Crystal structure of (7-[[bis(pyridin-2-ylmethyl)-amino-κ³N,N',N''methyl]-5-chloroquinolin-8-ol]-dibromidozinc(II))

Koji Kubono, a* Yukiyasu Kashiwagi, b Keita Tani a and Kunihiko Yokoi a

a Osaka Kyoiku University, 4-698-1 Asahigaoka, Kashiwara, Osaka 582-8582, Japan, and bOsaka Research Institute of Industrial Science and Technology, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan. *Correspondence e-mail: kubono@cc.osaka-kyoiku.ac.jp

In the title compound, [ZnBr₂(C₂₂H₁₉ClN₄O)], the Zn II atom adopts a distorted square-pyramidal coordination geometry, formed by two bromido ligands and three N atoms of the bis(pyridin-2-ylmethyl)amine moiety in the pentadentate ligand containing quinolinol. The Zn II atom is located well above the mean basal plane of the square-based pyramid. The apical position is occupied by a Br atom. The O and N atoms of the quinolinol moiety in the ligand are not coordinated to the Zn II atom. An intramolecular O—H⋯C1/C1/C1 N hydrogen bond, generating an S(5) ring motif, stabilizes the molecular structure. In the crystal, the molecules are linked by intermolecular C—H⋯C1/C1/C1 Br hydrogen bonds, generating ribbon structures containing alternating \( R_2^2(22) \) and \( R_2^2(14) \) rings. These ribbons are linked through an intermolecular C—H⋯Br hydrogen bond, forming a two-dimensional network sheet.

1. Chemical context

8-Quinolinol (Hq) is a notable bidentate ligand and an excellent analytical reagent for the determination of the concentration and separation of metal ions (Medlin, 1960; Eguchi et al., 2019). Hq derivatives and their metal complexes have wide applications in diverse areas such as pharmaceuticals (Lai et al., 2009) and organic light-emitting diodes (Li et al., 2020). Bis(pyridin-2-ylmethyl)amine [di(2-picoly)amine, dpa] is a well-known tridentate ligand and highly selective for Zn II. Its derivatives are utilized as chemosensors for detecting Zn II at low concentration in biological samples (Lin et al., 2013). In addition, some Zn II complexes with dpa derivatives comprise a binding site for polyphosphates such as diphosphate and adenosine triphosphate, and can act as respective anion sensors (Aoki et al., 2020; Bazany-Rodrı´guez et al., 2020). We, hence, developed the pentadentate ligand, 7-[[bis-(pyridin-2-ylmethyl)amino]methyl]-5-chloroquinolin-8-ol (HClqdpa) containing Hq and dpa moieties (Kubono et al., 2015). Subsequently, reactions between HClqdpa and Zn II salts were carried out in order to develop fluorescent anion sensors. In the course of these studies, a crystalline complex was obtained from the reaction with zinc(II) bromide. Here, the crystal structure of the respective title compound is reported.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The Zn II atom adopts a distorted square-pyramidal
geometry and coordinates two bromido ligands (Br1 and Br2) and three N atoms (N7, N8 and N9) of the dpa moiety in HClqdpd forming the ZnBr2(dpda) unit. The Hq moiety of the pentadentate ligand (HClqdpd) is not coordinated to the ZnII center. The five-coordinate geometry parameter, \( \tau = (\beta - \alpha)/60 \), derived from the two largest angles (\( \alpha < \beta \)) in a structure has ideal values of 0 for square-pyramidal and of 1 for trigonal–bipyramidal geometry (Addison et al., 1984). In the title compound it is equal to 0.138. The ZnII atom is located 0.5574 (3) Å above the mean basal plane (Br2/N8/N7/N9) of the square-based pyramid. The dpa moiety is meridionally bound to the ZnII atom. The apical position is occupied by the Br1 atom with the apical bond being slightly elongated to 2.4419 (4) Å compared to the equatorial Br2–Zn3 bond length of 2.4085 (4) Å. The Zn–N bond lengths in the title compound are 2.1455 (18) and 2.2670 (18) Å for the pyridyl N atoms are, hence, shorter and the bond length for the tertiary atom N7. In comparison, the Zn–N bond lengths in the crystal structure of a related complex with a mesityl methylene-appended dpa derivative are 2.093 (3), 2.066 (3), and 2.521 (3) Å (MUDWEQ; Acharya et al., 2020). The bond lengths for the pyridyl N atoms are, hence, shorter and the bond length for the tertiary N atom is longer than those in the title compound. The dihedral angles between the two pyridine rings in the title compound is 15.84 (13)°. In a related complex (MUDWEQ; Acharya et al., 2020), this dihedral angle between two pyridine rings is widened to 23.53 (18)°, concomitant with an increased \( \tau \) parameter of 0.211. The phenolic oxygen O5 of the Hq moiety is bound to hydrogen atom H5, which was found and refined freely. The proton, therefore, does not dissociate and no phenoxy function is formed. There is an intramolecular hydrogen bond, O5—H5⋯N6, generating an \( S(5) \) ring motif (Fig. 1 and Table 1). The quinoline ring system is slightly bent with an r.m.s. deviation of 0.018 (3) Å. In the quinoline ring system, the largest deviation from the mean plane is 0.020 (4) Å for carbon atom C15. The quinoline plane subtends dihedral angles of 24.14 (11) and 36.65 (11)° with the two pyridine rings.

