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# Bis(guanidinium) tris(pyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)zirconate(II) tetrahydrate

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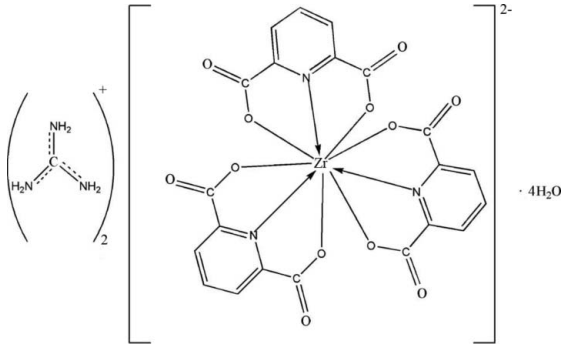
Key indicators: single-crystal X-ray study; $T$ = 120 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.056; $wR$ factor = 0.146; data-to-parameter ratio = 18.5.

In the title complex, $(CH_6N_3)_2[Zr(C_7H_3NO_4)_3]\cdot 4H_2O$, the $Zr^{IV}$ ion lies on a twofold rotation axes and is coordinated by six O and three N atoms of three tridentate pyridine-2,6-dicarboxylate ligands, forming a slightly distorted tricapped trigonal–prismatic geometry. In the crystal, O—H···O and N—H···O hydrogen bonds link the components into a three-dimensional network.

## Related literature

For related structures, see: Aghabozorg *et al.* (2005); Tabatabaee (2010); Tabatabaee *et al.* (2009, 2011*a*,*b*,*c*, 2012); Derikvand *et al.* (2010); Attar Gharamaleki *et al.* (2009).



## Experimental

### Crystal data

$(CH_6N_3)_2[Zr(C_7H_3NO_4)_3]\cdot 4H_2O$
$M_r$ = 778.77
Orthorhombic, *Pbcn*
$a$ = 17.2444 (9) Å
$b$ = 10.8583 (5) Å
$c$ = 16.5268 (8) Å
$V$ = 3094.6 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.45 mm$^{-1}$
$T$ = 120 K
0.17 × 0.15 × 0.07 mm

### Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min}$ = 0.884, $T_{max}$ = 0.970
32229 measured reflections
4116 independent reflections
2884 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.068

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.146
$S$ = 1.07
4116 reflections
223 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.87 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.47 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3*NA*···O1 | 0.77 | 2.23 | 3.003 (4) | 175 |
| N3—H3*NB*···O2$W^{i}$ | 0.86 | 2.15 | 2.930 (4) | 150 |
| N4—H4*NA*···O2$W^{i}$ | 0.83 | 2.04 | 2.818 (4) | 156 |
| N4—H4*NB*···O1$W^{ii}$ | 0.78 | 2.06 | 2.834 (4) | 175 |
| N5—H5*NA*···O2 | 0.88 | 1.95 | 2.828 (4) | 171 |
| N5—H5*NB*···O3$^{iii}$ | 0.79 | 2.45 | 3.143 (4) | 148 |
| N5—H5*NB*···O4$^{iii}$ | 0.79 | 2.52 | 3.171 (4) | 141 |
| O1*W*—H1*WA*···O3$^{iv}$ | 0.84 | 2.33 | 3.041 (3) | 143 |
| O1*W*—H1*WA*···O5$^{iv}$ | 0.84 | 2.38 | 3.076 (3) | 140 |
| O1*W*—H1*WB*···O6 | 0.89 | 1.87 | 2.761 (3) | 175 |
| O2*W*—H2*WA*···O5$^{iv}$ | 0.86 | 2.07 | 2.909 (3) | 165 |
| O2*W*—H2*WA*···O6$^{iv}$ | 0.86 | 2.57 | 3.085 (3) | 119 |
| O2*W*—H2*WB*···O4$^{v}$ | 0.94 | 1.84 | 2.745 (3) | 160 |

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*, *DIAMOND* (Brandenburg, 1999) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

The authors wish to express their deepest appreciation to the late Professor Dr. H Aghabozorg who has inspired, advised and assisted during this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5430).

## References

Aghabozorg, H., Moghimi, A., Manteghi, F. & Ranjbar, M. (2005). *Z. Anorg. Allg. Chem.* **631**, 909–913.
Attar Gharamaleki, J., Aghabozorg, H., Derikvand, Z. & Yousefi, M. (2009). *Acta Cryst.* E**65**, m824–m825.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (1998). *SAINT*, *SMART* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Derikvand, Z., Talei, G. R., Aghabozorg, H., Olmstead, M. M., Azadbakht, A., Nemati, A. & Attar Gharamaleki, J. (2010). *Chin. J. Chem.* **28**, 2167–2173.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tabatabaee, M. (2010). *Acta Cryst.* E**66**, m647–m648.
Tabatabaee, M., Abbasi, F., Kukovec, B. M. & Nasirizadeh, N. (2011*b*). *J. Coord. Chem.* **64**, 1718–1728.
Tabatabaee, M., Aghabozorg, H., Attar Gharamaleki, J. & Sharif, M. A. (2009). *Acta Cryst.* E**65**, m473–m474.

