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# [$\mu$-1,3-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl-$\kappa N^2$)propan-2-olato-$\kappa^2 O$:*O*]bis[(ethanol-$\kappa O$)zinc(II)] bis(perchlorate)

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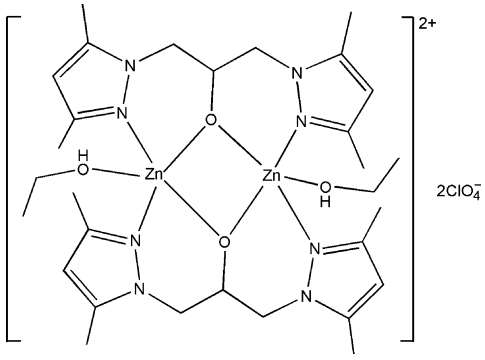
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.030; $wR$ factor = 0.083; data-to-parameter ratio = 14.0.

In the centrosymmetric dinuclear title complex, $[Zn_2(C_{13}H_{19}N_4O)_2(C_2H_5OH)_2](ClO_4)_2$, the $Zn^{II}$ atom is in a distorted trigonal-bipyramidal coordination geometry. The equatorial plane is constructed by one N atom and one O atom from two 1,3-bis(3,5-dimethylpyrazol-1-yl)propan-2-olate (bppo) ligands and one O atom from an ethanol molecule. One N atom and one O atom from the two bppo ligands occupy the axial positions. Intermolecular O—H···O hydrogen bonds between the ethanol molecules and perchlorate anions, and O···$\pi$ interactions between the perchlorate anions and pyrazole rings [O···centroid distances = 3.494 (3) and 3.413 (3) Å], lead to a chain structure along [010].

## Related literature

For related structures, see: Montoya *et al.* (2007).




## Experimental

### Crystal data

$[Zn_2(C_{13}H_{19}N_4O)_2(C_2H_6O)_2](ClO_4)_2$
$M_r$ = 916.42
Triclinic, $P\overline{1}$
$a$ = 8.8570 (18) Å
$b$ = 11.148 (2) Å
$c$ = 11.300 (2) Å
$\alpha$ = 111.13 (3)°
$\beta$ = 100.40 (3)°
$\gamma$ = 100.11 (3)°
$V$ = 987.8 (5) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 1.42 mm$^{-1}$
$T$ = 293 K
0.22 × 0.20 × 0.20 mm

### Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.765, $T_{max}$ = 0.765
7788 measured reflections
3482 independent reflections
3172 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
$S$ = 1.07
3482 reflections
249 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.22 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.076 (2) | Zn1—O6$^{i}$ | 2.0428 (16) |
| Zn1—N3$^{i}$ | 2.042 (2) | Zn1—O7 | 2.1292 (18) |
| Zn1—O6 | 1.9908 (16) | | |

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

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O7—H7$A$···O3 | 0.85 | 2.03 | 2.860 (3) | 165 |

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

We are grateful for support from Henan University of Urban Construction.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2370).

## References

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# supplementary materials

*Acta Cryst.* (2010). E**66**, m1520 [ **doi:10.1107/S160053681004479X** ]

# [$\mu$-1,3-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl-$\kappa N^2$)propan-2-olato-$\kappa^2 O$:*O*]bis[(ethanol-$\kappa O$)zinc(II)] bis(perchlorate)

**D.-M. Tian and C.-Y. Shi**

## Comment

Pyrazole-derived ligands have been extensively studied in recent years. These ligands are known as anionic or neutral groups to coordinate to metal centers through N atoms in monodentate and exobidentate modes. It is essential to study the syntheses and crystal structures of the complexes formed by pyrazole systematically, and to inquire into the factors that influence the formation and structure of such complexes. Such studies may lead to the design and synthesis of functional materials, and also provide a theoretical foundation for supramolecular chemistry and crystal engineering (Montoya *et al.*, 2007). As part of our studies on the synthesis and characterization of these compounds, we report here the synthesis and crystal structure of the title compound.