3. Supramolecular features

In the crystal, two molecules are associated through a pair of intermolecular C⋯H⋯Br hydrogen bonds \([C16–H16⋯Br2]^-\) and \([C22–H22⋯Br2]^-\) to the ZnII atom. The apical position is occupied by the Br2 atom with the apical bond being slightly elongated to 2.4419 (4) Å compared to the equatorial Br2—Zn3 bond length of 2.4085 (4) Å. The Zn—N bond lengths in the title compound are 2.1455 (18) and 2.1497 (18) Å for the pyridyl N atoms. The bond lengths for the tertiary atom N7. In comparison, the Zn—N bond lengths in the crystal structure of a related complex with a mesityl methylene-appended dpa derivative are 2.093 (3), 2.066 (3), and 2.521 (3) Å (MUDWEQ; Acharya et al., 2020). The bond lengths for the pyridyl N atoms are, hence, shorter and the bond length for the tertiary N atom is longer than those in the title compound. The dihedral angles between the two pyridine rings in the title compound is 15.84 (13)°. In a related complex (MUDWEQ; Acharya et al., 2020), this dihedral angle between two pyridine rings is widened to 23.53 (18)°, concomitant with an increased \( \tau \) parameter of 0.211. The phenolic oxygen O5 of the Hq moiety is bound to hydrogen atom H5, which was found and refined freely. The proton, therefore, does not dissociate and no phenoxy function is formed. There is an intramolecular hydrogen bond, O5—H5⋯N6, generating an \( S(5) \) ring motif (Fig. 1 and Table 1). The quinoline ring system is slightly bent with an r.m.s. deviation of 0.018 (3) Å. In the quinoline ring system, the largest deviation from the mean plane is 0.020 (4) Å for carbon atom C15. The quinoline plane subtends dihedral angles of 24.14 (11) and 36.65 (11)° with the two pyridine rings.

### Table 1

| Hydrogen-bond geometry (Å, °) | D—H⋯A          | D—H | H⋯A  | D⋯A  | D—H⋯A |
|------------------------------|-----------------|-----|------|------|-------|
| O5—H5⋯N6                    | 0.79 (4)        | 2.14 (4) | 2.653 (3) | 124 (3) |
| C16—H16⋯Br2i                | 0.95            | 2.87 | 3.808 (3) | 170   |
| C22—H22⋯Br2ii               | 0.95            | 2.88 | 3.581 (3) | 131   |
| C29—H29⋯Br1iii              | 0.95            | 2.90 | 3.798 (3) | 158   |

Symmetry codes: (i) \(-x + 1, -y, -z\); (ii) \(x + 1, y - 1, z\); (iii) \(-x + 1, -y + 1, -z + 1\).

Br2i; symmetry code: (i) \(1 - x, -y, -z\) (Table 1), forming a centrosymmetric dimer with an \( R_2(2) \) ring motif. Another pair of intermolecular C⋯H⋯Br hydrogen bonds is observed \([C29—H29⋯Br1ii]\); symmetry code: (iii) \(1 - x, 1 - y, 1 - z\) (Table 1), which forms another centrosymmetric dimer with an \( R_2(14) \) ring motif. The different hydrogen-bonded pairs of molecules are also linked to each other by these intermolecular C⋯H⋯Br hydrogen bonds, generating a ribbon structure along \([0\overline{1}1]\) based on alternating \( R_2(22) \) and \( R_2(14) \) hydrogen-bonding motifs (Fig. 2). In the crystal, molecules are further linked by an intermolecular C⋯H⋯Br hydrogen bond \([C22—H22⋯Br2ii]\); symmetry code: (ii) \(x + 1, y - 1, z\) (Table 1), forming a C(6) chain motif running along \([2\overline{2}0]\).
Eight structures are ion-pairs between H$_2$q+ derivatives and