Tabatabaee, M., Kukovec, B. M. & Kazeroonizadeh, M. (2011*a*). *Polyhedron*, **30**, 1114–1119.
Tabatabaee, M., Tahriri, M., Tahriri, M., Dušek, M. & Fejfarová, K. (2011*c*). *Acta Cryst.* E**67**, m769–m770.
Tabatabaee, M., Tahriri, M., Tahriri, M., Ozawa, Y., Neumuller, B., Fujioka, H. & Toriumi, K. (2012). *Polyhedron*, **33**, 336–340.

# supplementary materials

*Acta Cryst.* (2012). E**68**, m462–m463 [doi:10.1107/S1600536812011439]

## Bis(guanidinium) tris(pyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)zirconate(II) tetrahydrate

**Masoumeh Tabatabaee, Mahnaz Adineh, Zohreh Derikvand and Jafar Attar Gharamaleki**

### Comment

In recent years, our research group has been interested in the synthesis of proton transfer compounds and study of their behavior with metal ions. We have focused on the proton delivery of polycarboxylic acids. Pyridine-2,6-dicarboxylic acid ($pydcH_2$) is a very important carboxylate derivative and has attracted much interest in coordination chemistry. This is the acid we have utilized widely in our studies (Tabatabaee *et al.*, 2010, 2011*a*, 2011*b*, 2011*c*, 2012; Derikvand *et al.*, 2010; Attar Gharamaleki *et al.*, 2009). In this paper we report the crystal structure of the title complex (I). The $Zr^{IV}$ ion lies on a twofold rotation axis. The asymmetric unit and the symmetry complete cation is shown in Fig. 1. The $Zr^{IV}$ atom is coordinated by three tridentate pydc ligands forming a slightly distorted tricapped trigonal prismatic environment (Fig. 2). The Zr—N distances and Zr—O distances are consistent with those found in $(pydaH)_2[Zr(pydc)_3].5H_2O$ (Aghabozorg *et al.*, 2005). In the crystal, O—H···O and N—H···O hydrogen bonds (Table 1) link the components into a three-dimensional network (Fig. 3).

### Experimental

An aqueous solution of $ZrOCl_2.8H_2O$, (161 mg, 0.5 mmol) in water (5 ml) was added to a stirring solution of (20 ml) pyridine-2,6-dicarboxylic acid (176 mg, 1 mmol) and guanidine hydrochloride (95 mg, 1 mmol). The reaction mixture was stirred at 298K for 1 h. Colorless crystals of the title compound were obtained after 4 days by slow evaporation of the solvent at room temperature.

### Refinement

H atoms bonded to C atoms were placed in calculated positions. The H atoms of water molecules and $NH_2$ groups were located in difference Fourier maps and included in 'as found′ positions. All hydrogen atoms were refined in isotropic approximatiom in a riding-model approximation with $U_{iso}$(H) parameters equal to 1.2 $U_{eq}$(C), 1.5 $U_{eq}$(O,*N*).

### Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

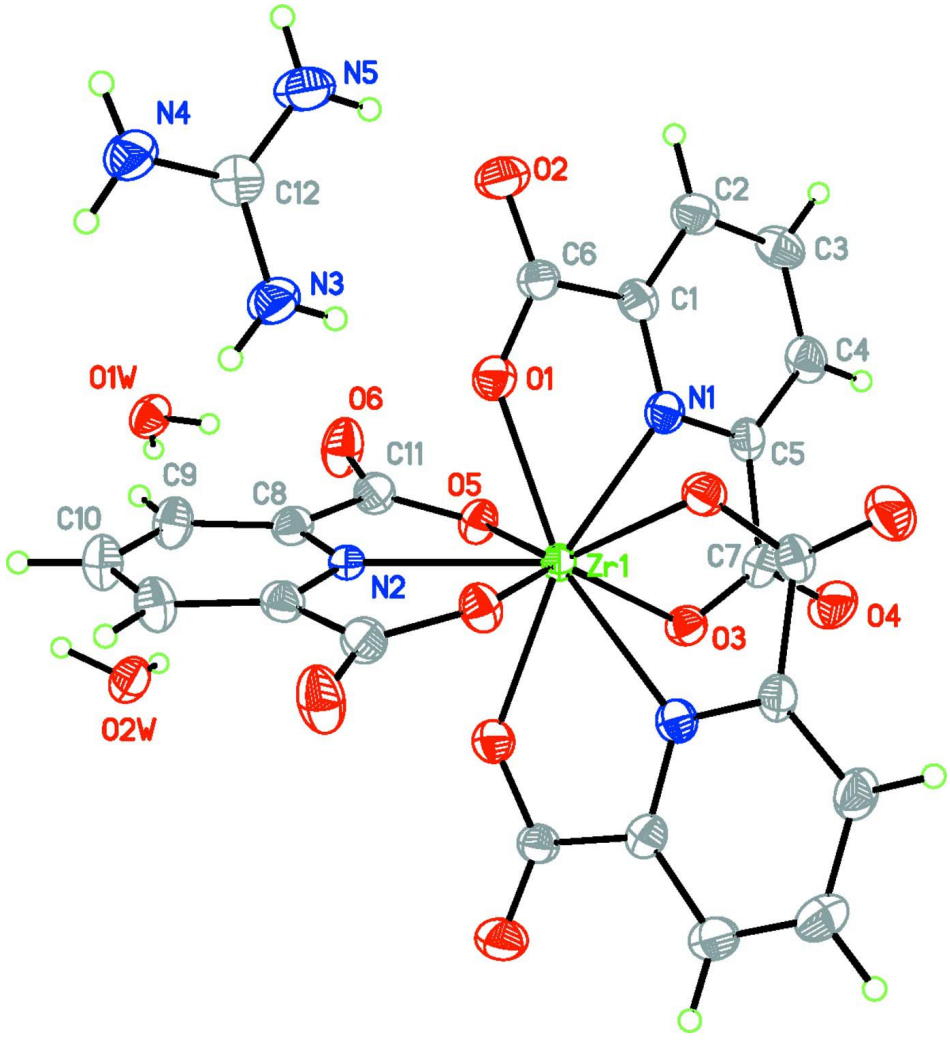



**Figure 1**

The molecular structure of (I) with ellipsoids drawn at the 50% probability level. The unlabeled atoms are related by the symmetry operator (-x+1, y, -z+1/2). Only the symmetry unique anions and water molecules are shown.

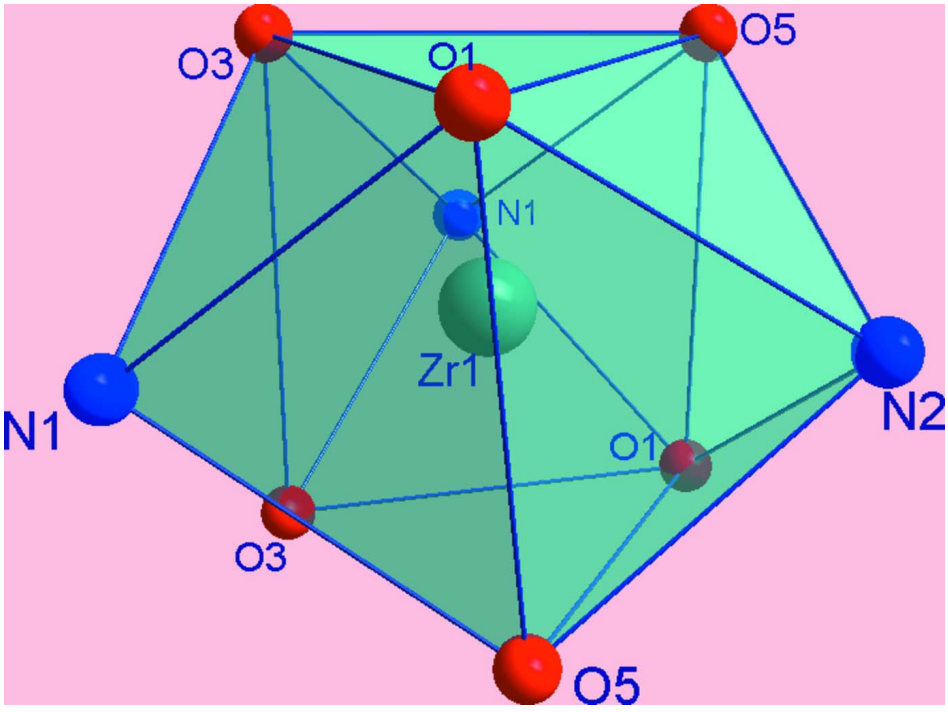



**Figure 2**

View of the coordination environment of the $Zr^{IV}$ ion.

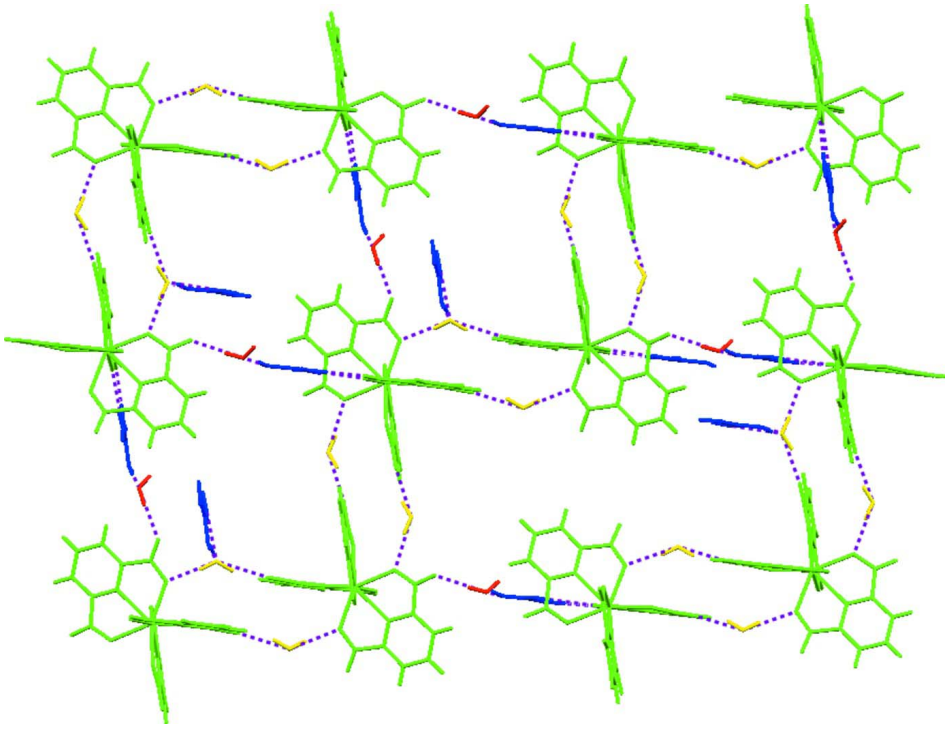


**Figure 3**

Part of the crystal structure of (I). The donor to acceptor distances of the hydrogen bonds are shown as dotted lines.