In the title compound (Fig. 1), the $Zn^{II}$ atom is five-coordinated by two O atoms and two N atoms from two 1,3-bis(3,5-dimethyl-pyrazol-1-yl)propan-2-olate (bppo) ligands and one O atom from an ethanol molecule in a distorted trigonal–bipyramidal geometry (Table 1). The equatorial plane is constructed by $N3^{i}$ and O6 from the two bppo ligands and O7 from the ethanol molecule. The N1 and $O6^{i}$ atoms occupy the axial positions [symmetry code: (i) 1 - x, -y, -z]. Two hydroxyl O atoms bridge the Zn atoms, forming a dinuclear complex. Intermolecular O—H···O hydrogen bonds between the ethanol molecules and perchlorate anions (Table 2) and O···π interactions between the perchlorate anions and pyrazole rings, O2···*Cg*1$^{ii}$ and O3···*Cg*2, [*Cg*1 and *Cg*2 are the centroids of C2/C3/C4/N3/N4 ring and C6/C7/C8/N1/N2 ring; symmetry code: (ii) x, -1 + y, z; O—centroid distances = 3.494 (3) and 3.413 (3) Å, respectively], lead to a chain structure along [010] (Fig. 2).

## Experimental

1,3-Bis(3,5-dimethyl-pyrazol-1-yl)propan-2-ol and $ZnCl_2.6H_2O$ were available commercially and were used without further purification. 1,3-Bis(3,5-dimethyl-pyrazol-1-yl)propan-2-ol (124 mg, 0.5 mmol) were dissolved in anhydrous alcohol (15 ml). To this solution was added $ZuCl_2.6H_2O$ (122 mg, 0.5 mmol) in anhydrous alcohol (10 ml). After keeping the resulting solution in air to evaporate about half of the solvent, blue prismatic crystals of the title compound were formed. The crystals were isolated, washed with alcohol three times and dried in a vacuum desiccator using silica gel (yield: 75%). Analysis, calculated for $C_{30}H_{50}Cl_2N_8O_{12}Zn_2$: C 39.32, H 5.50, N, 12.23%; found: C 39.42, H 5.28, N 12.35%.

## Refinement

H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93–0.98 Å and $U_{iso}$(H) = 1.2(1.5 for methyl)$U_{eq}$(C). Hydroxy H atom was located in a difference Fourier map and refined as a riding atom, with O—H = 0.85 Å and $U_{iso}$(H) = 1.5$U_{eq}$(O).

**Figures**

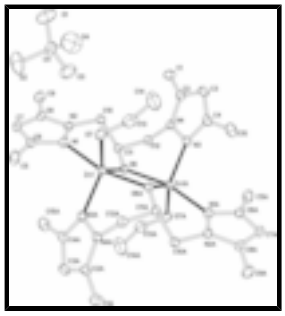

Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (A) 1 - *x*, -*y*, -*z*.]

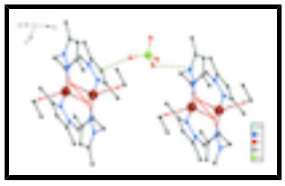

Fig. 2. The chain structure in the title compound. Dashed lines denote O···π interactions.

**[μ-1,3-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl-κ$N^2$)propan- 2-olato-κ$^2$*O*:*O*]bis[(ethanol-κ*O*)zinc(II)] bis(perchlorate)**