et al. Acharya propan-2-amine}dibromidozinc(II) (IHIJOB; Juraj (IHIJIV; Juraj one complex with a more typical geometry mentioned above being facially coordinated. This structure is a polymorph of 2020), which adopts a trigonal–bipyramidal geometry with dpa moiety (IRISEJ; Zhang 2012; TORLUH; Plenio being meridionally coordinated (YOZZOC; Abufarag, 1995; RUVCUI; S ˇkalamera et al.) for ZnII complexes with the [bis(pyridin-2-ylmethyl)amino]methyl fragment as ligand gave 517 hits, and among those, eight hits with two bromido ligands. Of these eight analogues, three structures are complexes with dpa among those, eight hits with two bromido ligands. Of these eight analogues, three structures are complexes with dpa bearing a tertiary N donor atom directly bound to an aromatic moiety (IRISEJ; Zhang et al., 2016; ZEGZOC; Gao et al., 2012; TORLUH; Plenio et al., 1996). In the remaining five dibromido ZnII complexes with dpa derivatives (comprising four compounds), the tertiary N atoms are bound to aliphatic carbon atoms as in the title complex. Four of these five closely related structures exhibit square-pyramidal geometries with dpa being meridionally coordinated (YOZZOC; Abufarag et al., 1995; RUVCUI; Škalamera et al., 2016; MUDWEQ; Acharya et al., 2020; IHJJIV; Juraj et al., 2020). The remaining exceptional structure is fac-[N,N’-bis[(pyridine-2-yl)methyl]-propan-2-amine]dibromidozinc(II) (HIJOB; Juraj et al., 2020), which adopts a trigonal–bipyramidal geometry with dpa being facially coordinated. This structure is a polymorph of one complex with a more typical geometry mentioned above (IHJJIV; Juraj et al., 2020). A search for molecular structures containing ZnII and the Hq moiety in which the H atom of the phenolic hydroxy group is not dissociated gave 29 hits (comprising 25 compounds). Of these, six structures (three compounds) are ion-pairs between tetrachloridozincate(II) and an 8-hydroxyquinolinol-1-ium (H$_2$q+) derivative, for example, (H$_2$q)[ZnCl$_4$] (FARFIP; Lamshöft et al., 2011). Eight structures are ion-pairs between H$_2$q+ derivatives and anionic complexes consisting of ZnX$_2$ (X = Cl, Br, or I) and quinolino-8-lato derivatives, e.g. 8-hydroxy-2-methylquinolino- linium diiodo(2-methylquinolin-8-lato)zinc(II) (AYOCOH; Najafi et al., 2011). Two structures are ion-pairs between H$_2$q+ derivatives and anionic ZnII complexes with other chelate ligands, e.g. bis(8-hydroxyquinolin-1-ium) tris(4-nitrophenol) bis(pyridine-2,6-carboxylato)zinc(II) trihydrate (MIYKEN; Singh et al., 2019). The remaining 13 structures (12 compounds) are ZnII chelate complexes containing the Hq ligand with an undissociated phenolic functional group, e.g., bis(8-hydroxyquinolin-2-carboxylato)zinc(II) trihydrate (QOCRAC; McDonald et al., 2008). A crystal structure of a ZnII complex containing the Hq moiety which is neither the counter-cation of an ion-pair nor bound to ZnII has not been reported yet. A search for ZnII complexes in which the entire ligand scaffold and substitution is also more analogous to the title compound, i.e. with [bis(pyridin-2-ylmethyl)amino]-methyl at the 2-position of Hq or respective derivatives, gave three hits (CIGJAF; Royzen et al., 2013; RIZROI; Xue et al., 2008; TEHDOA; Royzen et al., 2006). In the three structures, the phenolic hydroxy group is deprotonated and coordinated by ZnII.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42; May 2021; Groom et al., 2016) using ConQuest (Bruno et al., 2002) for ZnII complexes with the [bis(pyridin-2-ylmethyl)amino]methyl fragment as ligand gave 517 hits, and among those, eight hits with two bromido ligands. Of these eight analogues, three structures are complexes with dpa bearing a tertiary N donor atom directly bound to an aromatic moiety (IRISEJ; Zhang et al., 2016; ZEGZOC; Gao et al., 2012; TORLUH; Plenio et al., 1996). In the remaining five dibromido ZnII complexes with dpa derivatives (comprising four compounds), the tertiary N atoms are bound to aliphatic carbon atoms as in the title complex. Four of these five closely related structures exhibit square-pyramidal geometries with dpa being meridionally coordinated (YOZZOC; Abufarag et al., 1995; RUVCUI; Škalamera et al., 2016; MUDWEQ; Acharya et al., 2020; IHJJIV; Juraj et al., 2020). The remaining exceptional structure is fac-[N,N’-bis[(pyridine-2-yl)methyl]-propan-2-amine]dibromidozinc(II) (HIJOB; Juraj et al., 2020), which adopts a trigonal–bipyramidal geometry with dpa being facially coordinated. This structure is a polymorph of one complex with a more typical geometry mentioned above (IHJJIV; Juraj et al., 2020). A search for molecular structures containing ZnII and the Hq moiety in which the H atom of the phenolic hydroxy group is not dissociated gave 29 hits (comprising 25 compounds). Of these, six structures (three compounds) are ion-pairs between tetrachloridozincate(II) and an 8-hydroxyquinolinol-1-ium (H$_2$q+) derivative, for example, (H$_2$q)[ZnCl$_4$] (FARFIP; Lamshöft et al., 2011). Eight structures are ion-pairs between H$_2$q+ derivatives and anionic complexes consisting of ZnX$_2$ (X = Cl, Br, or I) and quinolino-8-lato derivatives, e.g. 8-hydroxy-2-methylquinolino-linium diiodo(2-methylquinolin-8-lato)zinc(II) (AYOCOH; Najafi et al., 2011). Two structures are ion-pairs between H$_2$q+ derivatives and anionic ZnII complexes with other chelate ligands, e.g. bis(8-hydroxyquinolin-1-ium) tris(4-nitrophenol) bis(pyridine-2,6-carboxylato)zinc(II) dihydrate (MIYKEN; Singh et al., 2019). The remaining 13 structures (12 compounds) are ZnII chelate complexes containing the Hq ligand with an undissociated phenolic functional group, e.g., bis(8-hydroxyquinolin-2-carboxylato)zinc(II) trihydrate (QOCRAC; McDonald et al., 2008). A crystal structure of a ZnII complex containing the Hq moiety which is neither the counter-cation of an ion-pair nor bound to ZnII has not been reported yet. A search for ZnII complexes in which the entire ligand scaffold and substitution is also more analogous to the title compound, i.e. with [bis(pyridin-2-ylmethyl)amino]-methyl at the 2-position of Hq or respective derivatives, gave three hits (CIGJAF; Royzen et al., 2013; RIZROI; Xue et al., 2008; TEHDOA; Royzen et al., 2006). In the three structures, the phenolic hydroxy group is deprotonated and coordinated by ZnII.

