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Crystal structure and Hirshfeld surface analysis of 7,7′-{[(pyridin-2-ylmethyl)azanediyl]bis(methylene)}-bis(5-chloroquinolin-8-ol)

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Keywords: crystal structure; 8-quinolinol; tripodal molecule; O—H···N hydrogen bonds; C—H···O interactions.

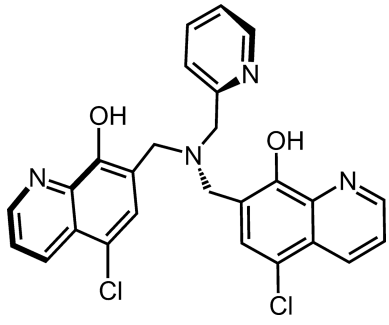
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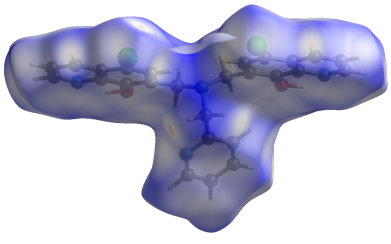
In the title compound, $C_{26}H_{20}Cl_2N_4O_2$, which is a tripodal molecule containing two quinolin-8-ol moieties, one pyridine ring and a tertiary amino group, two intramolecular O—H···N hydrogen bonds involving the hydroxy groups and N atoms of quinolin-8-ol moieties generate $S(5)$ ring motifs and stabilize the molecular conformation. In the crystal, two molecules are linked by intermolecular C—H···Cl hydrogen bonds, forming an inversion dimer with an $R_2^2(16)$ ring motif. A supramolecular chain structure is formed by intermolecular O—H···N hydrogen bonds running parallel to the b-axis direction. The two types of hydrogen-bonding interactions link the molecules into a sheet structure extending parallel to $(10\bar{2})$. A Hirshfeld surface analysis reveals that the most significant contributions for the crystal packing arise from H···H (40.0%), C···H/H···C (15.6%) and Cl···H/H···Cl (15.4%) contacts.

1. Chemical context

Quinolin-8-ol (Hq) and its derivatives are well-known chelating ligands and analytical reagents (Wiberley & Bassett, 1949; Rahier *et al.*, 2016; Meghna *et al.*, 2026). Metal complexes with Hq or its derivatives have wide-ranging applications in diverse areas such as magnetic materials, anticancer agents or organic light-emitting diodes (Zou *et al.*, 2019; Huang *et al.*, 2026; D'Souza *et al.*, 2008; Li *et al.*, 2020). Compounds having two Hq moieties can form polynuclear metal complexes, which have applications as luminescent sensors (Wu *et al.*, 2017). Moreover, polynuclear dimeric Hq complexes can efficiently capture anions, such as pyrophosphate, through their multiple metal ions, thereby offering the potential for use as a fluorescent anion probe.



In the context given above, we reported quinolinol-based potentially fluorescent ligands, *viz*. 7-{[bis(pyridin-2-ylmethyl)-amino]methyl}-5-chloroquinolin-8-ol (HClqdpa; its deprotonated anion, Clqdpa$^-$) and 1,1-bis(5-chloro-8-hydroxyquinolin-7-yl)-1-(pyridin-2-yl)methane (Kubono *et al.*, 2015; Kashiwagi



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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···N5	0.80 (3)	2.24 (2)	2.7337 (15)	121 (2)
O3—H3···N6^{i}	0.80 (3)	2.25 (2)	2.8362 (15)	131 (2)
O4—H4···N6	0.80 (2)	2.29 (2)	2.7485 (15)	117 (2)
O4—H4···N5^{ii}	0.80 (2)	2.22 (2)	2.8456 (15)	136 (2)
C34—H34*A*···Cl1^{iii}	0.99	2.78	3.7082 (15)	157