*Crystal data*

| | |
|---|---|
| $[Zn_2(C_{13}H_{19}N_4O)_2(C_2H_6O)_2](ClO_4)_2$ | $Z = 1$ |
| $M_r = 916.42$ | $F(000) = 476$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.541$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a = 8.8570$ (18) Å | Cell parameters from 2230 reflections |
| $b = 11.148$ (2) Å | θ = 2.3–25.7° |
| $c = 11.300$ (2) Å | μ = 1.42 mm$^{-1}$ |
| α = 111.13 (3)° | $T = 293$ K |
| β = 100.40 (3)° | Block, colourless |
| γ = 100.11 (3)° | 0.22 × 0.20 × 0.20 mm |
| $V = 987.8$ (5) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker APEX CCD diffractometer | 3482 independent reflections |
| Radiation source: fine-focus sealed tube | 3172 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.017$ |
| φ and ω scans | $\theta_{max} = 25.0°$, $\theta_{min} = 3.3°$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $h = -10 \rightarrow 10$ |
| $T_{min} = 0.765$, $T_{max} = 0.765$ | $k = -13 \rightarrow 13$ |
| 7788 measured reflections | $l = -13 \rightarrow 13$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.083$ | H-atom parameters constrained |
| $S = 1.07$ | $w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.4173P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 3482 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 249 parameters | $\Delta\rho_{max} = 0.50$ e Å$^{-3}$ |
| 2 restraints | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.44360 (3) | −0.13668 (2) | 0.00434 (2) | 0.03250 (11) |
| N1 | 0.3373 (2) | −0.18995 (19) | 0.13387 (19) | 0.0385 (4) |
| N2 | 0.3198 (2) | −0.09350 (19) | 0.24246 (19) | 0.0364 (4) |
| O6 | 0.40890 (17) | 0.04471 (14) | 0.07488 (15) | 0.0331 (3) |
| O7 | 0.6260 (2) | −0.21497 (19) | 0.07459 (19) | 0.0528 (5) |
| H7A | 0.6208 | −0.2359 | 0.1393 | 0.079* |
| C5 | 0.2447 (4) | −0.4353 (3) | 0.0179 (3) | 0.0597 (7) |
| H5A | 0.2756 | −0.4202 | −0.0538 | 0.089* |
| H5B | 0.1397 | −0.4941 | −0.0135 | 0.089* |
| H5C | 0.3182 | −0.4748 | 0.0544 | 0.089* |
| C6 | 0.2460 (3) | −0.3054 (2) | 0.1218 (2) | 0.0413 (5) |
| C7 | 0.1694 (3) | −0.2813 (3) | 0.2213 (3) | 0.0453 (6) |
| H7 | 0.0970 | −0.3442 | 0.2334 | 0.054* |
| C8 | 0.2202 (3) | −0.1478 (3) | 0.2983 (2) | 0.0413 (5) |
| C9 | 0.1855 (4) | −0.0683 (3) | 0.4239 (3) | 0.0606 (8) |
| H9A | 0.2773 | −0.0431 | 0.4961 | 0.091* |
| H9B | 0.0971 | −0.1210 | 0.4368 | 0.091* |
| H9C | 0.1599 | 0.0104 | 0.4193 | 0.091* |
| C10 | 0.4166 (3) | 0.0433 (2) | 0.2899 (2) | 0.0381 (5) |
| H10A | 0.5279 | 0.0435 | 0.3030 | 0.046* |
| H10B | 0.4016 | 0.0957 | 0.3743 | 0.046* |
| C11 | 0.3753 (3) | 0.1084 (2) | 0.1951 (2) | 0.0331 (5) |
| H11 | 0.2605 | 0.0997 | 0.1770 | 0.040* |
| C13 | 0.7924 (3) | −0.1751 (4) | 0.0899 (3) | 0.0641 (8) |
| H13A | 0.8108 | −0.1760 | 0.0076 | 0.077* |
| H13B | 0.8423 | −0.2383 | 0.1110 | 0.077* |
| C14 | 0.8653 (5) | −0.0412 (4) | 0.1945 (6) | 0.1128 (18) |
| H14A | 0.8059 | 0.0190 | 0.1808 | 0.169* |
| H14B | 0.9729 | −0.0113 | 0.1926 | 0.169* |
| H14C | 0.8647 | −0.0439 | 0.2783 | 0.169* |

