H11···O6$w^{i}$ | 0.84 | 1.80 | 2.627 (2) | 169 |
| O1$w$—H12···O9$w^{ii}$ | 0.84 | 1.99 | 2.789 (1) | 159 |
| O2$w$—H21···O1$w^{i}$ | 0.84 | 1.91 | 2.746 (2) | 173 |
| O2$w$—H22···O1$^{iii}$ | 0.84 | 1.90 | 2.737 (2) | 174 |
| O3$w$—H31···O4$^{iv}$ | 0.84 | 1.93 | 2.746 (2) | 165 |
| O3$w$—H32···O4$w^{iii}$ | 0.84 | 1.86 | 2.658 (2) | 158 |
| O4$w$—H4$w$1···O8$^{iii}$ | 0.84 | 1.85 | 2.693 (2) | 176 |
| O4$w$—H4$w$2···O8$w$ | 0.84 | 1.85 | 2.675 (2) | 169 |
| O5$w$—H51···O2$^{v}$ | 0.84 | 2.02 | 2.850 (2) | 168 |
| O5$w$—H52···O7$w$ | 0.84 | 2.01 | 2.813 (3) | 161 |
| O6$w$—H61···O5$w$ | 0.84 | 2.02 | 2.797 (2) | 153 |
| O6$w$—H62···O7$w^{vi}$ | 0.84 | 2.15 | 2.965 (3) | 164 |
| O7$w$—H71···O3 | 0.84 | 2.38 | 3.195 (2) | 163 |
| O7$w$—H72···O9$^{vii}$ | 0.84 | 2.07 | 2.900 (2) | 168 |
| O8$w$—H81···O3$^{viii}$ | 0.84 | 2.06 | 2.890 (2) | 172 |
| O8$w$—H82···O4$^{ix}$ | 0.84 | 2.33 | 3.148 (3) | 164 |
| O9$w$—H9···O2 | 0.84 | 1.89 | 2.716 (2) | 170 |

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iv) $x, -y+1, z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vii) $-x+1, -y+1, -z+1$; (viii) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (ix) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *RAPID-AUTO* (Rigaku, 2002); cell refinement: *RAPID-AUTO*; data reduction: *CrystalClear* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5183).

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# supplementary materials

*Acta Cryst.* (2010). E**66**, m271-m272 [ **doi:10.1107/S1600536810004198** ]

# Decaaqua-1$\kappa^5O$,4$\kappa^5O$-bis($\mu$-nitrilotriacetato)-1:2$\kappa^5O$:*N*,*O*',*O*'',*O*''';3:4$\kappa^5N$,*O*,*O*',*O*'':*O*'''-$\mu$-oxido-2:3$\kappa^2O$:*O*-diperoxido-2$\kappa^2O$,*O*';3$\kappa^2O$,*O*'-1,4-dicopper(II)-2,3-dititanium(IV) heptahydrate

**X.-H. Xie, B.-M. Wang and S. W. Ng**

## Experimental

To a suspension of nitrilotriacetic acid (1.91 g, 10 mol) in water (30 ml) was added titanium tetrabutoxide (3.40 ml). After 12 hours, the mixture was allowed to cool to 273 K; 30% hydrogen peroxide (5 ml) was added. The mixture was filtered. The pH of the filtrate was raised to 4.0. Copper chloride dihydrate (1.70 g, 10 mol) was added. The solution was kept at 279 K for a week. Green crystals were collected and washed with water; the yield was 90%. CH&N elemental analysis. Found (Calc. for $C_{12}H_{46}O_{34}N_2Cu_2Ti_2$): C 14.59 (14.63), H 4.75 (4.71), N 2.82% (2.84%). The crystals do not dissolve in organic solvents.

## Refinement

Carbon-bound H-atoms were allowed to ride on their parent atoms (C–H 0.97 Å) with U(H) set to 1.2$U_{eq}$(C). The water H-atoms were located in a difference Fourier map, and were initially refined with distance restraints of O–H 0.84 and H···H 1.37 Å; with U(H) set to 1.5$U_{eq}$(O). Once found, their positions were fixed.

