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Di- μ_2 -methoxo-bis[μ -3,10,18,25-tetra-azapentacyclo[17.4.4.3.1.1]triconta-1(31),2,4(9),5,7,10,12,14,16(32),-17,19(24),20,22,25,27,29-hexadecaene-31,32-diolato]dizinc(II)} bis(perchlorate) *N,N*-dimethylformamide disolvate

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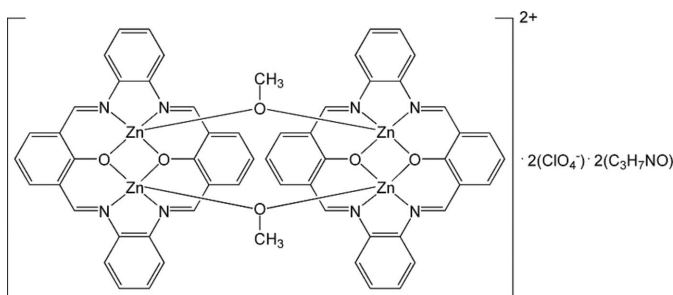
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in solvent or counterion; R factor = 0.045; wR factor = 0.123; data-to-parameter ratio = 13.4.

The title compound, $[\text{Zn}_4(\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2)_2(\text{CH}_3\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$, is a C_2 symmetric tetranuclear zinc(II) complex comprised of two $[\text{Zn}_2L]^{2+}$ units bridged by a pair of μ_2 -OMe ligands (where L is the doubly-deprotonated form of the macrocyclic dinucleating ligand derived from the [2 + 2] Schiff base condensation between 2-hydroxybenzene-1,3-dicarbaldehyde and 1,2-diaminobenzene). Each Zn^{II} atom has a distorted square-pyramidal coordination geometry and the $\text{Zn}_4(\mu\text{-OMe})_2$ unit lies in the cleft formed by two distinctly bent Schiff base ligands. The observed molecular shape is supported by an intramolecular π - π interaction between one of the phenolate rings on each of the two ligands [centroid-centroid distance = 3.491 (5) Å]. The methyl groups of the solvent molecule are disordered over two sets of sites in a 0.6:0.4 ratio.

Related literature

For the first examples of polynuclear transition metal complexes of Schiff base macrocyclic ligands, see: Pilkington & Robson (1970). For complexes comprising of macrocyclic ligands derived from 2-hydroxy-benzene-1,3-dicarbaldehyde and diamines or triamines, see: Vigato *et al.* (1990, 2007); Huang *et al.* (2006).



Experimental

Crystal data

$[\text{Zn}_4(\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2)_2(\text{CH}_3\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$
 $M_r = 1553.57$
 Monoclinic, $C2/c$
 $a = 30.9454$ (4) Å
 $b = 10.4512$ (2) Å
 $c = 20.5774$ (4) Å

$\beta = 112.019$ (1)°
 $V = 6169.65$ (19) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.70$ mm⁻¹
 $T = 123$ K
 $0.20 \times 0.20 \times 0.13$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1997)
 $T_{\text{min}} = 0.92$, $T_{\text{max}} = 1.0$

32276 measured reflections
 6063 independent reflections
 4245 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.123$
 $S = 1.03$
 6063 reflections
 453 parameters

17 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.86$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; 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: *CIFTAB* (Sheldrick, 1997).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2265).

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supporting information

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Di- μ_2 -methoxy-bis{[μ -3,10,18,25-tetraazapentacyclo-[17.4.4.3.1.1]tricont-1(31),2,4(9),5,7,10,12,14,16(32),17,19(24),20,22,25,27,29-hexadecaene-31,32-diolato]dizinc(II)} bis(perchlorate) *N,N*-dimethylformamide disolvate

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S1. Comment

The molecular structure of $[\text{Zn}_4\text{L}_2(\text{CH}_3\text{O})_2](\text{ClO}_4)_2 \times 2 \text{ DMF}$ (**1**) (Figure 1) features two Schiff base ligands, each of which coordinates a pair of zinc(II) centres. The dinuclear subunits are then bridged by two exogenous methoxy ligands. The two independent zinc(II) atoms have similar square-pyramidal coordination environments. The basal plane consists of nitrogen and oxygen atoms of the Schiff base ligand (mean deviation Zn1 0.004 (3) Å, Zn2 0.019 (3) Å); Zn1 and Zn2 lie out of these basal planes by 0.644 (1) and 0.654 (1) Å, respectively. The oxygen atoms, O3 and O3ⁱ (symmetry code: i 1 - x , y , 0.5 - z), of the bridging methoxy ligands occupy the apical positions. The two zinc(II) centres within each macrocyclic cavity are separated by 3.0136 (6) Å, whilst those bridged by the methoxy ligand are situated 3.4458 (5) Å apart.

Within the cation, there is an aromatic π - π interaction between the phenolic ring (C8—C13) from each of the Schiff base ligands. The centroid-centroid separation between them is 3.491 (5) Å and there is a distinct bending of the Schiff base ligand with the C8—C13 ring forming an angle of 27.44 (9) ° to the N1, N2, N3, N4 plane (*cf* 4.1 (1) ° for the other phenolic ring C15—C20). Overall, the cation adopts a 'cleft-shaped' structure with the associated ClO₄⁻ anions and DMF molecules located near the periphery of the cleft opening.