| | | | | |
|---|---|---|---|---|
| C12 | 0.4601 (3) | 0.2576 (2) | 0.2567 (2) | 0.0367 (5) |
| H12A | 0.4222 | 0.2976 | 0.1977 | 0.044* |
| H12B | 0.4328 | 0.2998 | 0.3385 | 0.044* |
| N3 | 0.7009 (2) | 0.25422 (18) | 0.17989 (19) | 0.0366 (4) |
| N4 | 0.6328 (2) | 0.28347 (18) | 0.28297 (18) | 0.0359 (4) |
| C1 | 0.7043 (4) | 0.3867 (3) | 0.5278 (3) | 0.0630 (8) |
| H1A | 0.6439 | 0.4506 | 0.5295 | 0.094* |
| H1B | 0.8007 | 0.4283 | 0.5977 | 0.094* |
| H1C | 0.6428 | 0.3136 | 0.5389 | 0.094* |
| C2 | 0.7442 (3) | 0.3366 (2) | 0.3990 (2) | 0.0437 (6) |
| C3 | 0.8885 (3) | 0.3381 (3) | 0.3704 (3) | 0.0501 (6) |
| H3 | 0.9877 | 0.3674 | 0.4306 | 0.060* |
| C15 | 0.9736 (3) | 0.2689 (3) | 0.1524 (3) | 0.0614 (8) |
| H15A | 0.9241 | 0.1944 | 0.0696 | 0.092* |
| H15B | 1.0653 | 0.2525 | 0.1974 | 0.092* |
| H15C | 1.0055 | 0.3479 | 0.1373 | 0.092* |
| C4 | 0.8579 (3) | 0.2875 (2) | 0.2346 (3) | 0.0433 (6) |
| O1 | 0.7169 (4) | −0.2927 (3) | 0.4897 (3) | 0.1003 (9) |
| O2 | 0.5741 (4) | −0.4532 (3) | 0.2842 (4) | 0.1233 (12) |
| O3 | 0.6271 (4) | −0.2330 (3) | 0.3209 (3) | 0.0955 (9) |
| O4 | 0.8318 (4) | −0.3383 (4) | 0.3177 (3) | 0.1242 (12) |
| Cl1 | 0.68858 (8) | −0.33052 (6) | 0.35237 (7) | 0.05214 (18) |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.03703 (16) | 0.02905 (16) | 0.03013 (16) | 0.00679 (10) | 0.01162 (11) | 0.01013 (11) |
| N1 | 0.0468 (11) | 0.0325 (10) | 0.0367 (11) | 0.0091 (8) | 0.0174 (9) | 0.0121 (8) |
| N2 | 0.0422 (10) | 0.0341 (10) | 0.0325 (10) | 0.0070 (8) | 0.0130 (8) | 0.0131 (8) |
| O6 | 0.0396 (8) | 0.0292 (8) | 0.0296 (8) | 0.0076 (6) | 0.0132 (6) | 0.0099 (6) |
| O7 | 0.0477 (10) | 0.0682 (12) | 0.0590 (12) | 0.0215 (9) | 0.0158 (9) | 0.0403 (10) |
| C5 | 0.078 (2) | 0.0344 (14) | 0.0638 (19) | 0.0087 (13) | 0.0274 (16) | 0.0154 (13) |
| C6 | 0.0462 (13) | 0.0354 (13) | 0.0418 (14) | 0.0060 (10) | 0.0114 (11) | 0.0175 (11) |
| C7 | 0.0459 (13) | 0.0442 (14) | 0.0467 (15) | 0.0021 (11) | 0.0137 (11) | 0.0231 (12) |
| C8 | 0.0449 (13) | 0.0474 (14) | 0.0365 (13) | 0.0088 (10) | 0.0155 (10) | 0.0218 (11) |
| C9 | 0.0747 (19) | 0.0637 (18) | 0.0458 (16) | 0.0113 (15) | 0.0313 (15) | 0.0207 (14) |
| C10 | 0.0417 (12) | 0.0356 (12) | 0.0318 (12) | 0.0043 (9) | 0.0096 (10) | 0.0104 (10) |
| C11 | 0.0325 (11) | 0.0335 (11) | 0.0330 (12) | 0.0086 (9) | 0.0139 (9) | 0.0105 (9) |
| C13 | 0.0497 (16) | 0.099 (3) | 0.066 (2) | 0.0353 (16) | 0.0243 (15) | 0.0470 (19) |
| C14 | 0.068 (2) | 0.086 (3) | 0.177 (5) | 0.002 (2) | −0.007 (3) | 0.072 (3) |
| C12 | 0.0416 (12) | 0.0318 (12) | 0.0366 (13) | 0.0108 (9) | 0.0159 (10) | 0.0107 (10) |
| N3 | 0.0364 (10) | 0.0339 (10) | 0.0340 (10) | 0.0066 (8) | 0.0112 (8) | 0.0079 (8) |
| N4 | 0.0401 (10) | 0.0319 (10) | 0.0304 (10) | 0.0054 (8) | 0.0095 (8) | 0.0082 (8) |