5. Synthesis and crystallization

The HClqpa ligand (97.7 mg, 0.250 mmol) was dissolved in 15 mL of hot acetonitrile. Then a solution of zinc(II) bromide...
(56.4 mg, 0.250 mmol) in 15 mL of hot acetonitrile was added to the ligand solution. The mixture was stirred for 20 min at 333 K. After removal of the solvent at room temperature in air for one week, colorless crystals of the title compound were obtained (yield 35%; m.p. 496–497 K). Analysis calculated for C₂₂H₁₉Br₂ClN₄OZn: C 42.89, H 3.11, N 9.09%; found: C 42.94, H 3.02, N 8.95%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy H atom was located in a difference-Fourier map and freely refined. The C-bound H atoms were positioned geometrically and refined using a riding model: C—H = 0.95–0.99 Å with U_{iso}(H) = 1.2 U_{eq}(C). One outlier reflex (002) was omitted from the refinement.

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Crystal structure of (7-{[bis(pyridin-2-ylmethyl)amino-κ₃N,N′,N″]methyl}-5-chloroquinolin-8-ol)dibromidozinc(II)

Koji Kubono, Yukiyasu Kashiwagi, Keita Tani and Kunihiko Yokoi

Computing details

Data collection: RAPID-AUTO (Rigaku, 2006); cell refinement: RAPID-AUTO (Rigaku, 2006); data reduction: RAPID-AUTO (Rigaku, 2006); program(s) used to solve structure: SIR92 (Altomare, et al., 1993); program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2015); molecular graphics: PLATON (Spek, 2020); software used to prepare material for publication: CrystalStructure (Rigaku, 2016).

(7-{[Bis(pyridin-2-ylmethyl)amino-κ₃N,N′,N″]methyl}-5-chloroquinolin-8-ol)dibromidozinc(II)

Crystal data

[ZnBr₂(C₂₂H₁₉ClN₄O)]  
M_r = 616.05  
Triclinic, P₁  
a = 7.6779 (3) Å  
b = 8.7860 (4) Å  
c = 18.1379 (8) Å  
α = 89.460 (6)°  
β = 89.617 (6)°  
γ = 66.878 (5)°  
V = 1125.21 (9) Å³  
Z = 2  
F(000) = 608.00  
D_x = 1.818 Mg m⁻³  
Mo Kα radiation, λ = 0.71075 Å  
Cell parameters from 9577 reflections  
θ = 2.5–27.4°  
µ = 4.78 mm⁻¹  
T = 173 K  
Block, colorless  
0.35 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID diffractometer  
Detector resolution: 10.000 pixels mm⁻¹  
ω scans  
Absorption correction: multi-scan  
(ABSCOR; Higashi, 1995)  
T_min = 0.316, T_max = 0.487  
5114 independent reflections  
4386 reflections with F^2 > 2.0σ(F^2)  
Rint = 0.017  
θ_max = 27.4°, θ_min = 2.8°  
h = −9→9  
k = −11→11  
l = −23→23  
11009 measured reflections