## Figures

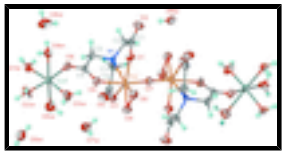


Fig. 1. Anisotropic displacement ellipsoid plot (Barbour, 2001) of $Cu_2Ti_2(O)(O_2)_2(H_2O)_{10}(C_6H_6NO_6)_2{\cdot}7H_2O$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

## Decaaqua-1$\kappa^5O$,4$\kappa^5O$-bis(μ-nitrilotriacetato)- 1:2$\kappa^5O$:*N*,*O*',*O*'',*O*'''; 3:4$\kappa^5N$,*O*,*O*',*O*'':*O*'''-μ-oxido- 2:3$\kappa^2O$:*O*-diperoxido- 2$\kappa^2O$,*O*';3$\kappa^2O$,*O*'-1,4-dicopper(II)- 2,3-dititanium(IV) heptahydrate

*Crystal data*

| | |
|---|---|
| $[Cu_2Ti_2(C_6H_6NO_6)_2O(O_2)_2(H_2O)_{10}]\cdot 7H_2O$ | $F(000) = 2024$ |
| $M_r = 985.39$ | $D_x = 1.925$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| Hall symbol: -C 2yc | Cell parameters from 13230 reflections |
| $a = 14.9312$ (10) Å | θ = 3.1–27.5° |
| $b = 13.2892$ (9) Å | μ = 1.81 mm$^{-1}$ |
| $c = 17.4449$ (10) Å | $T = 293$ K |
| β = 100.825 (2)° | Block, green |
| $V = 3399.9$ (4) Å$^3$ | 0.30 × 0.20 × 0.20 mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS Spider IP diffractometer | 3894 independent reflections |
| Radiation source: fine-focus sealed tube | 3408 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.033$ |
| ω scan | $\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$ |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $h = -19 \rightarrow 19$ |
| $T_{min} = 0.694$, $T_{max} = 1.000$ | $k = -17 \rightarrow 17$ |
| 16221 measured reflections | $l = -22 \rightarrow 22$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.075$ | H-atom parameters constrained |
| $S = 1.08$ | $w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 4.0704P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 3894 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 236 parameters | $\Delta\rho_{max} = 0.44$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.31$ e Å$^{-3}$ |

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.133265 (16) | 0.615605 (19) | 0.469933 (13) | 0.02095 (8) |
| Ti1 | 0.42419 (2) | 0.63347 (3) | 0.319688 (18) | 0.01718 (9) |
| O1 | 0.39888 (10) | 0.78937 (11) | 0.30661 (8) | 0.0241 (3) |
| O2 | 0.36186 (12) | 0.91179 (12) | 0.21923 (9) | 0.0331 (4) |
| O3 | 0.38194 (10) | 0.48763 (11) | 0.28694 (8) | 0.0254 (3) |
| O4 | 0.31766 (13) | 0.38625 (12) | 0.19110 (10) | 0.0355 (4) |
| O5 | 0.31248 (10) | 0.63343 (12) | 0.37559 (8) | 0.0263 (3) |
| O6 | 0.16254 (10) | 0.64622 (12) | 0.36729 (8) | 0.0254 (3) |
| O7 | 0.5000 | 0.63818 (16) | 0.2500 | 0.0239 (4) |
| O8 | 0.50228 (10) | 0.67667 (12) | 0.41151 (8) | 0.0280 (3) |
| O9 | 0.49544 (10) | 0.56625 (12) | 0.40498 (8) | 0.0296 (3) |
| O1w | 0.00795 (10) | 0.58467 (12) | 0.40849 (8) | 0.0254 (3) |
| H11 | −0.0307 | 0.6261 | 0.4188 | 0.038* |
| H12 | 0.0096 | 0.5890 | 0.3607 | 0.038* |
| O2w | 0.08783 (12) | 0.58514 (13) | 0.56735 (9) | 0.0358 (4) |
| H21 | 0.0557 | 0.5363 | 0.5765 | 0.054* |
| H22 | 0.0908 | 0.6269 | 0.6039 | 0.054* |
| O3w | 0.25339 (11) | 0.62901 (14) | 0.53336 (9) | 0.0360 (4) |