S2. Experimental

A solution of 2-hydroxy-benzene-1,3-dicarbaldehyde (2 mmol) in ethanol (10 ml) was added dropwise to a stirred solution of $\text{Zn}(\text{ClO}_4)_2 \times 6 \text{ H}_2\text{O}$ (2 mmol) and 1,2-diaminobenzene (2 mmol) in ethanol (20 ml). Triethylamine (2 mmol) was then added and the reaction mixture was stirred for 3 h at room temperature. The solvent was removed *in vacuo* and the resulting solid was recrystallized by slow diffusion of methanol into an *N,N*-dimethylformamide solution to give the title compound as yellow blocks in 64% yield. IR (cm⁻¹): 622 (ClO₄), 1090 (ClO₄), 1540 (C=C), 1615 (C=N). **CAUTION:** Although no problems were encountered in this work transition metal perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.

S3. Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{C})$.

The methyl groups of the solvent DMF molecule, C31 and C32, were modeled as disordered over two positions 0.8 Å apart (refined occupancies 0.60:0.40) and were refined with constrained N—C distances and anisotropic thermal

parameters.

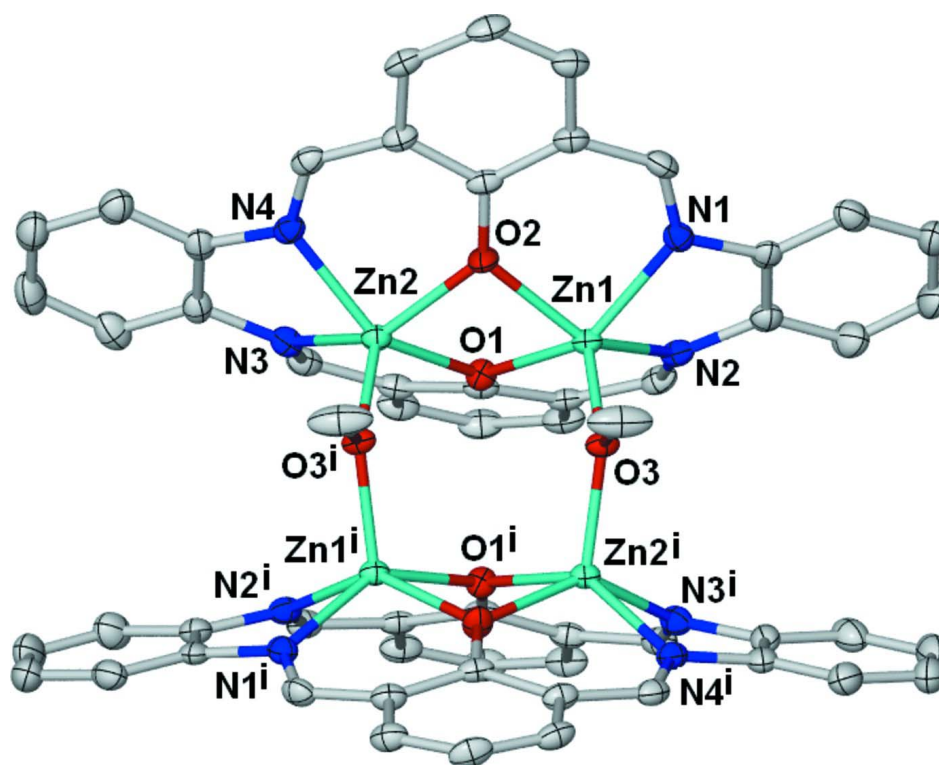


Figure 1

A view of the complex cation of (I) showing labeling of selected non-hydrogen atoms. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity. Atoms denoted 'i' are generated by the symmetry operator: $1 - x, y, 0.5 - z$.

Di- μ_2 -methoxy-bis{[μ -3,10,18,25-tetraazapentacyclo[17.4.4.3.1.1]triconta-1(31),2,4(9),5,7,10,12,14,16 (32),17,19 (24),20,22,25,27,29-hexadecaene-31,32- diolato]dizinc(II)} bis(perchlorate) *N,N*-dimethylformamide disolvate

Crystal data

$[\text{Zn}_4(\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2)_2(\text{CH}_3\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$

$M_r = 1553.57$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 30.9454(4)\ \text{\AA}$

$b = 10.4512(2)\ \text{\AA}$

$c = 20.5774(4)\ \text{\AA}$

$\beta = 112.019(1)^\circ$

$V = 6169.65(19)\ \text{\AA}^3$

$Z = 4$

$F(000) = 3168$

$D_x = 1.673\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3613 reflections

$\theta = 2.1\text{--}26.0^\circ$

$\mu = 1.70\ \text{mm}^{-1}$

$T = 123\ \text{K}$

Block, yellow

$0.20 \times 0.20 \times 0.13\ \text{mm}$

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal

monochromator

Detector resolution: $9\ \text{pixels mm}^{-1}$

Thin-slice φ and ω scans

Absorption correction: multi-scan

(*SORTAV*; Blessing, 1997)

$T_{\min} = 0.92, T_{\max} = 1.0$

32276 measured reflections
 6063 independent reflections
 4245 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.074$

$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 $h = -38 \rightarrow 38$
 $k = -12 \rightarrow 12$
 $l = -25 \rightarrow 25$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.123$
 $S = 1.03$
 6063 reflections
 453 parameters
 17 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 14.7497P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.86 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{\AA}^{-3}$

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. The methyl groups of the solvent DMF molecule, C31 and C32, were modeled as disordered over two positions 0.8 Å apart (refined occupancies 0.60:0.40) and were refined with constrained N—C distances and anisotropic thermal parameters.