| C1 | 0.080 (2) | 0.0609 (18) | 0.0336 (15) | 0.0046 (15) | 0.0084 (14) | 0.0131 (13) |
| C2 | 0.0550 (15) | 0.0314 (12) | 0.0344 (13) | 0.0021 (10) | 0.0037 (11) | 0.0098 (10) |
| C3 | 0.0450 (14) | 0.0431 (14) | 0.0467 (16) | 0.0014 (11) | −0.0047 (12) | 0.0134 (12) |
| C15 | 0.0406 (14) | 0.0656 (19) | 0.075 (2) | 0.0121 (13) | 0.0207 (14) | 0.0229 (16) |
| C4 | 0.0392 (12) | 0.0352 (13) | 0.0489 (15) | 0.0062 (10) | 0.0078 (11) | 0.0133 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 0.135 (2) | 0.135 (3) | 0.0666 (17) | 0.065 (2) | 0.0451 (17) | 0.0586 (18) |
| O2 | 0.125 (2) | 0.0526 (16) | 0.163 (3) | −0.0057 (15) | 0.031 (2) | 0.0271 (18) |
| O3 | 0.140 (2) | 0.0671 (16) | 0.0824 (18) | 0.0311 (16) | 0.0106 (17) | 0.0403 (14) |
| O4 | 0.088 (2) | 0.178 (3) | 0.116 (3) | 0.040 (2) | 0.0609 (19) | 0.051 (2) |
| Cl1 | 0.0664 (4) | 0.0457 (4) | 0.0509 (4) | 0.0129 (3) | 0.0249 (3) | 0.0234 (3) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.076 (2) | C11—H11 | 0.9800 |
| Zn1—N3$^{i}$ | 2.042 (2) | C13—C14 | 1.468 (6) |
| Zn1—O6 | 1.9908 (16) | C13—H13A | 0.9700 |
| Zn1—O6$^{i}$ | 2.0428 (16) | C13—H13B | 0.9700 |
| Zn1—O7 | 2.1292 (18) | C14—H14A | 0.9600 |
| Zn1—Zn1$^{i}$ | 3.0784 (9) | C14—H14B | 0.9600 |
| N1—C6 | 1.340 (3) | C14—H14C | 0.9600 |
| N1—N2 | 1.364 (3) | C12—N4 | 1.460 (3) |
| N2—C8 | 1.353 (3) | C12—H12A | 0.9700 |
| N2—C10 | 1.461 (3) | C12—H12B | 0.9700 |
| O6—C11 | 1.401 (3) | N3—C4 | 1.341 (3) |
| O6—Zn1$^{i}$ | 2.0428 (16) | N3—N4 | 1.370 (3) |
| O7—C13 | 1.422 (3) | N3—Zn1$^{i}$ | 2.042 (2) |
| O7—H7A | 0.8500 | N4—C2 | 1.346 (3) |
| C5—C6 | 1.496 (4) | C1—C2 | 1.491 (4) |
| C5—H5A | 0.9600 | C1—H1A | 0.9600 |
| C5—H5B | 0.9600 | C1—H1B | 0.9600 |
| C5—H5C | 0.9600 | C1—H1C | 0.9600 |
| C6—C7 | 1.385 (4) | C2—C3 | 1.372 (4) |
| C7—C8 | 1.366 (4) | C3—C4 | 1.385 (4) |
| C7—H7 | 0.9300 | C3—H3 | 0.9300 |
| C8—C9 | 1.497 (4) | C15—C4 | 1.495 (4) |
| C9—H9A | 0.9600 | C15—H15A | 0.9600 |
| C9—H9B | 0.9600 | C15—H15B | 0.9600 |
| C9—H9C | 0.9600 | C15—H15C | 0.9600 |
| C10—C11 | 1.522 (3) | O1—Cl1 | 1.414 (3) |
| C10—H10A | 0.9700 | O2—Cl1 | 1.401 (3) |
| C10—H10B | 0.9700 | O3—Cl1 | 1.422 (3) |
| C11—C12 | 1.534 (3) | O4—Cl1 | 1.402 (3) |
| O6—Zn1—N3$^{i}$ | 112.71 (8) | C10—C11—C12 | 111.32 (19) |
| O6—Zn1—O6$^{i}$ | 80.52 (7) | O6—C11—H11 | 107.6 |
| N3$^{i}$—Zn1—O6$^{i}$ | 89.87 (7) | C10—C11—H11 | 107.6 |
| O6—Zn1—N1 | 91.69 (7) | C12—C11—H11 | 107.6 |
| N3$^{i}$—Zn1—N1 | 106.21 (8) | O7—C13—C14 | 111.5 (3) |
| O6$^{i}$—Zn1—N1 | 163.86 (7) | O7—C13—H13A | 109.3 |
| O6—Zn1—O7 | 130.72 (8) | C14—C13—H13A | 109.3 |
| N3$^{i}$—Zn1—O7 | 115.77 (8) | O7—C13—H13B | 109.3 |
| O6$^{i}$—Zn1—O7 | 91.14 (7) | C14—C13—H13B | 109.3 |