**Bis(guanidinium) tris(pyridine-2,6-dicarboxylato- $\kappa^3O^2,N,O^6$)zirconate(II) tetrahydrate**

*Crystal data*

$(CH_6N_3)_2[Zr(C_7H_3NO_4)_3]\cdot 4H_2O$
$M_r = 778.77$
Orthorhombic, *Pbcn*
Hall symbol: -P 2n 2ab
$a = 17.2444$ (9) Å
$b = 10.8583$ (5) Å
$c = 16.5268$ (8) Å
$V = 3094.6$ (3) Å$^3$
$Z = 4$
$F(000) = 1592$
$D_x = 1.672$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4151 reflections
$\theta = 2.3$–$26.0°$
$\mu = 0.45$ mm$^{-1}$
$T = 120$ K
Prism, colorless
0.17 × 0.15 × 0.07 mm

*Data collection*

Bruker SMART 1000 CCD diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.884$, $T_{max} = 0.970$
32229 measured reflections
4116 independent reflections
2884 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 29.0°$, $\theta_{min} = 2.2°$
$h = -23\rightarrow23$
$k = -14\rightarrow14$
$l = -22\rightarrow22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.146$
$S = 1.07$
4116 reflections
223 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 8.430P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.87$ e Å$^{-3}$
$\Delta\rho_{min} = -0.47$ e Å$^{-3}$

*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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zr1 | 0.5000 | 0.72625 (4) | 0.2500 | 0.01631 (13) |
| O1 | 0.38154 (13) | 0.6592 (2) | 0.28200 (14) | 0.0245 (5) |
| O2 | 0.25204 (15) | 0.6675 (3) | 0.27362 (17) | 0.0349 (6) |
| O3 | 0.54360 (12) | 0.8668 (2) | 0.16530 (13) | 0.0226 (5) |
| O4 | 0.53142 (16) | 1.0370 (2) | 0.09047 (17) | 0.0362 (6) |