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) |
|-----|---------------|--------------|--------------|----------------------------------|-----------|
| Zn1 | 0.544502 (14) | 0.56311 (4) | 0.36676 (2) | 0.01940 (13) | |
| Zn2 | 0.440196 (15) | 0.56125 (4) | 0.29071 (2) | 0.01988 (13) | |
| Cl3 | 0.84640 (4) | 0.42735 (11) | 0.41666 (5) | 0.0349 (3) | |
| O1 | 0.49269 (8) | 0.6907 (2) | 0.31948 (12) | 0.0221 (6) | |
| O2 | 0.48877 (9) | 0.4672 (2) | 0.37215 (13) | 0.0246 (6) | |
| O3 | 0.56028 (9) | 0.4799 (2) | 0.29429 (12) | 0.0211 (6) | |
| O4 | 0.66347 (13) | -0.0167 (4) | 0.36447 (19) | 0.0604 (10) | |
| O5 | 0.80381 (13) | 0.4340 (5) | 0.4259 (2) | 0.0914 (17) | |
| O6 | 0.84744 (12) | 0.5253 (4) | 0.3665 (2) | 0.0599 (10) | |
| O7 | 0.88417 (12) | 0.4450 (4) | 0.48234 (17) | 0.0586 (10) | |
| O8 | 0.85150 (17) | 0.3080 (4) | 0.38887 (19) | 0.0873 (15) | |
| N1 | 0.58342 (11) | 0.4818 (3) | 0.46159 (16) | 0.0232 (7) | |
| N2 | 0.58800 (11) | 0.7109 (3) | 0.40917 (16) | 0.0240 (7) | |
| N3 | 0.39402 (11) | 0.7064 (3) | 0.27061 (16) | 0.0239 (7) | |
| N4 | 0.39069 (11) | 0.4756 (3) | 0.32117 (16) | 0.0236 (7) | |
| N5 | 0.68833 (17) | 0.1882 (4) | 0.3794 (3) | 0.0628 (13) | |
| C1 | 0.62745 (13) | 0.5440 (4) | 0.48975 (19) | 0.0245 (9) | |
| C2 | 0.63005 (13) | 0.6653 (4) | 0.46105 (19) | 0.0256 (9) | |
| C3 | 0.67245 (15) | 0.7315 (5) | 0.4850 (2) | 0.0376 (11) | |