| | | | |
|---|---|---|---|
| N1—Zn1—O7 | 83.23 (8) | H13A—C13—H13B | 108.0 |
| O6—Zn1—Zn1$^{i}$ | 40.88 (4) | C13—C14—H14A | 109.5 |
| N3$^{i}$—Zn1—Zn1$^{i}$ | 104.37 (6) | C13—C14—H14B | 109.5 |
| O6$^{i}$—Zn1—Zn1$^{i}$ | 39.63 (4) | H14A—C14—H14B | 109.5 |
| N1—Zn1—Zn1$^{i}$ | 131.04 (6) | C13—C14—H14C | 109.5 |
| O7—Zn1—Zn1$^{i}$ | 115.79 (6) | H14A—C14—H14C | 109.5 |
| C6—N1—N2 | 106.23 (19) | H14B—C14—H14C | 109.5 |
| C6—N1—Zn1 | 132.19 (16) | N4—C12—C11 | 112.81 (18) |
| N2—N1—Zn1 | 119.85 (14) | N4—C12—H12A | 109.0 |
| C8—N2—N1 | 110.49 (19) | C11—C12—H12A | 109.0 |
| C8—N2—C10 | 129.5 (2) | N4—C12—H12B | 109.0 |
| N1—N2—C10 | 119.68 (18) | C11—C12—H12B | 109.0 |
| C11—O6—Zn1 | 126.98 (13) | H12A—C12—H12B | 107.8 |
| C11—O6—Zn1$^{i}$ | 124.67 (13) | C4—N3—N4 | 105.54 (19) |
| Zn1—O6—Zn1$^{i}$ | 99.48 (7) | C4—N3—Zn1$^{i}$ | 134.36 (17) |
| C13—O7—Zn1 | 128.78 (17) | N4—N3—Zn1$^{i}$ | 117.88 (14) |
| C13—O7—H7A | 103.2 | C2—N4—N3 | 111.10 (19) |
| Zn1—O7—H7A | 118.4 | C2—N4—C12 | 129.4 (2) |
| C6—C5—H5A | 109.5 | N3—N4—C12 | 119.52 (18) |
| C6—C5—H5B | 109.5 | C2—C1—H1A | 109.5 |
| H5A—C5—H5B | 109.5 | C2—C1—H1B | 109.5 |
| C6—C5—H5C | 109.5 | H1A—C1—H1B | 109.5 |
| H5A—C5—H5C | 109.5 | C2—C1—H1C | 109.5 |
| H5B—C5—H5C | 109.5 | H1A—C1—H1C | 109.5 |
| N1—C6—C7 | 109.4 (2) | H1B—C1—H1C | 109.5 |
| N1—C6—C5 | 121.1 (2) | N4—C2—C3 | 106.6 (2) |
| C7—C6—C5 | 129.4 (2) | N4—C2—C1 | 122.5 (2) |
| C8—C7—C6 | 107.2 (2) | C3—C2—C1 | 130.8 (2) |
| C8—C7—H7 | 126.4 | C2—C3—C4 | 106.8 (2) |
| C6—C7—H7 | 126.4 | C2—C3—H3 | 126.6 |
| N2—C8—C7 | 106.7 (2) | C4—C3—H3 | 126.6 |
| N2—C8—C9 | 123.0 (2) | C4—C15—H15A | 109.5 |
| C7—C8—C9 | 130.2 (2) | C4—C15—H15B | 109.5 |
| C8—C9—H9A | 109.5 | H15A—C15—H15B | 109.5 |
| C8—C9—H9B | 109.5 | C4—C15—H15C | 109.5 |
| H9A—C9—H9B | 109.5 | H15A—C15—H15C | 109.5 |
| C8—C9—H9C | 109.5 | H15B—C15—H15C | 109.5 |
| H9A—C9—H9C | 109.5 | N3—C4—C3 | 109.9 (2) |
| H9B—C9—H9C | 109.5 | N3—C4—C15 | 121.5 (2) |
| N2—C10—C11 | 112.67 (19) | C3—C4—C15 | 128.6 (2) |
| N2—C10—H10A | 109.1 | O2—Cl1—O4 | 110.6 (2) |
| C11—C10—H10A | 109.1 | O2—Cl1—O1 | 110.3 (2) |
| N2—C10—H10B | 109.1 | O4—Cl1—O1 | 109.0 (2) |
| C11—C10—H10B | 109.1 | O2—Cl1—O3 | 107.9 (2) |
| H10A—C10—H10B | 107.8 | O4—Cl1—O3 | 110.9 (2) |
| O6—C11—C10 | 111.91 (18) | O1—Cl1—O3 | 108.07 (18) |
| O6—C11—C12 | 110.58 (18) | | |