| | | | | |
|---|---|---|---|---|
| O5 | 0.47334 (14) | 0.6443 (2) | 0.12914 (14) | 0.0236 (5) |
| O6 | 0.42065 (17) | 0.4926 (2) | 0.05627 (15) | 0.0354 (6) |
| N1 | 0.40034 (15) | 0.8418 (2) | 0.18731 (16) | 0.0214 (5) |
| N2 | 0.5000 | 0.5072 (3) | 0.2500 | 0.0171 (7) |
| C1 | 0.32630 (19) | 0.8123 (3) | 0.20019 (19) | 0.0225 (6) |
| C2 | 0.2655 (2) | 0.8764 (3) | 0.1641 (2) | 0.0292 (7) |
| H2A | 0.2131 | 0.8533 | 0.1731 | 0.035* |
| C3 | 0.2842 (2) | 0.9750 (3) | 0.1146 (2) | 0.0295 (7) |
| H3A | 0.2441 | 1.0216 | 0.0898 | 0.035* |
| C4 | 0.3609 (2) | 1.0061 (3) | 0.1010 (2) | 0.0273 (7) |
| H4A | 0.3743 | 1.0733 | 0.0670 | 0.033* |
| C5 | 0.41742 (19) | 0.9359 (3) | 0.13861 (19) | 0.0219 (6) |
| C6 | 0.31649 (18) | 0.7054 (3) | 0.25566 (19) | 0.0218 (6) |
| C7 | 0.50369 (18) | 0.9516 (3) | 0.12932 (18) | 0.0205 (6) |
| C8 | 0.47612 (18) | 0.4462 (3) | 0.18438 (19) | 0.0222 (6) |
| C9 | 0.4742 (2) | 0.3187 (3) | 0.1823 (2) | 0.0273 (7) |
| H9A | 0.4557 | 0.2761 | 0.1360 | 0.033* |
| C10 | 0.5000 | 0.2551 (4) | 0.2500 | 0.0284 (10) |
| H10A | 0.5000 | 0.1676 | 0.2500 | 0.034* |
| C11 | 0.45375 (19) | 0.5307 (3) | 0.1163 (2) | 0.0240 (6) |
| N3 | 0.33875 (17) | 0.4432 (3) | 0.38628 (19) | 0.0312 (7) |
| H3NA | 0.3482 | 0.5016 | 0.3616 | 0.047* |
| H3NB | 0.3752 | 0.4039 | 0.4112 | 0.047* |
| N4 | 0.25724 (18) | 0.3150 (3) | 0.45574 (18) | 0.0314 (7) |
| H4NA | 0.2971 | 0.2749 | 0.4652 | 0.047* |
| H4NB | 0.2158 | 0.2885 | 0.4626 | 0.047* |
| N5 | 0.20814 (17) | 0.4727 (3) | 0.3776 (2) | 0.0364 (8) |
| H5NA | 0.2166 | 0.5344 | 0.3439 | 0.055* |
| H5NB | 0.1654 | 0.4517 | 0.3865 | 0.055* |
| C12 | 0.26720 (19) | 0.4098 (3) | 0.4060 (2) | 0.0268 (7) |
| O1W | 0.39648 (14) | 0.2667 (2) | −0.01609 (15) | 0.0279 (5) |
| H1WA | 0.4195 | 0.2642 | −0.0607 | 0.042* |
| H1WB | 0.4026 | 0.3377 | 0.0100 | 0.042* |
| O2W | 0.58669 (15) | 0.2479 (2) | 0.01935 (16) | 0.0310 (6) |
| H2WA | 0.5768 | 0.2747 | −0.0287 | 0.047* |
| H2WB | 0.5631 | 0.1722 | 0.0319 | 0.047* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zr1 | 0.0173 (2) | 0.0148 (2) | 0.0169 (2) | 0.000 | −0.00061 (15) | 0.000 |
| O1 | 0.0241 (12) | 0.0232 (11) | 0.0261 (11) | −0.0009 (9) | −0.0003 (9) | 0.0031 (9) |
| O2 | 0.0217 (12) | 0.0369 (15) | 0.0462 (15) | −0.0031 (11) | 0.0017 (11) | 0.0095 (12) |
| O3 | 0.0213 (11) | 0.0233 (11) | 0.0232 (11) | −0.0011 (9) | 0.0001 (9) | 0.0015 (9) |
| O4 | 0.0327 (13) | 0.0314 (14) | 0.0444 (15) | −0.0070 (11) | −0.0008 (12) | 0.0144 (12) |
| O5 | 0.0280 (11) | 0.0211 (11) | 0.0216 (11) | −0.0035 (9) | −0.0030 (9) | 0.0003 (9) |
| O6 | 0.0521 (16) | 0.0249 (12) | 0.0292 (13) | −0.0054 (11) | −0.0141 (12) | −0.0004 (10) |
| N1 | 0.0231 (13) | 0.0206 (13) | 0.0205 (13) | −0.0005 (10) | 0.0002 (10) | −0.0013 (10) |