| | | | | |
|---|---|---|---|---|
| H31 | 0.2639 | 0.6289 | 0.5824 | 0.054* |
| H32 | 0.2965 | 0.6587 | 0.5181 | 0.054* |
| O4w | 0.09054 (10) | 0.77903 (12) | 0.47459 (8) | 0.0274 (3) |
| H4w1 | 0.0638 | 0.7931 | 0.5115 | 0.041* |
| H4w2 | 0.0566 | 0.7959 | 0.4325 | 0.041* |
| O5w | 0.17335 (12) | 0.44158 (13) | 0.44550 (9) | 0.0355 (4) |
| H51 | 0.1595 | 0.4244 | 0.3984 | 0.053* |
| H52 | 0.2304 | 0.4418 | 0.4585 | 0.053* |
| O6w | 0.12472 (12) | 0.30720 (14) | 0.55409 (10) | 0.0394 (4) |
| H61 | 0.1311 | 0.3329 | 0.5114 | 0.059* |
| H62 | 0.1168 | 0.2450 | 0.5476 | 0.059* |
| O7w | 0.36239 (13) | 0.41472 (15) | 0.45757 (11) | 0.0466 (5) |
| H71 | 0.3780 | 0.4405 | 0.4181 | 0.070* |
| H72 | 0.4018 | 0.4295 | 0.4970 | 0.070* |
| O8w | −0.01007 (15) | 0.80955 (16) | 0.33263 (11) | 0.0542 (5) |
| H81 | −0.0423 | 0.8616 | 0.3237 | 0.081* |
| H82 | 0.0404 | 0.8207 | 0.3196 | 0.081* |
| O9w | 0.5000 | 1.04750 (17) | 0.2500 | 0.0319 (5) |
| H9 | 0.4536 | 1.0105 | 0.2432 | 0.048* |
| N1 | 0.30344 (11) | 0.65163 (12) | 0.21958 (9) | 0.0170 (3) |
| C1 | 0.36250 (14) | 0.82322 (15) | 0.23904 (11) | 0.0221 (4) |
| C2 | 0.32017 (14) | 0.74543 (15) | 0.17992 (11) | 0.0224 (4) |
| H2A | 0.2631 | 0.7709 | 0.1504 | 0.027* |
| H2B | 0.3607 | 0.7322 | 0.1437 | 0.027* |
| C3 | 0.30488 (14) | 0.56253 (15) | 0.16936 (11) | 0.0227 (4) |
| H3A | 0.3465 | 0.5742 | 0.1337 | 0.027* |
| H3B | 0.2445 | 0.5513 | 0.1387 | 0.027* |
| C4 | 0.33482 (14) | 0.47085 (16) | 0.21844 (11) | 0.0227 (4) |
| C5 | 0.21789 (13) | 0.65676 (17) | 0.25076 (11) | 0.0224 (4) |
| H5A | 0.1768 | 0.6045 | 0.2264 | 0.027* |
| H5B | 0.1888 | 0.7211 | 0.2368 | 0.027* |
| C6 | 0.23267 (13) | 0.64436 (15) | 0.33827 (11) | 0.0191 (4) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.01981 (13) | 0.02595 (14) | 0.01754 (13) | −0.00436 (9) | 0.00469 (9) | −0.00037 (9) |
| Ti1 | 0.01574 (17) | 0.02177 (18) | 0.01442 (16) | 0.00001 (13) | 0.00386 (12) | 0.00014 (12) |
| O1 | 0.0284 (8) | 0.0214 (7) | 0.0208 (7) | 0.0008 (6) | 0.0002 (6) | −0.0029 (5) |
| O2 | 0.0396 (9) | 0.0210 (8) | 0.0352 (8) | −0.0057 (7) | −0.0017 (7) | 0.0041 (6) |
| O3 | 0.0290 (8) | 0.0202 (7) | 0.0249 (7) | −0.0009 (6) | −0.0005 (6) | 0.0013 (6) |
| O4 | 0.0464 (10) | 0.0203 (8) | 0.0360 (9) | 0.0004 (7) | −0.0019 (7) | −0.0053 (6) |
| O5 | 0.0173 (7) | 0.0438 (9) | 0.0180 (6) | 0.0002 (6) | 0.0042 (5) | 0.0011 (6) |
| O6 | 0.0192 (7) | 0.0363 (8) | 0.0220 (7) | −0.0003 (6) | 0.0070 (5) | 0.0019 (6) |
| O7 | 0.0205 (10) | 0.0325 (11) | 0.0195 (9) | 0.000 | 0.0062 (8) | 0.000 |
| O8 | 0.0249 (8) | 0.0365 (9) | 0.0213 (7) | −0.0015 (7) | 0.0006 (6) | −0.0035 (6) |
| O9 | 0.0281 (8) | 0.0350 (9) | 0.0243 (7) | 0.0051 (7) | 0.0013 (6) | 0.0063 (6) |