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

et al., 2020). Of these ligands, HClqdpa contains Hq and bis(pyridin-2-ylmethyl)amine moieties, and it can form Zn^{II} complexes with different Zn–ligand ratios, such as the mononuclear Zn–HClqdpa = 1:1 complex, $ZnBr_2$(HClqdpa) (Kubono *et al.*, 2022), the dinuclear Zn–Clqdpa^{-} = 2:1 complex, Zn_2Cl_3(Clqdpa) (Kubono *et al.*, 2024) and the dinuclear Zn–Clqdpa^{-} = 2:2 complex, $[Zn_2(Clqdpa)_2](ClO_4)_2$ (Kubono *et al.*, 2026). In the crystalline state, Zn_2Cl_3(Clqdpa) and $[Zn_2(Clqdpa)_2](ClO_4)_2$ exhibit fluorescence, whereas $ZnBr_2$(HClqdpa) is non-fluorescent. In contrast, all three complexes exhibit fluorescence in solution with polar solvents such as methanol, acetone or acetonitrile. Compounds with two Hq moieties are expected to form a wider variety of polynuclear complexes compared to HClqdpa. Herein, we present the molecular and crystal structures and Hirshfeld surface analysis of such a compound, namely, the title compound, 7,7′-{[(pyridin-2-ylmethyl)azanediyl]bis(methylene)}bis(5-chloroquinolin-8-ol).

2. Structural commentary

The title compound is a tripodal molecule possessing two Hq moieties, one pyridine moiety and a tertiary amino group; its molecular structure is shown in Fig. 1. The quinoline rings are almost planar, with r.m.s. deviations of 0.006 (1) Å for N5/C9–C17 and 0.002 (1) Å for N6/C18–C26. There are two intramolecular O—H···N hydrogen bonds involving the hydroxy groups and N atoms of Hq moieties (O3—H3···N5 and O4—H4···N6), generating *S*(5) ring motifs (Table 1). The N(tertiary amine)—C—C—C(bonded to an OH group) torsion angles N8—C32—C10—C9 and N8—C33—C19—C18 are 146.40 (12) and −170.06 (11)°, respectively. The N(pyridine)—C—C—N(tertiary amine) torsion angle N7—C27—C34—N8 is −102.50 (14)° and the C—N(tertiary amine)—C angles C32—N8—C34, C33—N8—C32 and C33—N8—C34 are 113.45 (10), 112.30 (10) and 112.11 (10)°, respectively. The quinoline rings are almost parallel to one another and have an interplanar dihedral angle of 2.04 (4)°, whereas the dihedral angle between the planes of a quinoline ring and a pyridine ring is 37.44 (6)° for N5/C9–C17 and 39.46 (6)° for N6/C18–C26.

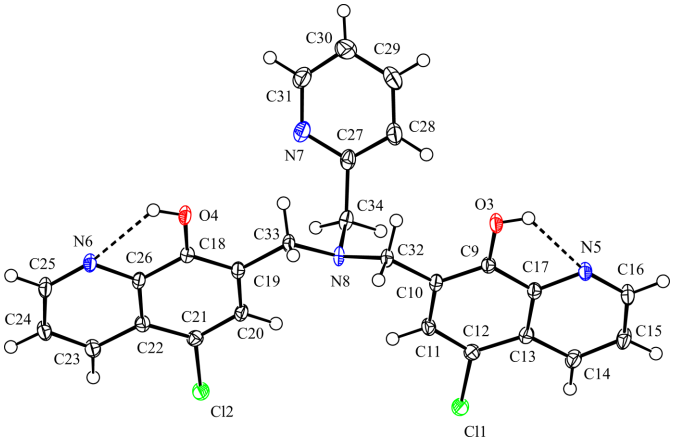


Figure 1
The molecular structure of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radius and the intramolecular O—H···N hydrogen bonds are shown as dashed lines.

3. Supramolecular features

In the crystal, two molecules are linked by pairwise intermolecular C—H···Cl hydrogen bonds (C34—H34*A*···Cl1^{iii}; the symmetry code refers to Table 1), forming an inversion dimer with an $R_2^2(16)$ ring motif (Fig. 2). A supramolecular chain structure is formed by intermolecular O—H···N hydrogen bonds (O3—H3···N6^{i} and O4—H4···N5^{ii}; the symmetry codes refer to Table 1) along the *b*-axis direction. The two intermolecular hydrogen bonds originate from the same hydroxy groups as the intramolecular interactions, so these the hydrogen bonds are bifurcated (Fig. 3). The N atoms of the pyridine ring and of the tertiary amino group are not involved in hydrogen-bonding interactions. The molecules are linked by the two types of hydrogen bonds, generating a sheet structure extending parallel to $(10\overline{2})$ (Fig. 4).