| N2 | 0.0149 (15) | 0.0161 (16) | 0.0203 (16) | 0.000 | 0.0013 (13) | 0.000 |
| C1 | 0.0236 (15) | 0.0212 (14) | 0.0228 (15) | 0.0026 (12) | −0.0013 (12) | 0.0011 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0220 (16) | 0.0310 (18) | 0.0345 (19) | 0.0021 (13) | −0.0010 (14) | 0.0036 (15) |
| C3 | 0.0256 (17) | 0.0336 (18) | 0.0294 (17) | 0.0077 (14) | −0.0024 (14) | 0.0045 (15) |
| C4 | 0.0311 (17) | 0.0233 (16) | 0.0276 (16) | 0.0032 (13) | −0.0045 (13) | 0.0055 (13) |
| C5 | 0.0260 (15) | 0.0163 (14) | 0.0235 (15) | 0.0008 (12) | −0.0029 (12) | −0.0002 (12) |
| C6 | 0.0192 (14) | 0.0226 (15) | 0.0235 (15) | −0.0006 (11) | 0.0006 (12) | −0.0015 (12) |
| C7 | 0.0258 (15) | 0.0177 (13) | 0.0179 (13) | −0.0029 (12) | −0.0011 (12) | −0.0001 (11) |
| C8 | 0.0199 (14) | 0.0238 (16) | 0.0230 (15) | −0.0014 (12) | 0.0018 (11) | −0.0023 (13) |
| C9 | 0.0365 (18) | 0.0214 (16) | 0.0239 (16) | −0.0030 (14) | −0.0006 (13) | −0.0025 (13) |
| C10 | 0.040 (3) | 0.020 (2) | 0.025 (2) | 0.000 | −0.003 (2) | 0.000 |
| C11 | 0.0244 (15) | 0.0240 (16) | 0.0235 (15) | −0.0002 (12) | −0.0027 (12) | −0.0022 (12) |
| N3 | 0.0240 (14) | 0.0321 (16) | 0.0375 (17) | −0.0040 (12) | 0.0005 (12) | 0.0113 (13) |
| N4 | 0.0269 (15) | 0.0324 (16) | 0.0348 (16) | −0.0033 (12) | 0.0041 (12) | 0.0093 (13) |
| N5 | 0.0208 (14) | 0.0441 (19) | 0.0444 (19) | −0.0014 (13) | 0.0018 (13) | 0.0160 (15) |
| C12 | 0.0275 (17) | 0.0300 (17) | 0.0228 (16) | −0.0002 (14) | −0.0002 (12) | 0.0000 (13) |
| O1W | 0.0299 (12) | 0.0258 (12) | 0.0280 (12) | −0.0058 (10) | 0.0040 (10) | −0.0057 (10) |
| O2W | 0.0336 (13) | 0.0273 (12) | 0.0323 (13) | −0.0075 (10) | −0.0053 (11) | 0.0050 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zr1—O3 | 2.203 (2) | C3—H3A | 0.9500 |
| Zr1—O3$^{i}$ | 2.203 (2) | C4—C5 | 1.384 (4) |
| Zr1—O1$^{i}$ | 2.232 (2) | C4—H4A | 0.9500 |
| Zr1—O1 | 2.232 (2) | C5—C7 | 1.505 (4) |
| Zr1—O5 | 2.234 (2) | C8—C9 | 1.384 (5) |
| Zr1—O5$^{i}$ | 2.234 (2) | C8—C11 | 1.503 (5) |
| Zr1—N1$^{i}$ | 2.366 (3) | C9—C10 | 1.388 (4) |
| Zr1—N1 | 2.366 (3) | C9—H9A | 0.9500 |
| Zr1—N2 | 2.378 (4) | C10—C9$^{i}$ | 1.388 (4) |
| O1—C6 | 1.304 (4) | C10—H10A | 0.9500 |
| O2—C6 | 1.222 (4) | N3—C12 | 1.327 (4) |
| O3—C7 | 1.294 (4) | N3—H3NA | 0.7713 |
| O4—C7 | 1.225 (4) | N3—H3NB | 0.8647 |
| O5—C11 | 1.297 (4) | N4—C12 | 1.329 (4) |
| O6—C11 | 1.217 (4) | N4—H4NA | 0.8289 |
| N1—C1 | 1.333 (4) | N4—H4NB | 0.7790 |
| N1—C5 | 1.334 (4) | N5—C12 | 1.312 (4) |
| N2—C8 | 1.336 (4) | N5—H5NA | 0.8832 |
| N2—C8$^{i}$ | 1.336 (4) | N5—H5NB | 0.7861 |
| C1—C2 | 1.393 (5) | O1W—H1WA | 0.8370 |
| C1—C6 | 1.489 (5) | O1W—H1WB | 0.8899 |
| C2—C3 | 1.386 (5) | O2W—H2WA | 0.8620 |
| C2—H2A | 0.9500 | O2W—H2WB | 0.9408 |
| C3—C4 | 1.382 (5) | | |