| O1w | 0.0247 (8) | 0.0285 (8) | 0.0241 (7) | −0.0044 (6) | 0.0076 (6) | −0.0029 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2w | 0.0535 (11) | 0.0327 (9) | 0.0258 (7) | −0.0203 (8) | 0.0190 (7) | −0.0081 (7) |
| O3w | 0.0266 (8) | 0.0562 (11) | 0.0233 (7) | −0.0132 (8) | 0.0001 (6) | 0.0062 (7) |
| O4w | 0.0268 (8) | 0.0330 (8) | 0.0224 (7) | −0.0010 (6) | 0.0049 (6) | −0.0035 (6) |
| O5w | 0.0370 (9) | 0.0380 (9) | 0.0310 (8) | 0.0004 (7) | 0.0052 (7) | −0.0032 (7) |
| O6w | 0.0345 (9) | 0.0426 (10) | 0.0420 (9) | −0.0011 (8) | 0.0098 (7) | −0.0002 (8) |
| O7w | 0.0379 (10) | 0.0545 (12) | 0.0443 (10) | −0.0041 (9) | −0.0006 (8) | 0.0179 (9) |
| O8w | 0.0553 (13) | 0.0572 (13) | 0.0454 (11) | 0.0194 (10) | −0.0024 (9) | 0.0064 (9) |
| O9w | 0.0229 (11) | 0.0308 (12) | 0.0402 (12) | 0.000 | 0.0008 (9) | 0.000 |
| N1 | 0.0187 (8) | 0.0169 (8) | 0.0159 (7) | −0.0022 (6) | 0.0044 (6) | −0.0008 (6) |
| C1 | 0.0199 (10) | 0.0219 (10) | 0.0247 (9) | −0.0014 (8) | 0.0047 (7) | 0.0007 (8) |
| C2 | 0.0262 (10) | 0.0216 (10) | 0.0186 (9) | −0.0034 (8) | 0.0020 (7) | 0.0043 (8) |
| C3 | 0.0285 (11) | 0.0207 (10) | 0.0183 (9) | 0.0008 (8) | 0.0028 (7) | −0.0030 (7) |
| C4 | 0.0211 (9) | 0.0244 (10) | 0.0233 (9) | 0.0014 (8) | 0.0060 (7) | −0.0022 (8) |
| C5 | 0.0161 (9) | 0.0312 (11) | 0.0198 (9) | 0.0008 (8) | 0.0033 (7) | 0.0006 (8) |
| C6 | 0.0199 (9) | 0.0183 (9) | 0.0200 (9) | −0.0017 (7) | 0.0060 (7) | −0.0010 (7) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—O3w | 1.9308 (16) | O3w—H31 | 0.8399 |
| Cu1—O6 | 1.9639 (14) | O3w—H32 | 0.8400 |
| Cu1—O2w | 1.9862 (15) | O4w—H4w1 | 0.8400 |
| Cu1—O1w | 2.0163 (15) | O4w—H4w2 | 0.8399 |
| Cu1—O4w | 2.2693 (16) | O5w—H51 | 0.8401 |
| Cu1—O5w | 2.4462 (17) | O5w—H52 | 0.8400 |
| Ti1—O7 | 1.8110 (3) | O6w—H61 | 0.8400 |
| Ti1—O9 | 1.8838 (14) | O6w—H62 | 0.8400 |
| Ti1—O8 | 1.8850 (14) | O7w—H71 | 0.8400 |
| Ti1—O5 | 2.0843 (14) | O7w—H72 | 0.8401 |
| Ti1—O3 | 2.0845 (15) | O8w—H81 | 0.8400 |
| Ti1—O1 | 2.1106 (15) | O8w—H82 | 0.8400 |
| Ti1—N1 | 2.2751 (16) | O9w—H9 | 0.8401 |
| O1—C1 | 1.283 (2) | N1—C2 | 1.470 (2) |
| O2—C1 | 1.226 (3) | N1—C3 | 1.475 (2) |
| O3—C4 | 1.287 (2) | N1—C5 | 1.481 (2) |
| O4—C4 | 1.229 (3) | C1—C2 | 1.512 (3) |
| O5—C6 | 1.254 (2) | C2—H2A | 0.9700 |
| O6—C6 | 1.246 (2) | C2—H2B | 0.9700 |
| O7—Ti1$^{i}$ | 1.8110 (3) | C3—C4 | 1.508 (3) |
| O8—O9 | 1.474 (2) | C3—H3A | 0.9700 |
| O1w—H11 | 0.8400 | C3—H3B | 0.9700 |
| O1w—H12 | 0.8401 | C5—C6 | 1.510 (3) |
| O2w—H21 | 0.8400 | C5—H5A | 0.9700 |
| O2w—H22 | 0.8400 | C5—H5B | 0.9700 |
| O3w—Cu1—O6 | 99.30 (6) | Cu1—O2w—H22 | 122.5 |
| O3w—Cu1—O2w | 87.61 (7) | H21—O2w—H22 | 108.5 |
| O6—Cu1—O2w | 173.02 (7) | Cu1—O3w—H31 | 124.0 |
| O3w—Cu1—O1w | 173.18 (7) | Cu1—O3w—H32 | 123.1 |
| O6—Cu1—O1w | 84.30 (6) | H31—O3w—H32 | 108.4 |
| O2w—Cu1—O1w | 88.93 (6) | Cu1—O4w—H4w1 | 114.7 |