Refinement

Refinement on F^2  
R[F^2 > 2σ(F^2)] = 0.027  
wR(F^2) = 0.059  
S = 1.07  
5114 reflections  
284 parameters  
0 restraints  
Primary atom site location: structure-invariant direct methods  
Secondary atom site location: difference Fourier map  
Hydrogen site location: inferred from neighbouring sites  
H atoms treated by a mixture of independent and constrained refinement  
w = 1/[σ^2(F^2) + (0.024P)^2 + 0.8532P]  
where P = (F^2 + 2F_c^2)/3  
(Δσ) max < 0.001

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Computing details

Data collection: RAPID-AUTO (Rigaku, 2006); cell refinement: RAPID-AUTO (Rigaku, 2006); data reduction: RAPID-AUTO (Rigaku, 2006); program(s) used to solve structure: SIR92 (Altomare, et al., 1993); program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2015); molecular graphics: PLATON (Spek, 2020); software used to prepare material for publication: CrystalStructure (Rigaku, 2016).
$\Delta \rho_{\text{max}} = 0.59 \text{ e Å}^{-3}$  
$\Delta \rho_{\text{min}} = -0.65 \text{ e Å}^{-3}$

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on $F^2$. R-factor (gt) are based on $F$. The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R-factor (gt).

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{Å}^2$)

|   | $x$     | $y$     | $z$     | $U_{	ext{iso}}^2/U_{	ext{eq}}$ |
|---|---------|---------|---------|----------------------------------|
|Br1| 0.27928 (3) | 0.13134 (3) | 0.42388 (2) | 0.02925 (7) |
|Br2| 0.21673 (4) | 0.34246 (3) | 0.22122 (2) | 0.03710 (7) |
|Zn3| 0.43550 (3) | 0.18902 (3) | 0.31584 (2) | 0.02169 (7) |
|Cl4| 0.52345 (11) | 0.31327 (11) | 0.04318 (5) | 0.0578 (2) |
|O5 | 1.0962 (2) | -0.2077 (2) | 0.21912 (11) | 0.0350 (4) |
|N6 | 1.0498 (3) | -0.2729 (3) | 0.07984 (13) | 0.0399 (5) |
|N7 | 0.7489 (3) | 0.0783 (2) | 0.34256 (10) | 0.0226 (4) |
|N8 | 0.5357 (3) | -0.0510 (2) | 0.26615 (11) | 0.0249 (4) |
|N9 | 0.4920 (3) | 0.3899 (2) | 0.36144 (10) | 0.0252 (4) |
|C10| 0.9635 (3) | -0.0864 (3) | 0.17935 (13) | 0.0259 (5) |
|C11| 0.8577 (3) | 0.0643 (3) | 0.21048 (13) | 0.0248 (5) |
|C12| 0.7210 (3) | 0.1857 (3) | 0.16621 (14) | 0.0294 (5) |
|H12| 0.649031 | 0.290977 | 0.186741 | 0.035* |
|C13| 0.6895 (4) | 0.1560 (3) | 0.09501 (15) | 0.0337 (5) |
|C14| 0.7945 (4) | 0.0008 (3) | 0.06192 (14) | 0.0337 (6) |
|C15| 0.7731 (5) | -0.0458 (4) | -0.01112 (16) | 0.0489 (8) |
|H15| 0.679789 | 0.029174 | -0.042671 | 0.059* |
|C16| 0.8870 (5) | -0.1980 (5) | -0.03553 (17) | 0.0595 (10) |
|H16| 0.873842 | -0.230341 | -0.084318 | 0.071* |
|C17| 1.0237 (5) | -0.3070 (4) | 0.01133 (17) | 0.0521 (8) |
|H17| 1.102771 | -0.412396 | -0.007394 | 0.063* |
|C18| 0.9343 (3) | -0.1194 (3) | 0.10505 (13) | 0.0297 (5) |
|C19| 0.8847 (3) | 0.1035 (3) | 0.28896 (13) | 0.0291 (5) |
|H19A| 1.015382 | 0.032903 | 0.304228 | 0.035* |
|H19B| 0.870946 | 0.220136 | 0.291434 | 0.035* |
|C20| 0.7877 (3) | -0.0985 (3) | 0.35371 (14) | 0.0278 (5) |
|H20A| 0.736052 | -0.114214 | 0.402007 | 0.033* |
|H20B| 0.926284 | -0.163249 | 0.354144 | 0.033* |
|C21| 0.6994 (3) | -0.1604 (3) | 0.29331 (13) | 0.0255 (5) |
|C22| 0.7819 (4) | -0.3211 (3) | 0.26675 (15) | 0.0334 (6) |
|H22| 0.896330 | -0.397844 | 0.287479 | 0.040* |
|C23| 0.6955 (4) | -0.3673 (3) | 0.21001 (17) | 0.0401 (6) |
|H23| 0.751460 | -0.475780 | 0.190356 | 0.048* |
|C24| 0.5265 (4) | -0.2547 (3) | 0.18174 (16) | 0.0396 (6) |
|H24| 0.464442 | -0.284338 | 0.142650 | 0.048* |
Atomic displacement parameters (Å²)