| | | | |
|---|---|---|---|
| O6—Zn1—N1—C6 | 144.8 (2) | C10—N2—C8—C7 | −174.6 (2) |
| $N3^{i}$—Zn1—N1—C6 | 30.5 (2) | N1—N2—C8—C9 | 176.0 (2) |
| $O6^{i}$—Zn1—N1—C6 | −154.6 (2) | C10—N2—C8—C9 | 3.1 (4) |
| O7—Zn1—N1—C6 | −84.4 (2) | C6—C7—C8—N2 | 2.3 (3) |
| $Zn1^{i}$—Zn1—N1—C6 | 157.08 (19) | C6—C7—C8—C9 | −175.3 (3) |
| O6—Zn1—N1—N2 | −18.00 (17) | C8—N2—C10—C11 | −120.3 (3) |
| $N3^{i}$—Zn1—N1—N2 | −132.25 (17) | N1—N2—C10—C11 | 67.4 (3) |
| $O6^{i}$—Zn1—N1—N2 | 42.6 (3) | Zn1—O6—C11—C10 | 17.7 (2) |
| O7—Zn1—N1—N2 | 112.83 (18) | $Zn1^{i}$—O6—C11—C10 | −122.81 (16) |
| $Zn1^{i}$—Zn1—N1—N2 | −5.7 (2) | Zn1—O6—C11—C12 | 142.41 (15) |
| C6—N1—N2—C8 | 0.5 (3) | $Zn1^{i}$—O6—C11—C12 | 1.9 (2) |
| Zn1—N1—N2—C8 | 167.30 (16) | N2—C10—C11—O6 | −64.4 (2) |
| C6—N1—N2—C10 | 174.2 (2) | N2—C10—C11—C12 | 171.27 (17) |
| Zn1—N1—N2—C10 | −19.0 (3) | Zn1—O7—C13—C14 | 67.8 (4) |
| $N3^{i}$—Zn1—O6—C11 | 126.18 (16) | O6—C11—C12—N4 | −60.2 (2) |
| $O6^{i}$—Zn1—O6—C11 | −147.97 (19) | C10—C11—C12—N4 | 64.9 (2) |
| N1—Zn1—O6—C11 | 17.82 (17) | C4—N3—N4—C2 | 1.5 (2) |
| O7—Zn1—O6—C11 | −64.70 (18) | $Zn1^{i}$—N3—N4—C2 | 166.94 (15) |
| $Zn1^{i}$—Zn1—O6—C11 | −147.97 (19) | C4—N3—N4—C12 | −179.55 (19) |
| $N3^{i}$—Zn1—O6—$Zn1^{i}$ | −85.85 (8) | $Zn1^{i}$—N3—N4—C12 | −14.1 (2) |
| $O6^{i}$—Zn1—O6—$Zn1^{i}$ | 0.0 | C11—C12—N4—C2 | −111.0 (3) |
| N1—Zn1—O6—$Zn1^{i}$ | 165.79 (8) | C11—C12—N4—N3 | 70.2 (3) |
| O7—Zn1—O6—$Zn1^{i}$ | 83.27 (10) | N3—N4—C2—C3 | −1.9 (3) |
| O6—Zn1—O7—C13 | −62.0 (3) | C12—N4—C2—C3 | 179.3 (2) |
| $N3^{i}$—Zn1—O7—C13 | 106.8 (2) | N3—N4—C2—C1 | 175.6 (2) |
| $O6^{i}$—Zn1—O7—C13 | 16.4 (2) | C12—N4—C2—C1 | −3.3 (4) |
| N1—Zn1—O7—C13 | −148.4 (2) | N4—C2—C3—C4 | 1.5 (3) |
| $Zn1^{i}$—Zn1—O7—C13 | −15.8 (2) | C1—C2—C3—C4 | −175.6 (3) |
| N2—N1—C6—C7 | 1.0 (3) | N4—N3—C4—C3 | −0.5 (3) |
| Zn1—N1—C6—C7 | −163.53 (18) | $Zn1^{i}$—N3—C4—C3 | −162.39 (18) |
| N2—N1—C6—C5 | −175.6 (2) | N4—N3—C4—C15 | 179.5 (2) |
| Zn1—N1—C6—C5 | 20.0 (4) | $Zn1^{i}$—N3—C4—C15 | 17.6 (4) |
| N1—C6—C7—C8 | −2.0 (3) | C2—C3—C4—N3 | −0.7 (3) |
| C5—C6—C7—C8 | 174.1 (3) | C2—C3—C4—C15 | 179.4 (3) |
| N1—N2—C8—C7 | −1.8 (3) | | |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O7—H7A···O3 | 0.85 | 2.03 | 2.860 (3) | 165 |