| | | | |
|---|---|---|---|
| O3w—Cu1—O4w | 97.37 (7) | Cu1—O4w—H4w2 | 110.6 |
| O6—Cu1—O4w | 86.94 (6) | H4w1—O4w—H4w2 | 108.4 |
| O2w—Cu1—O4w | 91.20 (6) | Cu1—O5w—H51 | 113.8 |
| O1w—Cu1—O4w | 88.57 (6) | Cu1—O5w—H52 | 102.6 |
| O3w—Cu1—O5w | 87.46 (7) | H51—O5w—H52 | 108.4 |
| O6—Cu1—O5w | 86.18 (6) | H61—O6w—H62 | 108.4 |
| O2w—Cu1—O5w | 95.19 (6) | H71—O7w—H72 | 108.4 |
| O1w—Cu1—O5w | 87.00 (6) | H81—O8w—H82 | 108.5 |
| O4w—Cu1—O5w | 172.15 (5) | C2—N1—C3 | 112.23 (14) |
| O7—Ti1—O9 | 102.42 (6) | C2—N1—C5 | 111.62 (16) |
| O7—Ti1—O8 | 101.25 (5) | C3—N1—C5 | 111.40 (15) |
| O9—Ti1—O8 | 46.04 (7) | C2—N1—Ti1 | 105.73 (11) |
| O7—Ti1—O5 | 165.95 (4) | C3—N1—Ti1 | 105.83 (11) |
| O9—Ti1—O5 | 90.75 (6) | C5—N1—Ti1 | 109.69 (11) |
| O8—Ti1—O5 | 91.38 (6) | O2—C1—O1 | 125.10 (19) |
| O7—Ti1—O3 | 92.48 (8) | O2—C1—C2 | 118.93 (18) |
| O9—Ti1—O3 | 82.68 (6) | O1—C1—C2 | 115.94 (17) |
| O8—Ti1—O3 | 128.55 (6) | N1—C2—C1 | 110.17 (15) |
| O5—Ti1—O3 | 84.28 (6) | N1—C2—H2A | 109.6 |
| O7—Ti1—O1 | 90.88 (8) | C1—C2—H2A | 109.6 |
| O9—Ti1—O1 | 127.87 (6) | N1—C2—H2B | 109.6 |
| O8—Ti1—O1 | 82.10 (6) | C1—C2—H2B | 109.6 |
| O5—Ti1—O1 | 84.72 (6) | H2A—C2—H2B | 108.1 |
| O3—Ti1—O1 | 147.58 (6) | N1—C3—C4 | 110.31 (15) |
| O7—Ti1—N1 | 89.21 (4) | N1—C3—H3A | 109.6 |
| O9—Ti1—N1 | 154.83 (7) | C4—C3—H3A | 109.6 |
| O8—Ti1—N1 | 153.44 (7) | N1—C3—H3B | 109.6 |
| O5—Ti1—N1 | 76.74 (6) | C4—C3—H3B | 109.6 |
| O3—Ti1—N1 | 74.50 (6) | H3A—C3—H3B | 108.1 |
| O1—Ti1—N1 | 73.32 (6) | O4—C4—O3 | 123.8 (2) |
| C1—O1—Ti1 | 118.67 (13) | O4—C4—C3 | 120.05 (18) |
| C4—O3—Ti1 | 120.00 (13) | O3—C4—C3 | 116.06 (18) |
| C6—O5—Ti1 | 121.52 (12) | N1—C5—C6 | 113.20 (16) |
| C6—O6—Cu1 | 135.58 (13) | N1—C5—H5A | 108.9 |
| Ti1—O7—Ti1$^{i}$ | 176.04 (14) | C6—C5—H5A | 108.9 |
| O9—O8—Ti1 | 66.94 (8) | N1—C5—H5B | 108.9 |
| O8—O9—Ti1 | 67.02 (8) | C6—C5—H5B | 108.9 |
| Cu1—O1w—H11 | 111.0 | H5A—C5—H5B | 107.8 |
| Cu1—O1w—H12 | 108.4 | O6—C6—O5 | 125.48 (17) |
| H11—O1w—H12 | 108.4 | O6—C6—C5 | 115.73 (17) |
| Cu1—O2w—H21 | 128.2 | O5—C6—C5 | 118.79 (17) |
| O7—Ti1—O1—C1 | 60.95 (14) | O1—Ti1—N1—C2 | 34.18 (11) |
| O9—Ti1—O1—C1 | 167.48 (14) | O7—Ti1—N1—C3 | 62.26 (13) |
| O8—Ti1—O1—C1 | 162.18 (15) | O9—Ti1—N1—C3 | −56.2 (2) |
| O5—Ti1—O1—C1 | −105.68 (15) | O8—Ti1—N1—C3 | 176.38 (14) |
| O3—Ti1—O1—C1 | −35.1 (2) | O5—Ti1—N1—C3 | −118.19 (12) |
| N1—Ti1—O1—C1 | −27.96 (14) | O3—Ti1—N1—C3 | −30.53 (11) |
| O7—Ti1—O3—C4 | −67.06 (15) | O1—Ti1—N1—C3 | 153.42 (13) |