|    | U¹¹ | U²² | U³³ | U¹₂ | U¹₃ | U²₃ |
|----|-----|-----|-----|-----|-----|-----|
| Br1| 0.02994 (12) | 0.03405 (13) | 0.02819 (12) | −0.01729 (10) | 0.00204 (9) | −0.00401 (9) |
| Br2| 0.03370 (13) | 0.03205 (13) | 0.03195 (13) | 0.00201 (10) | −0.00934 (10) | −0.00635 (10) |
| Zn3| 0.01991 (12) | 0.01955 (12) | 0.02461 (13) | −0.00657 (10) | −0.00128 (10) | −0.00394 (10) |
| Cl4| 0.0467 (4) | 0.0467 (5) | 0.0546 (5) | −0.0144 (4) | −0.0121 (4) | 0.0322 (4) |
| O5| 0.0269 (9) | 0.0347 (10) | 0.0364 (10) | −0.0046 (8) | 0.0016 (8) | 0.0014 (8) |
| N6| 0.0514 (14) | 0.0411 (13) | 0.0359 (12) | −0.0276 (11) | 0.0146 (11) | −0.0090 (10) |
| N7| 0.0225 (9) | 0.0236 (9) | 0.0229 (9) | −0.0104 (8) | −0.0006 (7) | −0.0011 (7) |
| N8| 0.0220 (9) | 0.0220 (9) | 0.0308 (10) | −0.0089 (8) | 0.0037 (8) | −0.0054 (8) |
| N9| 0.0297 (10) | 0.0228 (9) | 0.0243 (10) | −0.0114 (8) | 0.0001 (8) | −0.0022 (8) |
| C10| 0.0246 (11) | 0.0282 (11) | 0.0273 (12) | −0.0131 (10) | 0.0011 (9) | 0.0033 (9) |
| C11| 0.0240 (11) | 0.0275 (11) | 0.0266 (11) | −0.0140 (9) | 0.0021 (9) | −0.0002 (9) |
| C12| 0.0289 (12) | 0.0257 (12) | 0.0354 (13) | −0.0128 (10) | 0.0030 (10) | 0.0036 (10) |
| C13| 0.0309 (12) | 0.0373 (14) | 0.0351 (13) | −0.0161 (11) | −0.0043 (11) | 0.0146 (11) |
| C14| 0.0398 (14) | 0.0455 (15) | 0.0274 (12) | −0.0295 (13) | −0.0022 (11) | 0.0052 (11) |
| C15| 0.0577 (19) | 0.074 (2) | 0.0294 (14) | −0.0417 (18) | −0.0053 (13) | 0.0042 (14) |
| C16| 0.082 (2) | 0.087 (3) | 0.0349 (16) | −0.060 (2) | 0.0105 (16) | −0.0206 (17) |
| C17| 0.072 (2) | 0.0547 (19) | 0.0442 (17) | −0.0404 (18) | 0.0201 (16) | −0.0204 (15) |
| C18| 0.0347 (13) | 0.0332 (13) | 0.0286 (12) | −0.0216 (11) | 0.0066 (10) | −0.0022 (10) |
| C19| 0.0277 (12) | 0.0354 (13) | 0.0284 (12) | −0.0167 (10) | 0.0039 (9) | −0.0059 (10) |
| C20| 0.0231 (11) | 0.0241 (11) | 0.0335 (13) | −0.0063 (9) | −0.0015 (10) | 0.0020 (10) |
| C21| 0.0226 (10) | 0.0211 (11) | 0.0334 (12) | −0.0092 (9) | 0.0071 (9) | −0.0021 (9) |
| C22| 0.0290 (12) | 0.0198 (11) | 0.0488 (16) | −0.0067 (10) | 0.0130 (11) | −0.0038 (11) |
| C23| 0.0406 (15) | 0.0268 (13) | 0.0563 (17) | −0.0169 (12) | 0.0190 (13) | −0.0170 (12) |
| C24| 0.0438 (15) | 0.0392 (15) | 0.0447 (16) | −0.0255 (13) | 0.0087 (12) | −0.0165 (12) |
| C25| 0.0287 (12) | 0.0323 (13) | 0.0389 (14) | −0.0142 (11) | 0.0032 (11) | −0.0102 (11) |
| C26| 0.0251 (11) | 0.0328 (12) | 0.0225 (11) | −0.0137 (10) | −0.0033 (9) | −0.0009 (9) |
| C27| 0.0313 (12) | 0.0322 (12) | 0.0200 (10) | −0.0189 (10) | 0.0046 (9) | −0.0044 (9) |
| C28| 0.0456 (15) | 0.0472 (15) | 0.0254 (12) | −0.0327 (13) | 0.0033 (11) | −0.0065 (11) |
| C29| 0.0684 (19) | 0.0396 (15) | 0.0326 (14) | −0.0393 (15) | 0.0181 (13) | −0.0140 (11) |
Geometric parameters (Å, °)