| | | | | |
|------|--------------|------------|--------------|-------------|
| H3 | 0.6747 | 0.8128 | 0.4658 | 0.045* |
| C4 | 0.71091 (15) | 0.6788 (5) | 0.5362 (2) | 0.0424 (12) |
| H4 | 0.7395 | 0.7245 | 0.5524 | 0.051* |
| C5 | 0.70858 (15) | 0.5603 (5) | 0.5645 (2) | 0.0374 (11) |
| H5 | 0.7355 | 0.5256 | 0.5999 | 0.045* |
| C6 | 0.66721 (14) | 0.4916 (4) | 0.5414 (2) | 0.0319 (10) |
| H6 | 0.6658 | 0.4096 | 0.5605 | 0.038* |
| C7 | 0.57915 (14) | 0.8310 (4) | 0.3979 (2) | 0.0266 (9) |
| H7 | 0.6043 | 0.8888 | 0.4185 | 0.032* |
| C8 | 0.53386 (14) | 0.8859 (4) | 0.35607 (19) | 0.0230 (8) |
| C9 | 0.49187 (13) | 0.8162 (4) | 0.32477 (18) | 0.0214 (8) |
| C10 | 0.44868 (14) | 0.8847 (4) | 0.30100 (18) | 0.0243 (9) |
| C11 | 0.44939 (15) | 1.0188 (4) | 0.3043 (2) | 0.0306 (10) |
| H11 | 0.4207 | 1.0642 | 0.2884 | 0.037* |
| C12 | 0.49064 (15) | 1.0866 (4) | 0.3302 (2) | 0.0322 (10) |
| H12 | 0.4904 | 1.1774 | 0.3295 | 0.039* |
| C13 | 0.53222 (16) | 1.0211 (4) | 0.3570 (2) | 0.0304 (10) |
| H13 | 0.5605 | 1.0679 | 0.3765 | 0.037* |
| C14 | 0.40247 (14) | 0.8270 (4) | 0.27734 (19) | 0.0270 (9) |
| H14 | 0.3765 | 0.8832 | 0.2660 | 0.032* |
| C15 | 0.34817 (13) | 0.6556 (4) | 0.2554 (2) | 0.0270 (9) |
| C16 | 0.34680 (13) | 0.5339 (4) | 0.2840 (2) | 0.0260 (9) |
| C17 | 0.30367 (14) | 0.4767 (5) | 0.2720 (2) | 0.0348 (10) |
| H17 | 0.3022 | 0.3953 | 0.2916 | 0.042* |
| C18 | 0.26309 (16) | 0.5393 (5) | 0.2314 (2) | 0.0390 (11) |
| H18 | 0.2337 | 0.5008 | 0.2235 | 0.047* |
| C19 | 0.26487 (15) | 0.6566 (5) | 0.2025 (2) | 0.0409 (12) |
| H19 | 0.2367 | 0.6974 | 0.1739 | 0.049* |
| C20 | 0.30707 (15) | 0.7164 (4) | 0.2143 (2) | 0.0356 (10) |
| H20 | 0.3079 | 0.7981 | 0.1945 | 0.043* |
| C21 | 0.39648 (14) | 0.3803 (4) | 0.36304 (19) | 0.0256 (9) |
| H21 | 0.3692 | 0.3429 | 0.3658 | 0.031* |
| C22 | 0.44099 (13) | 0.3244 (4) | 0.40659 (19) | 0.0239 (9) |
| C23 | 0.48531 (13) | 0.3777 (4) | 0.41457 (19) | 0.0228 (8) |
| C24 | 0.52560 (14) | 0.3311 (4) | 0.46991 (19) | 0.0256 (9) |
| C25 | 0.52120 (15) | 0.2229 (4) | 0.5082 (2) | 0.0285 (9) |
| H25 | 0.5482 | 0.1902 | 0.5444 | 0.034* |
| C26 | 0.47916 (15) | 0.1639 (4) | 0.4945 (2) | 0.0310 (10) |
| H26 | 0.4775 | 0.0872 | 0.5182 | 0.037* |
| C27 | 0.43931 (15) | 0.2168 (4) | 0.4462 (2) | 0.0281 (9) |
| H27 | 0.4100 | 0.1794 | 0.4395 | 0.034* |
| C28 | 0.57110 (14) | 0.3906 (4) | 0.49350 (19) | 0.0262 (9) |
| H28 | 0.5939 | 0.3601 | 0.5361 | 0.031* |
| C29 | 0.5691 (2) | 0.3485 (4) | 0.3017 (2) | 0.0519 (14) |
| H29A | 0.5406 | 0.3016 | 0.2747 | 0.078* |
| H29B | 0.5793 | 0.3250 | 0.3513 | 0.078* |
| H29C | 0.5936 | 0.3269 | 0.2842 | 0.078* |
| C30 | 0.67208 (19) | 0.0813 (6) | 0.3976 (3) | 0.0556 (15) |