4. Hirshfeld surface analysis

A Hirshfeld surface (HS) analysis (Spackman & Jayatilaka, 2009) was carried out using *CrystalExplorer* (Spackman *et al.*,

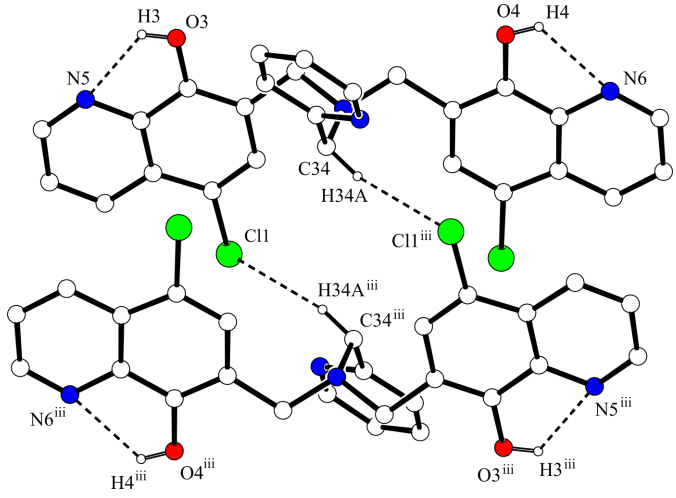


Figure 2
Formation of a centrosymmetric dimer by C—H···Cl hydrogen bonds. The intramolecular O—H···N and intermolecular C—H···Cl hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions have been omitted for clarity. (The symmetry code refers to Table 1.)

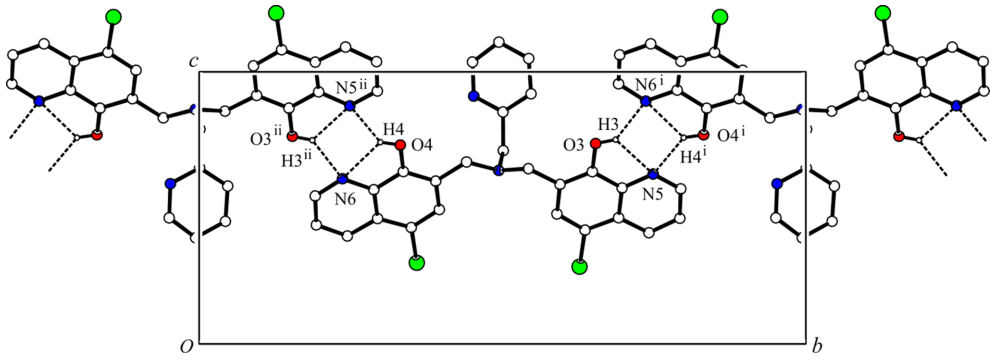


Figure 3
A packing diagram of the title compound viewed along the *a* axis, showing the formation of a supramolecular chain structure. The intermolecular and intramolecular O—H···N hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions have been omitted for clarity. (The symmetry codes refer to Table 1.)

2021) to visualize the intermolecular interactions and contacts in the crystal of the title compound. In the HS plotted over d_{norm} (Fig. 5), the contact distances equal, shorter and longer than the sum of van der Waals radii are shown by white, red and blue colours, respectively. The percentage contributions of the intermolecular interactions to the total HS were quantified by two-dimensional fingerprint plots (McKinnon *et al.*, 2007). The fingerprint plots of d_i *versus* d_e shown in Fig. 6 reveal that the most significant contributions arise from H···H (40.0%), C···H/H···C (15.6%) and Cl···H/H···Cl (15.4%) contacts. Smaller contributions are observed for H···N/N···H (7.2%), C···C (6.1%), O···H/H···O (4.3%), Cl···C/C···Cl (4.3%), N···C/C···N (2.9%), O···C/C···O (2.7%), Cl···N/N···Cl (0.9%) and N···N (0.5%) interactions.