|         |  |  |  |  |  |  |
|---------|---|---|---|---|---|---|
| Br1—Zn3 | 2.4419 (4) | C16—C17 | 1.396 (5) |
| Br2—Zn3 | 2.4085 (4) | C16—H16 | 0.9500 |
| Zn3—N8  | 2.1455 (18) | C17—H17 | 0.9500 |
| Zn3—N9  | 2.1497 (18) | C19—H19A | 0.9900 |
| Zn3—N7  | 2.2670 (18) | C19—H19B | 0.9900 |
| C14—C13 | 1.740 (3) | C20—C21 | 1.506 (3) |
| O5—C10  | 1.355 (3) | C20—H20A | 0.9900 |
| O5—H5   | 0.79 (4) | C20—H20B | 0.9900 |
| N6—C17  | 1.316 (4) | C21—C22 | 1.390 (3) |
| N6—C18  | 1.371 (3) | C22—C23 | 1.376 (4) |
| N7—C20  | 1.474 (3) | C22—H22 | 0.9500 |
| N7—C26  | 1.478 (3) | C23—C24 | 1.385 (4) |
| N7—C19  | 1.498 (3) | C23—H23 | 0.9500 |
| N8—C21  | 1.341 (3) | C24—C25 | 1.387 (3) |
| N8—C25  | 1.341 (3) | C24—H24 | 0.9500 |
| N9—C27  | 1.339 (3) | C25—H25 | 0.9500 |
| N9—C31  | 1.342 (3) | C26—C27 | 1.512 (3) |
| C10—C11 | 1.377 (3) | C26—H26A | 0.9900 |
| C10—C18 | 1.419 (3) | C26—H26B | 0.9900 |
| C11—C12 | 1.414 (3) | C27—C28 | 1.391 (3) |
| C11—C19 | 1.502 (3) | C28—C29 | 1.386 (4) |
| C12—C13 | 1.362 (4) | C28—H28 | 0.9500 |
| C12—H12 | 0.9500 | C29—C30 | 1.374 (4) |
| C13—C14 | 1.420 (4) | C29—H29 | 0.9500 |
| C14—C18 | 1.409 (4) | C30—C31 | 1.381 (3) |
| C14—C15 | 1.419 (4) | C30—H30 | 0.9500 |
| C15—C16 | 1.355 (5) | C31—H31 | 0.9500 |
| C15—H15 | 0.9500 |

Geometric parameters (Å, °)

|         |  |  |  |  |  |  |
|---------|---|---|---|---|---|---|
| N8—Zn3—N9 | 149.88 (7) | C14—C18—C10 | 120.6 (2) |
| N8—Zn3—N7  | 76.13 (7) | N7—C19—C11 | 114.29 (18) |
| N9—Zn3—N7  | 75.20 (7) | N7—C19—H19A | 108.7 |
| N8—Zn3—Br2 | 98.53 (5) | C11—C19—H19A | 108.7 |
| N9—Zn3—Br2 | 98.16 (5) | N7—C19—H19B | 108.7 |
| N7—Zn3—Br2 | 141.63 (5) | C11—C19—H19B | 108.7 |
| N8—Zn3—Br1 | 98.76 (5) | H19A—C19—H19B | 107.6 |
| N9—Zn3—Br1 | 97.48 (5) | N7—C20—C21 | 110.67 (19) |
| N7—Zn3—Br1 | 105.26 (5) | N7—C20—H20A | 109.5 |
| Br2—Zn3—Br1 | 113.102 (14) | C21—C20—H20A | 109.5 |
| C10—O5—H5 | 104 (3) | N7—C20—H20B | 109.5 |
| C17—N6—C18 | 116.6 (3) | C21—C20—H20B | 109.5 |
| C20—N7—C26 | 112.22 (18) | H20A—C20—H20B | 108.1 |
| C20—N7—C19 | 111.92 (18) | N8—C21—C22 | 121.6 (2) |
C26—N7—C19 108.08 (16)
C20—N7—Zn3 102.79 (13)
C26—N7—Zn3 102.85 (13)
C19—N7—Zn3 118.69 (14)
C21—N8—C25 119.2 (2)
C21—N8—Zn3 114.94 (14)
C25—N8—Zn3 125.90 (16)
C27—N9—C31 119.2 (2)
C27—N9—Zn3 115.53 (15)
C31—N9—Zn3 125.38 (16)
O5—C10—C11 120.9 (2)
O5—C10—C18 118.3 (2)
C11—C10—C18 120.8 (2)
C10—C11—C12 118.2 (2)
C10—C11—C19 122.2 (2)
C12—C11—C19 119.6 (2)
C13—C12—C11 122.0 (2)
C13—C12—H12 119.0
C11—C12—H12 119.0
C12—C13—C14 120.0 (2)
C12—C13—C14 119.3 (2)
C14—C13—C14 119.7 (2)
C18—C14—C15 116.3 (3)
C18—C14—C13 117.4 (2)
C15—C14—C13 126.3 (3)
C15—C14—C14 119.5 (3)
C15—C14—H15 120.2
C14—C15—H15 120.2
C15—C16—C17 119.7 (3)
C15—C16—H16 120.1
C16—C16—H16 120.1
N6—C17—C16 124.0 (3)
N6—C17—H17 118.0
C16—C17—H17 118.0
N6—C18—C14 123.9 (2)
N6—C18—C10 115.5 (2)
O5—C10—C11—C12 −179.8 (2)
C18—C10—C11—C12 −0.7 (3)
O5—C10—C11—C19 0.8 (3)
C18—C10—C11—C19 179.9 (2)
C10—C11—C12—C13 1.3 (3)
C19—C11—C12—C13 −179.3 (2)
C11—C12—C13—C14 −0.3 (4)
C11—C12—C13—C14 −178.28 (18)
C12—C13—C14—C18 −1.4 (4)
C14—C13—C14—C18 176.63 (18)
C12—C13—C14—C15 179.1 (2)
O5—C10—C11—C12 155.72 (18)
C18—C10—C11—C12 122.4 (2)
O5—C10—C11—C19 45.9 (2)
C18—C10—C11—C19 122.3 (2)
C10—C11—C12—C13 194.1 (2)
C19—C11—C12—C13 179.6 (2)
C11—C12—C13—C14 146.4 (2)
C12—C13—C14—C18 1.6 (4)
C12—C13—C14—C15 −178.2 (2)