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| O3—Zr1—O3$^{i}$ | 92.30 (12) | N1—C1—C6 | 113.2 (3) |
| O3—Zr1—O1$^{i}$ | 76.29 (8) | C2—C1—C6 | 124.6 (3) |
| O3$^{i}$—Zr1—O1$^{i}$ | 133.53 (8) | C3—C2—C1 | 117.6 (3) |
| O3—Zr1—O1 | 133.53 (8) | C3—C2—H2A | 121.2 |
| O3$^{i}$—Zr1—O1 | 76.29 (8) | C1—C2—H2A | 121.2 |
| O1$^{i}$—Zr1—O1 | 141.94 (12) | C4—C3—C2 | 120.5 (3) |

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| O3—Zr1—O5 | 77.18 (8) | C4—C3—H3A | 119.8 |
| O3$^{i}$—Zr1—O5 | 140.67 (8) | C2—C3—H3A | 119.8 |
| O1$^{i}$—Zr1—O5 | 81.18 (9) | C3—C4—C5 | 117.8 (3) |
| O1—Zr1—O5 | 83.89 (9) | C3—C4—H4A | 121.1 |
| O3—Zr1—O5$^{i}$ | 140.67 (8) | C5—C4—H4A | 121.1 |
| O3$^{i}$—Zr1—O5$^{i}$ | 77.18 (8) | N1—C5—C4 | 122.5 (3) |
| O1$^{i}$—Zr1—O5$^{i}$ | 83.89 (9) | N1—C5—C7 | 111.5 (3) |
| O1—Zr1—O5$^{i}$ | 81.18 (9) | C4—C5—C7 | 126.0 (3) |
| O5—Zr1—O5$^{i}$ | 133.07 (12) | O2—C6—O1 | 124.9 (3) |
| O3—Zr1—N1$^{i}$ | 70.31 (8) | O2—C6—C1 | 121.0 (3) |
| O3$^{i}$—Zr1—N1$^{i}$ | 66.58 (8) | O1—C6—C1 | 114.1 (3) |
| O1$^{i}$—Zr1—N1$^{i}$ | 67.17 (9) | O4—C7—O3 | 124.9 (3) |
| O1—Zr1—N1$^{i}$ | 137.20 (9) | O4—C7—C5 | 121.7 (3) |
| O5—Zr1—N1$^{i}$ | 138.75 (9) | O3—C7—C5 | 113.4 (3) |
| O5$^{i}$—Zr1—N1$^{i}$ | 70.75 (9) | N2—C8—C9 | 121.6 (3) |
| O3—Zr1—N1 | 66.58 (8) | N2—C8—C11 | 112.6 (3) |
| O3$^{i}$—Zr1—N1 | 70.31 (8) | C9—C8—C11 | 125.9 (3) |
| O1$^{i}$—Zr1—N1 | 137.20 (9) | C8—C9—C10 | 118.1 (3) |
| O1—Zr1—N1 | 67.17 (9) | C8—C9—H9A | 121.0 |
| O5—Zr1—N1 | 70.75 (9) | C10—C9—H9A | 121.0 |
| O5$^{i}$—Zr1—N1 | 138.75 (9) | C9—C10—C9$^{i}$ | 120.2 (4) |
| N1$^{i}$—Zr1—N1 | 115.98 (13) | C9—C10—H10A | 119.9 |
| O3—Zr1—N2 | 133.85 (6) | C9$^{i}$—C10—H10A | 119.9 |
| O3$^{i}$—Zr1—N2 | 133.85 (6) | O6—C11—O5 | 125.4 (3) |
| O1$^{i}$—Zr1—N2 | 70.97 (6) | O6—C11—C8 | 121.6 (3) |
| O1—Zr1—N2 | 70.97 (6) | O5—C11—C8 | 113.1 (3) |
| O5—Zr1—N2 | 66.54 (6) | C12—N3—H3NA | 123.4 |
| O5$^{i}$—Zr1—N2 | 66.54 (6) | C12—N3—H3NB | 115.1 |
| N1$^{i}$—Zr1—N2 | 122.01 (6) | H3NA—N3—H3NB | 120.4 |
| N1—Zr1—N2 | 122.01 (6) | C12—N4—H4NA | 114.6 |
| C6—O1—Zr1 | 125.7 (2) | C12—N4—H4NB | 119.6 |
| C7—O3—Zr1 | 127.11 (19) | H4NA—N4—H4NB | 122.8 |
| C11—O5—Zr1 | 125.4 (2) | C12—N5—H5NA | 119.5 |
| C1—N1—C5 | 119.5 (3) | C12—N5—H5NB | 120.7 |
| C1—N1—Zr1 | 119.9 (2) | H5NA—N5—H5NB | 119.5 |
| C5—N1—Zr1 | 120.7 (2) | N5—C12—N3 | 119.5 (3) |
| C8—N2—C8$^{i}$ | 120.5 (4) | N5—C12—N4 | 121.6 (3) |
| C8—N2—Zr1 | 119.8 (2) | N3—C12—N4 | 118.9 (3) |
| C8$^{i}$—N2—Zr1 | 119.8 (2) | H1WA—O1W—H1WB | 113.4 |
| N1—C1—C2 | 122.2 (3) | H2WA—O2W—H2WB | 114.3 |