| | | | | | |
|------|------------|-------------|-------------|-----------|----------|
| H30 | 0.6669 | 0.0828 | 0.4403 | 0.067* | |
| C31 | 0.7049 (6) | 0.2897 (15) | 0.4349 (9) | 0.084 (4) | 0.60 (2) |
| H31A | 0.7168 | 0.3629 | 0.4169 | 0.126* | 0.60 (2) |
| H31B | 0.7299 | 0.2550 | 0.4763 | 0.126* | 0.60 (2) |
| H31C | 0.6789 | 0.3174 | 0.4478 | 0.126* | 0.60 (2) |
| C32 | 0.6894 (5) | 0.1867 (13) | 0.3083 (6) | 0.056 (3) | 0.60 (2) |
| H32A | 0.7017 | 0.2683 | 0.2992 | 0.084* | 0.60 (2) |
| H32B | 0.6577 | 0.1740 | 0.2737 | 0.084* | 0.60 (2) |
| H32C | 0.7094 | 0.1167 | 0.3047 | 0.084* | 0.60 (2) |
| C31' | 0.6860 (5) | 0.3255 (11) | 0.4007 (12) | 0.055 (5) | 0.40 (2) |
| H31D | 0.7025 | 0.3803 | 0.3789 | 0.082* | 0.40 (2) |
| H31E | 0.7007 | 0.3329 | 0.4518 | 0.082* | 0.40 (2) |
| H31F | 0.6533 | 0.3523 | 0.3852 | 0.082* | 0.40 (2) |
| C32' | 0.7093 (8) | 0.1998 (19) | 0.3261 (9) | 0.053 (5) | 0.40 (2) |
| H32D | 0.7171 | 0.2896 | 0.3220 | 0.080* | 0.40 (2) |
| H32E | 0.6871 | 0.1696 | 0.2808 | 0.080* | 0.40 (2) |
| H32F | 0.7377 | 0.1479 | 0.3400 | 0.080* | 0.40 (2) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|--------------|---------------|
| Zn1 | 0.0232 (2) | 0.0180 (2) | 0.0188 (2) | -0.00098 (19) | 0.00989 (18) | -0.00027 (17) |
| Zn2 | 0.0236 (2) | 0.0188 (2) | 0.0191 (2) | 0.00050 (19) | 0.01015 (18) | -0.00067 (17) |
| Cl3 | 0.0274 (5) | 0.0398 (6) | 0.0327 (5) | -0.0016 (5) | 0.0057 (4) | -0.0034 (5) |
| O1 | 0.0236 (14) | 0.0164 (14) | 0.0265 (14) | -0.0006 (11) | 0.0095 (11) | -0.0011 (11) |
| O2 | 0.0236 (14) | 0.0262 (15) | 0.0252 (14) | -0.0023 (12) | 0.0104 (12) | 0.0083 (11) |
| O3 | 0.0287 (15) | 0.0167 (13) | 0.0220 (13) | 0.0045 (11) | 0.0143 (12) | 0.0041 (10) |
| O4 | 0.070 (3) | 0.049 (2) | 0.060 (2) | -0.018 (2) | 0.022 (2) | -0.0024 (19) |
| O5 | 0.034 (2) | 0.174 (5) | 0.064 (3) | 0.005 (3) | 0.0168 (19) | 0.042 (3) |
| O6 | 0.044 (2) | 0.063 (3) | 0.065 (2) | -0.0124 (18) | 0.0112 (18) | 0.0204 (19) |
| O7 | 0.041 (2) | 0.085 (3) | 0.0386 (19) | 0.0051 (19) | 0.0016 (16) | -0.0150 (18) |
| O8 | 0.148 (4) | 0.048 (2) | 0.045 (2) | 0.012 (3) | 0.012 (2) | -0.0124 (19) |
| N1 | 0.0244 (18) | 0.0235 (18) | 0.0214 (16) | 0.0011 (14) | 0.0083 (14) | -0.0013 (13) |
| N2 | 0.0283 (18) | 0.0236 (19) | 0.0238 (16) | -0.0044 (15) | 0.0141 (14) | -0.0020 (13) |
| N3 | 0.0260 (18) | 0.0233 (19) | 0.0216 (16) | 0.0037 (15) | 0.0079 (14) | 0.0001 (13) |
| N4 | 0.0251 (18) | 0.0249 (18) | 0.0237 (17) | -0.0037 (14) | 0.0123 (14) | -0.0042 (14) |
| N5 | 0.080 (3) | 0.049 (3) | 0.087 (3) | -0.022 (3) | 0.063 (3) | -0.023 (2) |
| C1 | 0.024 (2) | 0.033 (2) | 0.0184 (18) | -0.0023 (17) | 0.0112 (16) | -0.0079 (16) |
| C2 | 0.026 (2) | 0.032 (2) | 0.0217 (19) | -0.0006 (18) | 0.0121 (17) | -0.0037 (17) |
| C3 | 0.036 (3) | 0.043 (3) | 0.033 (2) | -0.012 (2) | 0.012 (2) | -0.003 (2) |
| C4 | 0.028 (2) | 0.064 (3) | 0.034 (2) | -0.015 (2) | 0.011 (2) | -0.006 (2) |
| C5 | 0.027 (2) | 0.057 (3) | 0.028 (2) | 0.001 (2) | 0.0106 (19) | -0.001 (2) |
| C6 | 0.033 (2) | 0.039 (3) | 0.023 (2) | 0.007 (2) | 0.0098 (18) | -0.0001 (19) |
| C7 | 0.031 (2) | 0.026 (2) | 0.028 (2) | -0.0110 (18) | 0.0171 (18) | -0.0076 (17) |
| C8 | 0.036 (2) | 0.019 (2) | 0.0206 (19) | -0.0018 (18) | 0.0183 (17) | 0.0006 (15) |
| C9 | 0.033 (2) | 0.0176 (19) | 0.0182 (18) | 0.0005 (17) | 0.0147 (16) | 0.0007 (15) |
| C10 | 0.039 (2) | 0.017 (2) | 0.0196 (19) | 0.0014 (18) | 0.0147 (18) | 0.0024 (15) |
| C11 | 0.044 (3) | 0.023 (2) | 0.029 (2) | 0.010 (2) | 0.018 (2) | 0.0056 (17) |