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Cl4—C13—C14—C15  −2.9 (4)  C21—C22—C23—C24  −1.5 (4)
C18—C14—C15—C16  −1.0 (4)  C22—C23—C24—C25  0.2 (4)
C13—C14—C15—C16  178.5 (3)  C21—N8—C25—C24  −1.3 (4)
C14—C15—C16—C17  0.0 (5)  Zn3—N8—C25—C24  178.66 (19)
C18—N6—C17—C16  −0.5 (4)  C23—C24—C25—N8  1.3 (4)
C15—C16—C17—N6  0.8 (5)  C20—N7—C26—C27  −158.30 (18)
C17—N6—C18—C14  −0.7 (4)  C19—N7—C26—C27  77.8 (2)
C17—N6—C18—C10  179.2 (2)  C22—N7—C26—C27  −48.52 (19)
C15—C14—C18—C10  1.4 (4)  C31—N9—C27—C26  −0.5 (3)
C13—C14—C18—C16  −0.7 (4)  C31—N9—C27—C28  0.2 (2)
C18—N6—C14—C18  −1.0 (3)  Zn3—N9—C27—C28  176.6 (2)
C13—C14—C18—C10  178.5 (5)  Zn3—N9—C27—C29  −176.89 (17)
C15—C14—C18—N6  −1.7 (3)  C26—C27—C28—C29  1.5 (4)
C11—C10—C18—N6  179.1 (3)  C27—C28—C29—C30  −0.3 (4)
O5—C10—C18—N6  −1.7 (3)  C29—C30—C31—N9  1.3 (4)
C12—C11—C19—N7  84.1 (3)  Zn3—N9—C31—C30  −175.09 (18)
C13—C14—C18—C10  −178.1 (2)  Zn3—N9—C31—C30  −49.1 (2)
C15—C14—C18—C16  −178.8 (2)  Zn3—N9—C31—C30  70.4 (3)
C11—C10—C18—C14  −96.5 (3)  Zn3—N9—C31—C30  84.1 (3)
C12—C11—C19—N7  84.1 (3)  Zn3—N9—C31—C30  −165.5 (2)
C10—C11—C19—N7  84.1 (3)  Zn3—N9—C31—C30  −49.1 (2)
C10—C11—C19—N7  −178.1 (2)  Zn3—N9—C31—C30  −175.09 (18)
C12—C11—C19—N7  84.1 (3)  Zn3—N9—C31—C30  −49.1 (2)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H  | H···A  | D···A  | D—H···A |
|---------|------|-------|-------|---------|
| O5—H5···N6 | 0.79 (4) | 2.14 (4) | 2.653 (3) | 124 (3) |
| C16—H16···Br2i | 0.95 | 2.87 | 3.808 (3) | 170 |
| C22—H22···Br2a | 0.95 | 2.88 | 3.581 (3) | 131 |
| C29—H29···Br1ii | 0.95 | 2.90 | 3.798 (3) | 158 |

Symmetry codes: (i) −x+1, −y, −z; (ii) x+1, y−1, z; (iii) −x+1, −y+1, −z+1.