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| O3—Zr1—O1—C6 | −5.4 (3) | O3—Zr1—N2—C8$^{i}$ | 130.96 (17) |
| O3$^{i}$—Zr1—O1—C6 | 74.6 (2) | O3$^{i}$—Zr1—N2—C8$^{i}$ | −49.04 (17) |
| O1$^{i}$—Zr1—O1—C6 | −138.4 (3) | O1$^{i}$—Zr1—N2—C8$^{i}$ | 83.72 (17) |
| O5—Zr1—O1—C6 | −71.2 (3) | O1—Zr1—N2—C8$^{i}$ | −96.28 (17) |
| O5$^{i}$—Zr1—O1—C6 | 153.4 (3) | O5—Zr1—N2—C8$^{i}$ | 172.17 (17) |
| N1$^{i}$—Zr1—O1—C6 | 104.6 (3) | O5$^{i}$—Zr1—N2—C8$^{i}$ | −7.83 (17) |
| N1—Zr1—O1—C6 | 0.5 (2) | N1$^{i}$—Zr1—N2—C8$^{i}$ | 38.12 (17) |
| N2—Zr1—O1—C6 | −138.4 (3) | N1—Zr1—N2—C8$^{i}$ | −141.88 (17) |

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| O3$^{i}$—Zr1—O3—C7 | −59.3 (2) | C5—N1—C1—C2 | 0.3 (5) |
| O1$^{i}$—Zr1—O3—C7 | 166.3 (3) | Zr1—N1—C1—C2 | −179.3 (2) |
| O1—Zr1—O3—C7 | 13.9 (3) | C5—N1—C1—C6 | 179.9 (3) |
| O5—Zr1—O3—C7 | 82.4 (2) | Zr1—N1—C1—C6 | 0.4 (4) |
| O5$^{i}$—Zr1—O3—C7 | −131.8 (2) | N1—C1—C2—C3 | −1.2 (5) |
| N1$^{i}$—Zr1—O3—C7 | −123.4 (3) | C6—C1—C2—C3 | 179.2 (3) |
| N1—Zr1—O3—C7 | 8.1 (2) | C1—C2—C3—C4 | 1.1 (5) |
| N2—Zr1—O3—C7 | 120.7 (2) | C2—C3—C4—C5 | −0.2 (5) |
| O3—Zr1—O5—C11 | 166.3 (3) | C1—N1—C5—C4 | 0.7 (5) |
| O3$^{i}$—Zr1—O5—C11 | −116.0 (3) | Zr1—N1—C5—C4 | −179.7 (2) |
| O1$^{i}$—Zr1—O5—C11 | 88.4 (3) | C1—N1—C5—C7 | −177.9 (3) |
| O1—Zr1—O5—C11 | −56.4 (3) | Zr1—N1—C5—C7 | 1.7 (3) |
| O5$^{i}$—Zr1—O5—C11 | 15.4 (2) | C3—C4—C5—N1 | −0.7 (5) |
| N1$^{i}$—Zr1—O5—C11 | 127.9 (2) | C3—C4—C5—C7 | 177.7 (3) |
| N1—Zr1—O5—C11 | −124.3 (3) | Zr1—O1—C6—O2 | 179.8 (3) |
| N2—Zr1—O5—C11 | 15.4 (2) | Zr1—O1—C6—C1 | −0.4 (4) |
| O3—Zr1—N1—C1 | 175.0 (3) | N1—C1—C6—O2 | 179.8 (3) |
| O3$^{i}$—Zr1—N1—C1 | −83.4 (2) | C2—C1—C6—O2 | −0.6 (5) |
| O1$^{i}$—Zr1—N1—C1 | 143.0 (2) | N1—C1—C6—O1 | 0.0 (4) |
| O1—Zr1—N1—C1 | −0.4 (2) | C2—C1—C6—O1 | 179.7 (3) |
| O5—Zr1—N1—C1 | 91.0 (2) | Zr1—O3—C7—O4 | 170.7 (2) |
| O5$^{i}$—Zr1—N1—C1 | −43.3 (3) | Zr1—O3—C7—C5 | −9.9 (4) |
| N1$^{i}$—Zr1—N1—C1 | −133.3 (3) | N1—C5—C7—O4 | −176.1 (3) |
| N2—Zr1—N1—C1 | 46.7 (3) | C4—C5—C7—O4 | 5.4 (5) |
| O3—Zr1—N1—C5 | −4.5 (2) | N1—C5—C7—O3 | 4.5 (4) |
| O3$^{i}$—Zr1—N1—C5 | 97.1 (2) | C4—C5—C7—O3 | −174.0 (3) |
| O1$^{i}$—Zr1—N1—C5 | −36.6 (3) | C8$^{i}$—N2—C8—C9 | 0.9 (2) |
| O1—Zr1—N1—C5 | −180.0 (3) | Zr1—N2—C8—C9 | −179.1 (2) |
| O5—Zr1—N1—C5 | −88.5 (2) | C8$^{i}$—N2—C8—C11 | −178.4 (3) |
| O5$^{i}$—Zr1—N1—C5 | 137.1 (2) | Zr1—N2—C8—C11 | 1.6 (3) |
| N1$^{i}$—Zr1—N1—C5 | 47.2 (2) | N2—C8—C9—C10 | −1.8 (5) |
| N2—Zr1—N1—C5 | −132.8 (2) | C11—C8—C9—C10 | 177.4 (3) |
| O3—Zr1—N2—C8 | −49.04 (17) | C8—C9—C10—C9$^{i}$ | 0.9 (2) |
| O3$^{i}$—Zr1—N2—C8 | 130.96 (17) | Zr1—O5—C11—O6 | 160.2 (3) |
| O1$^{i}$—Zr1—N2—C8 | −96.28 (17) | Zr1—O5—C11—C8 | −19.8 (4) |
| O1—Zr1—N2—C8 | 83.72 (17) | N2—C8—C11—O6 | −169.6 (3) |
| O5—Zr1—N2—C8 | −7.83 (17) | C9—C8—C11—O6 | 11.1 (5) |
| O5$^{i}$—Zr1—N2—C8 | 172.17 (17) | N2—C8—C11—O5 | 10.4 (4) |
| N1$^{i}$—Zr1—N2—C8 | −141.88 (17) | C9—C8—C11—O5 | −168.9 (3) |
| N1—Zr1—N2—C8 | 38.12 (17) | | |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*NA*···O1 | 0.77 | 2.23 | 3.003 (4) | 175 |
| N3—H3*NB*···O2*W*$^{i}$ | 0.86 | 2.15 | 2.930 (4) | 150 |
| N4—H4*NA*···O2*W*$^{i}$ | 0.83 | 2.04 | 2.818 (4) | 156 |
| N4—H4*NB*···O1*W*$^{ii}$ | 0.78 | 2.06 | 2.834 (4) | 175 |

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|---|---|---|---|---|
| N5—H5*NA*···O2 | 0.88 | 1.95 | 2.828 (4) | 171 |
| N5—H5*NB*···O3$^{iii}$ | 0.79 | 2.45 | 3.143 (4) | 148 |
| N5—H5*NB*···O4$^{iii}$ | 0.79 | 2.52 | 3.171 (4) | 141 |
| O1*W*—H1*WA*···O3$^{iv}$ | 0.84 | 2.33 | 3.041 (3) | 143 |
| O1*W*—H1*WA*···O5$^{iv}$ | 0.84 | 2.38 | 3.076 (3) | 140 |
| O1*W*—H1*WB*···O6 | 0.89 | 1.87 | 2.761 (3) | 175 |
| O2*W*—H2*WA*···O5$^{iv}$ | 0.86 | 2.07 | 2.909 (3) | 165 |
| O2*W*—H2*WA*···O6$^{iv}$ | 0.86 | 2.57 | 3.085 (3) | 119 |
| O2*W*—H2*WB*···O4$^{v}$ | 0.94 | 1.84 | 2.745 (3) | 160 |

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) −*x*+1/2, −*y*+1/2, *z*+1/2; (iii) *x*−1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1, −*y*+1, −*z*; (v) *x*, *y*−1, *z*.