| | | | | | | |
|------|-----------|-----------|-------------|--------------|-------------|--------------|
| C12 | 0.052 (3) | 0.019 (2) | 0.034 (2) | 0.001 (2) | 0.026 (2) | 0.0038 (18) |
| C13 | 0.047 (3) | 0.024 (2) | 0.029 (2) | -0.006 (2) | 0.023 (2) | -0.0013 (17) |
| C14 | 0.034 (2) | 0.026 (2) | 0.023 (2) | 0.0091 (19) | 0.0133 (17) | 0.0036 (17) |
| C15 | 0.024 (2) | 0.031 (2) | 0.025 (2) | 0.0039 (18) | 0.0075 (17) | -0.0062 (17) |
| C16 | 0.025 (2) | 0.033 (2) | 0.022 (2) | 0.0021 (18) | 0.0106 (17) | -0.0069 (16) |
| C17 | 0.031 (2) | 0.043 (3) | 0.031 (2) | -0.003 (2) | 0.0134 (19) | -0.0067 (19) |
| C18 | 0.028 (2) | 0.054 (3) | 0.034 (2) | -0.002 (2) | 0.010 (2) | -0.009 (2) |
| C19 | 0.028 (2) | 0.054 (3) | 0.035 (2) | 0.012 (2) | 0.006 (2) | -0.005 (2) |
| C20 | 0.037 (3) | 0.038 (3) | 0.028 (2) | 0.009 (2) | 0.0090 (19) | -0.0039 (19) |
| C21 | 0.029 (2) | 0.027 (2) | 0.026 (2) | -0.0064 (18) | 0.0163 (18) | -0.0072 (17) |
| C22 | 0.031 (2) | 0.020 (2) | 0.026 (2) | -0.0016 (17) | 0.0168 (17) | -0.0017 (16) |
| C23 | 0.034 (2) | 0.017 (2) | 0.0239 (19) | -0.0004 (17) | 0.0187 (17) | -0.0009 (16) |
| C24 | 0.034 (2) | 0.024 (2) | 0.0229 (19) | -0.0008 (18) | 0.0150 (18) | -0.0003 (16) |
| C25 | 0.036 (2) | 0.028 (2) | 0.027 (2) | 0.0057 (19) | 0.0163 (18) | 0.0030 (17) |
| C26 | 0.045 (3) | 0.023 (2) | 0.035 (2) | 0.000 (2) | 0.028 (2) | 0.0049 (18) |
| C27 | 0.037 (2) | 0.023 (2) | 0.034 (2) | -0.0046 (19) | 0.025 (2) | -0.0035 (17) |
| C28 | 0.031 (2) | 0.029 (2) | 0.0173 (18) | 0.0051 (18) | 0.0074 (17) | 0.0031 (16) |
| C29 | 0.104 (4) | 0.024 (2) | 0.048 (3) | 0.011 (3) | 0.051 (3) | 0.005 (2) |
| C30 | 0.060 (4) | 0.064 (4) | 0.054 (3) | -0.027 (3) | 0.034 (3) | -0.012 (3) |
| C31 | 0.089 (6) | 0.071 (6) | 0.087 (6) | -0.005 (4) | 0.027 (4) | -0.019 (4) |
| C32 | 0.036 (7) | 0.077 (8) | 0.069 (7) | -0.008 (6) | 0.035 (6) | 0.023 (6) |
| C31' | 0.042 (9) | 0.045 (9) | 0.070 (12) | -0.022 (7) | 0.013 (8) | -0.018 (8) |
| C32' | 0.057 (7) | 0.047 (6) | 0.059 (6) | 0.004 (5) | 0.026 (5) | 0.006 (4) |

Geometric parameters (Å, °)

| | | | |
|---------------------|------------|---------|-----------|
| Zn1—O3 | 1.940 (2) | C10—C11 | 1.404 (6) |
| Zn1—N2 | 2.019 (3) | C10—C14 | 1.457 (6) |
| Zn1—O1 | 2.031 (2) | C11—C12 | 1.380 (6) |
| Zn1—O2 | 2.034 (3) | C11—H11 | 0.9500 |
| Zn1—N1 | 2.054 (3) | C12—C13 | 1.377 (6) |
| Zn1—Zn2 | 3.0134 (6) | C12—H12 | 0.9500 |
| Zn2—O3 ⁱ | 1.940 (2) | C13—H13 | 0.9500 |
| Zn2—N3 | 2.018 (3) | C14—H14 | 0.9500 |
| Zn2—O1 | 2.025 (2) | C15—C20 | 1.390 (5) |
| Zn2—O2 | 2.036 (3) | C15—C16 | 1.408 (6) |
| Zn2—N4 | 2.064 (3) | C16—C17 | 1.398 (6) |
| Cl3—O5 | 1.403 (4) | C17—C18 | 1.384 (6) |
| Cl3—O8 | 1.405 (4) | C17—H17 | 0.9500 |
| Cl3—O7 | 1.429 (3) | C18—C19 | 1.373 (7) |
| Cl3—O6 | 1.462 (4) | C18—H18 | 0.9500 |
| O1—C9 | 1.316 (4) | C19—C20 | 1.384 (6) |
| O2—C23 | 1.310 (4) | C19—H19 | 0.9500 |
| O3—C29 | 1.396 (5) | C20—H20 | 0.9500 |
| O3—Zn2 ⁱ | 1.940 (2) | C21—C22 | 1.455 (5) |
| O4—C30 | 1.204 (6) | C21—H21 | 0.9500 |
| N1—C28 | 1.293 (5) | C22—C27 | 1.401 (5) |
| N1—C1 | 1.422 (5) | C22—C23 | 1.432 (5) |