**Fig. 1**

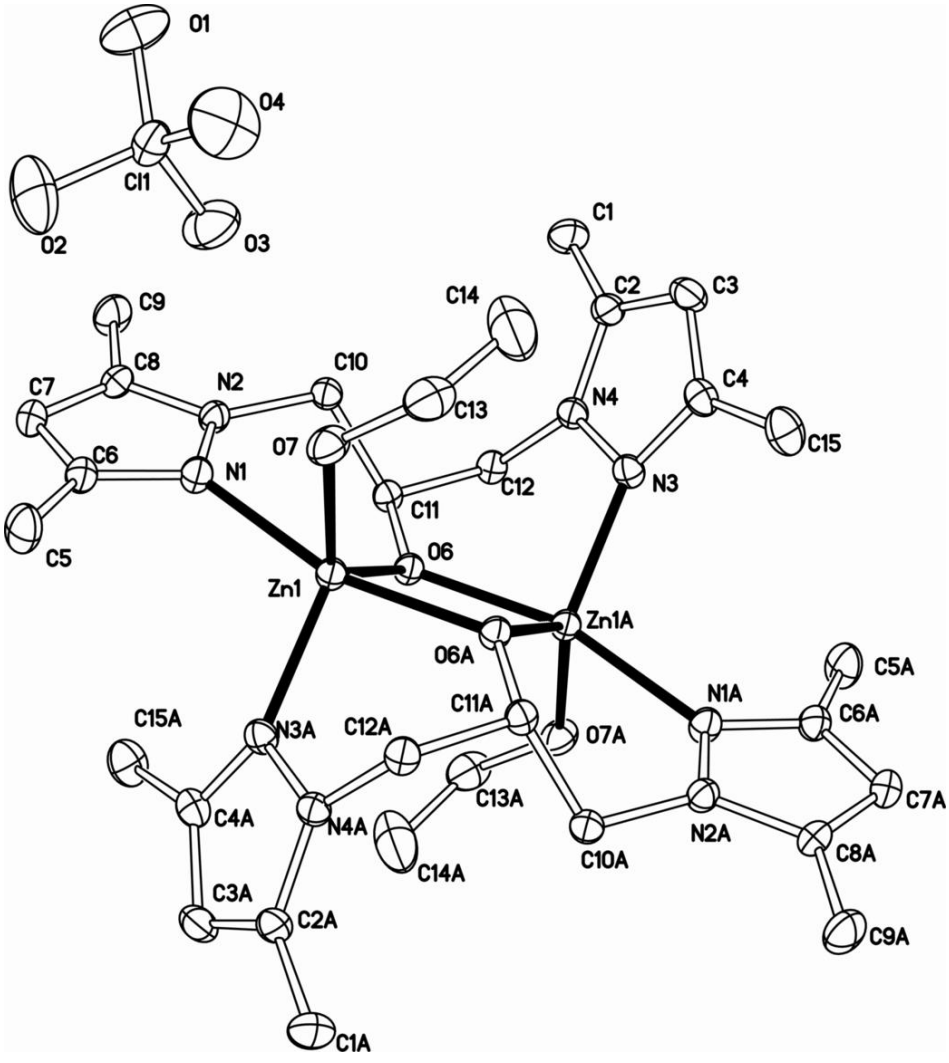
O1
O4
Cl1
O2
O3
C1
C2
C3
C14
C9
C8
C10
C7
N2
C4
C13
N4
O7
C15
C6
N1
C12
N3
C11
C5
O6
Zn1
Zn1A
O6A
C5A
N1A
C11A
C15A
N3A
C12A
O7A
C6A
C13A
C7A
C4A
N4A
N2A
C14A
C10A
C8A
C3A
C2A
C9A
C1A

**Fig. 2**