| | | | |
|---|---|---|---|
| O9—Ti1—O3—C4 | −169.27 (15) | O7—Ti1—N1—C5 | −177.46 (14) |
| O8—Ti1—O3—C4 | −173.57 (14) | O9—Ti1—N1—C5 | 64.1 (2) |
| O5—Ti1—O3—C4 | 99.23 (15) | O8—Ti1—N1—C5 | −63.3 (2) |
| O1—Ti1—O3—C4 | 28.5 (2) | O5—Ti1—N1—C5 | 2.08 (12) |
| N1—Ti1—O3—C4 | 21.43 (14) | O3—Ti1—N1—C5 | 89.74 (13) |
| O7—Ti1—O5—C6 | 0.3 (4) | O1—Ti1—N1—C5 | −86.31 (13) |
| O9—Ti1—O5—C6 | −159.50 (16) | Ti1—O1—C1—O2 | −163.57 (17) |
| O8—Ti1—O5—C6 | 154.45 (16) | Ti1—O1—C1—C2 | 14.5 (2) |
| O3—Ti1—O5—C6 | −76.94 (16) | C3—N1—C2—C1 | −152.71 (16) |
| O1—Ti1—O5—C6 | 72.52 (16) | C5—N1—C2—C1 | 81.41 (19) |
| N1—Ti1—O5—C6 | −1.55 (15) | Ti1—N1—C2—C1 | −37.80 (18) |
| O3w—Cu1—O6—C6 | 21.7 (2) | O2—C1—C2—N1 | −163.33 (19) |
| O1w—Cu1—O6—C6 | −152.5 (2) | O1—C1—C2—N1 | 18.4 (2) |
| O4w—Cu1—O6—C6 | 118.6 (2) | C2—N1—C3—C4 | 151.50 (17) |
| O5w—Cu1—O6—C6 | −65.1 (2) | C5—N1—C3—C4 | −82.5 (2) |
| O7—Ti1—O8—O9 | −96.49 (10) | Ti1—N1—C3—C4 | 36.65 (18) |
| O5—Ti1—O8—O9 | 89.71 (9) | Ti1—O3—C4—O4 | 170.04 (17) |
| O3—Ti1—O8—O9 | 5.92 (11) | Ti1—O3—C4—C3 | −6.4 (2) |
| O1—Ti1—O8—O9 | 174.19 (9) | N1—C3—C4—O4 | 160.50 (19) |
| N1—Ti1—O8—O9 | 152.02 (13) | N1—C3—C4—O3 | −22.9 (2) |
| O7—Ti1—O9—O8 | 93.73 (10) | C2—N1—C5—C6 | −119.28 (18) |
| O5—Ti1—O9—O8 | −91.20 (9) | C3—N1—C5—C6 | 114.39 (18) |
| O3—Ti1—O9—O8 | −175.33 (9) | Ti1—N1—C5—C6 | −2.4 (2) |
| O1—Ti1—O9—O8 | −7.30 (11) | Cu1—O6—C6—O5 | −11.1 (3) |
| N1—Ti1—O9—O8 | −150.44 (14) | Cu1—O6—C6—C5 | 169.07 (15) |
| O7—Ti1—N1—C2 | −56.98 (13) | Ti1—O5—C6—O6 | −179.24 (16) |
| O9—Ti1—N1—C2 | −175.44 (15) | Ti1—O5—C6—C5 | 0.6 (3) |
| O8—Ti1—N1—C2 | 57.15 (19) | N1—C5—C6—O6 | −178.72 (17) |
| O5—Ti1—N1—C2 | 122.57 (13) | N1—C5—C6—O5 | 1.4 (3) |
| O3—Ti1—N1—C2 | −149.77 (13) | | |