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|-------------------------|-------------|-------------|-----------|
| N2—C7 | 1.287 (5) | C23—C24 | 1.423 (5) |
| N2—C2 | 1.421 (5) | C24—C25 | 1.413 (5) |
| N3—C14 | 1.285 (5) | C24—C28 | 1.447 (5) |
| N3—C15 | 1.435 (5) | C25—C26 | 1.370 (6) |
| N4—C21 | 1.285 (5) | C25—H25 | 0.9500 |
| N4—C16 | 1.422 (5) | C26—C27 | 1.377 (6) |
| N5—C30 | 1.335 (6) | C26—H26 | 0.9500 |
| N5—C32' | 1.475 (9) | C27—H27 | 0.9500 |
| N5—C32 | 1.477 (11) | C28—H28 | 0.9500 |
| N5—C31 | 1.501 (12) | C29—H29A | 0.9800 |
| N5—C31' | 1.510 (9) | C29—H29B | 0.9800 |
| C1—C6 | 1.402 (5) | C29—H29C | 0.9800 |
| C1—C2 | 1.413 (6) | C30—H30 | 0.9500 |
| C2—C3 | 1.399 (6) | C31—H31A | 0.9800 |
| C3—C4 | 1.375 (6) | C31—H31B | 0.9800 |
| C3—H3 | 0.9500 | C31—H31C | 0.9800 |
| C4—C5 | 1.381 (7) | C32—H32A | 0.9800 |
| C4—H4 | 0.9500 | C32—H32B | 0.9800 |
| C5—C6 | 1.387 (6) | C32—H32C | 0.9800 |
| C5—H5 | 0.9500 | C31'—H31D | 0.9800 |
| C6—H6 | 0.9500 | C31'—H31E | 0.9800 |
| C7—C8 | 1.459 (5) | C31'—H31F | 0.9800 |
| C7—H7 | 0.9500 | C32'—H32D | 0.9800 |
| C8—C13 | 1.415 (6) | C32'—H32E | 0.9800 |
| C8—C9 | 1.417 (5) | C32'—H32F | 0.9800 |
| C9—C10 | 1.431 (5) | | |
| O3—Zn1—N2 | 110.85 (12) | C8—C9—C10 | 118.6 (3) |
| O3—Zn1—O1 | 107.89 (10) | C11—C10—C9 | 119.2 (4) |
| N2—Zn1—O1 | 89.05 (12) | C11—C10—C14 | 115.1 (4) |
| O3—Zn1—O2 | 106.49 (11) | C9—C10—C14 | 125.6 (4) |
| N2—Zn1—O2 | 142.66 (12) | C12—C11—C10 | 121.8 (4) |
| O1—Zn1—O2 | 79.43 (10) | C12—C11—H11 | 119.1 |
| O3—Zn1—N1 | 108.52 (11) | C10—C11—H11 | 119.1 |
| N2—Zn1—N1 | 81.23 (13) | C13—C12—C11 | 119.4 (4) |
| O1—Zn1—N1 | 143.43 (11) | C13—C12—H12 | 120.3 |
| O2—Zn1—N1 | 87.22 (11) | C11—C12—H12 | 120.3 |
| O3—Zn1—Zn2 | 97.31 (8) | C12—C13—C8 | 121.6 (4) |
| N2—Zn1—Zn2 | 129.80 (9) | C12—C13—H13 | 119.2 |
| O1—Zn1—Zn2 | 41.93 (7) | C8—C13—H13 | 119.2 |
| O2—Zn1—Zn2 | 42.26 (7) | N3—C14—C10 | 125.2 (4) |
| N1—Zn1—Zn2 | 128.55 (9) | N3—C14—H14 | 117.4 |
| O3 ⁱ —Zn2—N3 | 112.30 (11) | C10—C14—H14 | 117.4 |
| O3 ⁱ —Zn2—O1 | 106.91 (10) | C20—C15—C16 | 120.2 (4) |
| N3—Zn2—O1 | 89.22 (12) | C20—C15—N3 | 124.6 (4) |
| O3 ⁱ —Zn2—O2 | 106.50 (11) | C16—C15—N3 | 115.2 (3) |
| N3—Zn2—O2 | 141.19 (11) | C17—C16—C15 | 119.3 (4) |
| O1—Zn2—O2 | 79.53 (10) | C17—C16—N4 | 124.6 (4) |