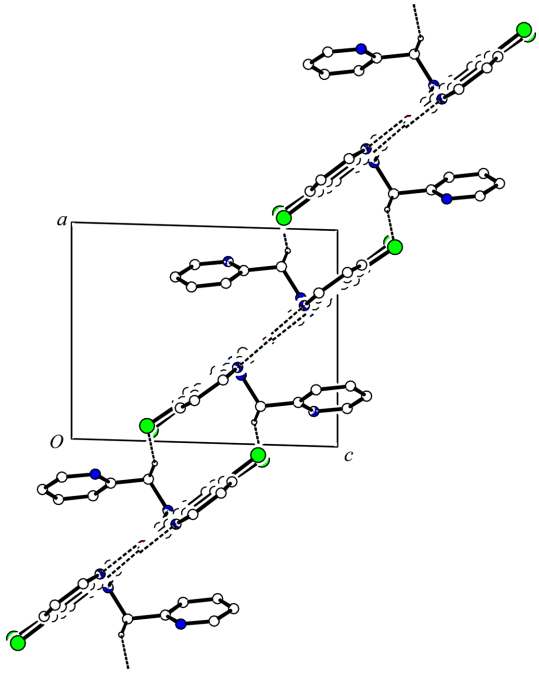


Figure 4
A portion of the crystal packing of the title compound, viewed along the *b* axis, showing the hydrogen-bonded sheet structure, with intermolecular O—H···N and C—H···Cl hydrogen bonds shown as dashed lines. H atoms not involved in the interactions have been omitted for clarity.

5. Database survey

A search of the Cambridge Structural Database (CSD; update of February 2026; Groom *et al.*, 2016) using *ConQuest* (Bruno *et al.*, 2002) for compounds containing the Hq moiety gave 796 hits. A search for the fragment 7-(aminomethyl)quinolin-8-olate gave 50 hits of which 25 structures are ligands without metal ions, and the remaining 25 structures are metal complexes. Of the 25 ligand structures, 18 stuctures contain a hydroxy group in the Hq moiety, and only one of the 18

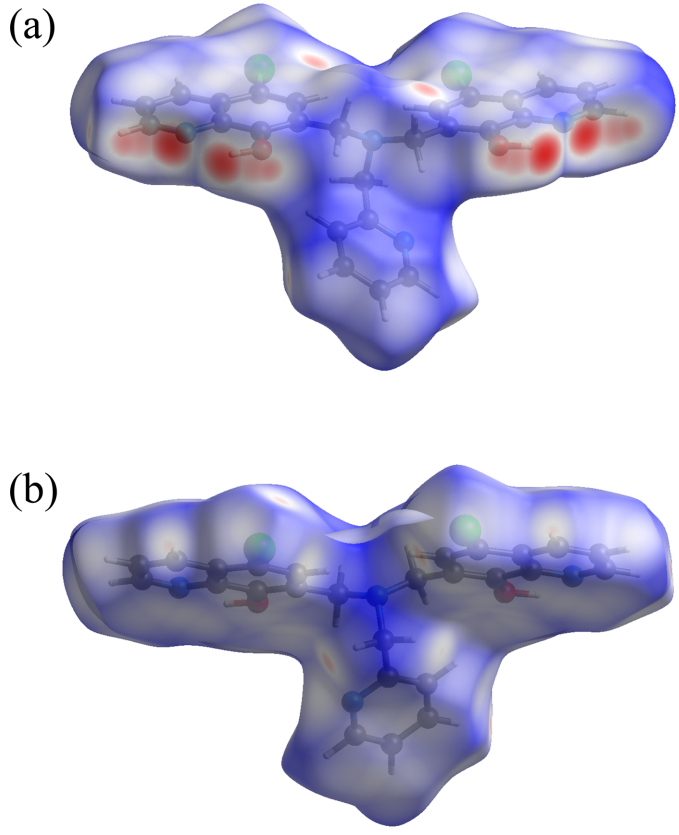


Figure 5
Hirshfeld surface mapped over d_{norm} for the title compoud, showing (*a*) a front view and (*b*) a back view.