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2.

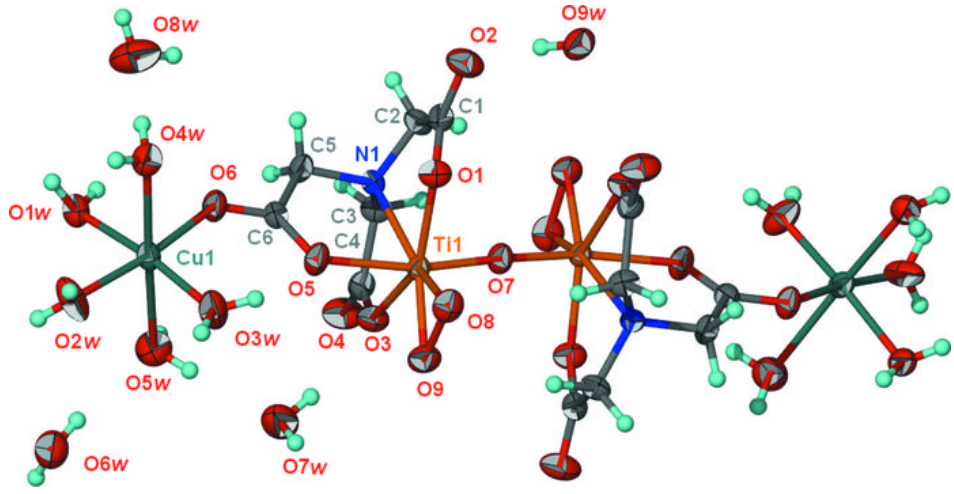
*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1w—H11···O6w$^{ii}$ | 0.84 | 1.80 | 2.627 (2) | 169 |
| O1w—H12···O9w$^{iii}$ | 0.84 | 1.99 | 2.789 (1) | 159 |
| O2w—H21···O1w$^{ii}$ | 0.84 | 1.91 | 2.746 (2) | 173 |
| O2w—H22···O1$^{iv}$ | 0.84 | 1.90 | 2.737 (2) | 174 |
| O3w—H31···O4$^{v}$ | 0.84 | 1.93 | 2.746 (2) | 165 |
| O3w—H32···O4w$^{iv}$ | 0.84 | 1.86 | 2.658 (2) | 158 |
| O4w—H4w1···O8$^{iv}$ | 0.84 | 1.85 | 2.693 (2) | 176 |
| O4w—H4w2···O8w | 0.84 | 1.85 | 2.675 (2) | 169 |
| O5w—H51···O2$^{vi}$ | 0.84 | 2.02 | 2.850 (2) | 168 |
| O5w—H52···O7w | 0.84 | 2.01 | 2.813 (3) | 161 |
| O6w—H61···O5w | 0.84 | 2.02 | 2.797 (2) | 153 |
| O6w—H62···O7w$^{vii}$ | 0.84 | 2.15 | 2.965 (3) | 164 |