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| O3 ⁱ —Zn2—N4 | 109.14 (11) | C15—C16—N4 | 116.1 (3) |
| N3—Zn2—N4 | 80.73 (13) | C18—C17—C16 | 119.6 (4) |
| O1—Zn2—N4 | 143.75 (11) | C18—C17—H17 | 120.2 |
| O2—Zn2—N4 | 86.77 (11) | C16—C17—H17 | 120.2 |
| O3 ⁱ —Zn2—Zn1 | 96.64 (8) | C19—C18—C17 | 120.6 (4) |
| N3—Zn2—Zn1 | 129.79 (9) | C19—C18—H18 | 119.7 |
| O1—Zn2—Zn1 | 42.11 (7) | C17—C18—H18 | 119.7 |
| O2—Zn2—Zn1 | 42.20 (7) | C18—C19—C20 | 121.0 (4) |
| N4—Zn2—Zn1 | 128.13 (9) | C18—C19—H19 | 119.5 |
| O5—C13—O8 | 110.8 (3) | C20—C19—H19 | 119.5 |
| O5—C13—O7 | 110.0 (2) | C19—C20—C15 | 119.2 (4) |
| O8—C13—O7 | 108.8 (2) | C19—C20—H20 | 120.4 |
| O5—C13—O6 | 109.4 (2) | C15—C20—H20 | 120.4 |
| O8—C13—O6 | 107.4 (2) | N4—C21—C22 | 125.9 (4) |
| O7—C13—O6 | 110.5 (2) | N4—C21—H21 | 117.1 |
| C9—O1—Zn2 | 130.6 (2) | C22—C21—H21 | 117.1 |
| C9—O1—Zn1 | 130.6 (2) | C27—C22—C23 | 119.2 (4) |
| Zn2—O1—Zn1 | 95.96 (11) | C27—C22—C21 | 116.6 (3) |
| C23—O2—Zn1 | 132.1 (2) | C23—C22—C21 | 124.0 (3) |
| C23—O2—Zn2 | 132.3 (2) | O2—C23—C24 | 120.8 (3) |
| Zn1—O2—Zn2 | 95.54 (10) | O2—C23—C22 | 121.0 (3) |
| C29—O3—Zn2 ⁱ | 117.7 (2) | C24—C23—C22 | 118.2 (3) |
| C29—O3—Zn1 | 116.9 (2) | C25—C24—C23 | 118.8 (4) |
| Zn2 ⁱ —O3—Zn1 | 125.25 (13) | C25—C24—C28 | 116.2 (4) |
| C28—N1—C1 | 123.4 (3) | C23—C24—C28 | 124.9 (3) |
| C28—N1—Zn1 | 127.4 (3) | C26—C25—C24 | 121.9 (4) |
| C1—N1—Zn1 | 109.2 (2) | C26—C25—H25 | 119.1 |
| C7—N2—C2 | 122.4 (3) | C24—C25—H25 | 119.1 |
| C7—N2—Zn1 | 127.3 (3) | C25—C26—C27 | 119.4 (4) |
| C2—N2—Zn1 | 110.1 (2) | C25—C26—H26 | 120.3 |
| C14—N3—C15 | 122.1 (3) | C27—C26—H26 | 120.3 |
| C14—N3—Zn2 | 128.0 (3) | C26—C27—C22 | 121.6 (4) |
| C15—N3—Zn2 | 109.4 (2) | C26—C27—H27 | 119.2 |
| C21—N4—C16 | 123.9 (3) | C22—C27—H27 | 119.2 |
| C21—N4—Zn2 | 127.4 (3) | N1—C28—C24 | 125.6 (3) |
| C16—N4—Zn2 | 108.6 (2) | N1—C28—H28 | 117.2 |
| C30—N5—C32' | 126.5 (9) | C24—C28—H28 | 117.2 |
| C30—N5—C32 | 114.8 (7) | O3—C29—H29A | 109.5 |
| C30—N5—C31 | 115.8 (7) | O3—C29—H29B | 109.5 |
| C32'—N5—C31 | 112.8 (11) | H29A—C29—H29B | 109.5 |
| C32—N5—C31 | 129.3 (10) | O3—C29—H29C | 109.5 |
| C30—N5—C31' | 130.5 (7) | H29A—C29—H29C | 109.5 |
| C32'—N5—C31' | 102.7 (11) | H29B—C29—H29C | 109.5 |
| C32—N5—C31' | 108.6 (11) | O4—C30—N5 | 125.5 (5) |
| C6—C1—C2 | 119.8 (4) | O4—C30—H30 | 117.3 |
| C6—C1—N1 | 124.4 (4) | N5—C30—H30 | 117.3 |
| C2—C1—N1 | 115.9 (3) | N5—C31—H31A | 109.5 |
| C3—C2—C1 | 119.3 (4) | N5—C31—H31B | 109.5 |

| | | | |
|-----------|-----------|----------------|-------|
| C3—C2—N2 | 124.9 (4) | H31A—C31—H31B | 109.5 |
| C1—C2—N2 | 115.8 (3) | N5—C31—H31C | 109.5 |
| C4—C3—C2 | 120.0 (4) | H31A—C31—H31C | 109.5 |
| C4—C3—H3 | 120.0 | H31B—C31—H31C | 109.5 |
| C2—C3—H3 | 120.0 | N5—C32—H32A | 109.5 |
| C3—C4—C5 | 121.0 (4) | N5—C32—H32B | 109.5 |
| C3—C4—H4 | 119.5 | H32A—C32—H32B | 109.5 |
| C5—C4—H4 | 119.5 | N5—C32—H32C | 109.5 |
| C4—C5—C6 | 120.5 (4) | H32A—C32—H32C | 109.5 |
| C4—C5—H5 | 119.8 | H32B—C32—H32C | 109.5 |
| C6—C5—H5 | 119.8 | N5—C31'—H31D | 109.5 |
| C5—C6—C1 | 119.5 (4) | N5—C31'—H31E | 109.5 |
| C5—C6—H6 | 120.3 | H31D—C31'—H31E | 109.5 |
| C1—C6—H6 | 120.3 | N5—C31'—H31F | 109.5 |
| N2—C7—C8 | 125.6 (4) | H31D—C31'—H31F | 109.5 |
| N2—C7—H7 | 117.2 | H31E—C31'—H31F | 109.5 |
| C8—C7—H7 | 117.2 | N5—C32'—H32D | 109.5 |
| C13—C8—C9 | 119.2 (4) | N5—C32'—H32E | 109.5 |
| C13—C8—C7 | 114.6 (4) | H32D—C32'—H32E | 109.5 |
| C9—C8—C7 | 125.5 (3) | N5—C32'—H32F | 109.5 |
| O1—C9—C8 | 120.5 (3) | H32D—C32'—H32F | 109.5 |
| O1—C9—C10 | 121.0 (3) | H32E—C32'—H32F | 109.5 |

Symmetry code: (i) $-x+1, y, -z+1/2$.