structures comprises two Hq moieties and is an azacrown compound (CSD refcode RELNUR; Bordunov *et al.*, 1996). Another of the 18 structures is that of the compound HClqdpa (RUTSIK; Kubono *et al.*, 2015), which is closely related to the title compound. In contrast to the latter, the molecular structure of HClqdpa exhibits an intramolecular O—H···N hydrogen bond between the H atom of hydroxy group in the Hq moiety and an N atom of a pyridine ring, generating an *S*(9) ring motif. Of the remaining seven ligand structures, six structures are quinolin-8-olate esters, and one structure is a zwitterion of Hq. Of the 25 metal complex structures, two structures are *catena* complexes and 15 are mononuclear complexes, with one of the latter being a Zn–HClqdpa = 1:1 complex, $ZnBr_2$(HClqdpa) (VAXNUH; Kubono *et al.*, 2022). Of the remaining eight metal complexes, six structures are dinuclear Zn^{II} complexes; these include a Zn–$Clqdpa^-$ = 2:1 complex, Zn_2Cl_3(Clqdpa) (PUCTOA; Kubono *et al.*, 2024), and a Zn–$Clqdpa^-$ = 2:2 complex acetonitrile clathrate, $[Zn_2(Clqdpa)_2](ClO_4)_2{\cdot}CH_3CN$ (IRURAS; Kubono *et al.*, 2026). Of the remaining two complexes, one is trinuclear Cu^{II} complex (CIFDEB; Aragoni *et al.*, 2007) and the other is a tetranulear Cu^{II} complex (LIJZOV; Bencini *et al.*, 2013). A crystal structure containing an Hq–CH_2–N–CH_2–Hq fragment like in the title compound has not yet been reported.

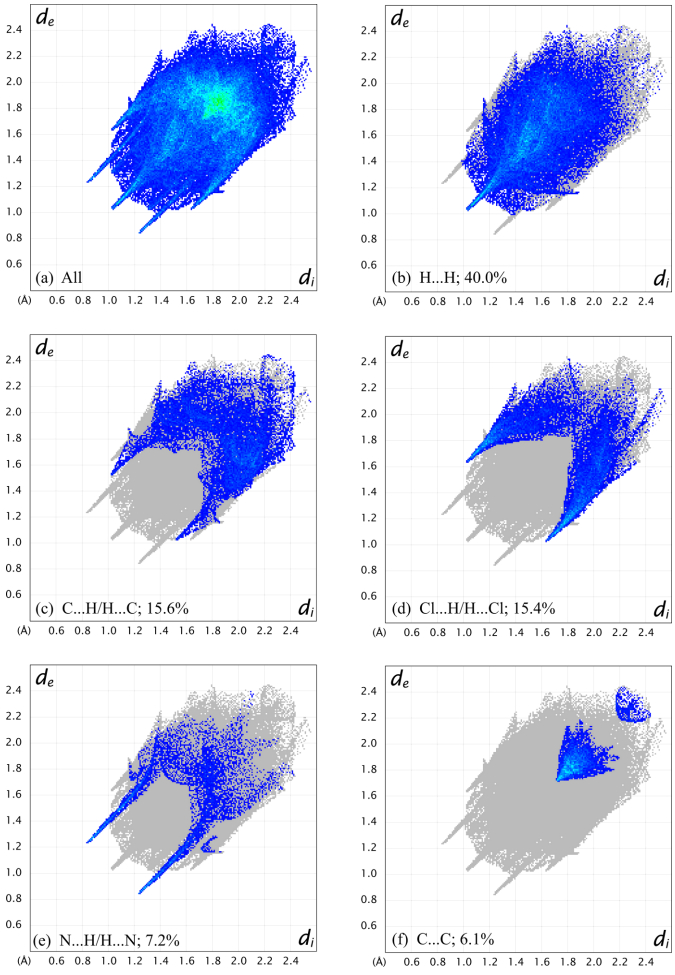


Figure 6
Two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C, (*d*) Cl···H/H···Cl, (*e*) N···H/H···N and (*f*) C···C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{26}H_{20}Cl_2N_4O_2$
M_r	491.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.6388 (1), 23.6574 (3), 10.6210 (1)
β (°)	91.706 (1)
V (Å^3)	2169.67 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.97
Crystal size (mm)	0.29 × 0.08 × 0.03
Data collection	
Diffractometer	Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.825, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15927, 4344, 3986
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.631
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.087, 1.07
No. of reflections	4344
No. of parameters	315
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.28

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *PLATON* (Spek, 2020) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Synthesis and crystallization