| | | | | |
|---|---|---|---|---|
| O7w—H71···O3 | 0.84 | 2.38 | 3.195 (2) | 163 |
| O7w—H72···O9$^{viii}$ | 0.84 | 2.07 | 2.900 (2) | 168 |
| O8w—H81···O3$^{ix}$ | 0.84 | 2.06 | 2.890 (2) | 172 |
| O8w—H82···O4$^{x}$ | 0.84 | 2.33 | 3.148 (3) | 164 |
| O9w—H9···O2 | 0.84 | 1.89 | 2.716 (2) | 170 |

Symmetry codes: (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*−1/2, *y*−1/2, *z*; (iv) −*x*+1/2, −*y*+3/2, −*z*+1; (v) *x*, −*y*+1, *z*+1/2; (vi) −*x*+1/2, *y*−1/2, −*z*+1/2; (vii) −*x*+1/2, −*y*+1/2, −*z*+1; (viii) −*x*+1, −*y*+1, −*z*+1; (ix) *x*−1/2, *y*+1/2, *z*; (x) −*x*+1/2, *y*+1/2, −*z*+1/2.

**Fig. 1**


O8w
O9w
O2
C2
C1
O4w
C5
N1
O6
O1
O1w
C3
C6
C4
Ti1
Cu1
O5
O7
O8
O2w
O3w
O4
O3
O5w
O9
O6w
O7w