A suspension of paraformaldehyde (0.36 g, 12 mmol), 2-picolyamine (0.504 g, 5 mmol) and 5-chloroquinolin-8-ol (1.80 g, 10 mmol) in 120 ml of methanol was heated for 48 h at 333 K. The solvent was removed *in vacuo* to give an oily product, which was precipitated by addition of diethyl ether. The crude solid was recrystallized from methanol/diethyl ether solution to obtain colourless crystals of the title compound (yield 11%, m.p. 429.7–431.5 K). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.96 (*s*, 2H), 4.02 (*s*, 4H), 7.19–7.22 (*m*, 1H), 7.40 (*d*, J = 7.6 Hz, 1H), 7.49 (*dd*, J = 8.4, 4.2 Hz, 2H), 7.51 (*s*, 2H), 7.65–7.69 (*m*, 1H), 8.43 (*dd*, J = 8.4, 1.4 Hz, 2H), 8.67 (*d*, J = 4.8 Hz, 1H), 8.87 (*dd*, J = 4.2, 1.4 Hz, 2H).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy H atoms were located in a difference Fourier map and refined freely. All H atoms bound to C atoms were positioned geometrically and refined

using a riding model, with C—H = 0.95–0.99 Å and U_{iso}(H) = 1.2U_{eq}(C).

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Koji Kubono, Atsuya Hori, Keita Tani and Yukiyasu Kashiwagi

Computing details

7,7′-{[(Pyridin-2-ylmethyl)azanediyl]bis(methylene)}bis(5-chloroquinolin-8-ol)

Crystal data

$C_{26}H_{20}Cl_2N_4O_2$
$M_r = 491.36$
Monoclinic, $P2_1/c$
$a = 8.6388$ (1) Å
$b = 23.6574$ (3) Å
$c = 10.6210$ (1) Å
$\beta = 91.706$ (1)°
$V = 2169.67$ (4) Å^3
$Z = 4$
$F(000) = 1016$
$D_x = 1.504$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 10576 reflections
$\theta = 3.7$–$76.3°$
$\mu = 2.97$ mm^{-1}
$T = 100$ K
Block, colourless
0.29 × 0.08 × 0.03 mm

Data collection

Rigaku XtaLAB Synergy Dualflex diffractometer with a HyPix detector
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2023)
$T_{min} = 0.825$, $T_{max} = 1.000$
15927 measured reflections
4344 independent reflections
3986 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 76.6°$, $\theta_{min} = 3.7°$
$h = -10 \rightarrow 10$
$k = -28 \rightarrow 29$
$l = -13 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.087$
$S = 1.07$
4344 reflections
315 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.6088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.07026 (4)	0.62698 (2)	0.28385 (3)	0.02009 (10)
Cl2	0.04938 (4)	0.35874 (2)	0.29830 (3)	0.02006 (10)
O3	0.47394 (11)	0.65359 (4)	0.73661 (9)	0.0193 (2)
H3	0.478 (3)	0.6866 (11)	0.751 (2)	0.052 (7)*
O4	0.48319 (11)	0.33157 (4)	0.73117 (9)	0.0176 (2)
H4	0.501 (3)	0.2986 (10)	0.7417 (19)	0.044 (6)*
N5	0.35276 (13)	0.74843 (5)	0.62451 (10)	0.0169 (2)
N8	0.31763 (13)	0.49382 (4)	0.63780 (11)	0.0155 (2)
N6	0.37967 (13)	0.23619 (5)	0.60722 (10)	0.0168 (2)
N7	0.15964 (14)	0.45263 (5)	0.91091 (11)	0.0229 (3)
C9	0.37995 (15)	0.64805 (5)	0.63336 (12)	0.0150 (3)
C17	0.31562 (15)	0.69706 (5)	0.57323 (12)	0.0150 (3)
C16	0.29263 (16)	0.79372 (6)	0.56996 (13)	0.0206 (3)
H16	0.317608	0.829544	0.605500	0.025*
C15	0.19367 (17)	0.79234 (6)	0.46228 (13)	0.0221 (3)
H15	0.152689	0.826338	0.427318	0.027*
C14	0.15755 (16)	0.74135 (6)	0.40893 (13)	0.0197 (3)
H14	0.092357	0.739498	0.335416	0.024*
C13	0.21797 (15)	0.69136 (6)	0.46400 (12)	0.0161 (3)
C12	0.18772 (15)	0.63600 (6)	0.41852 (12)	0.0164 (3)
C11	0.24910 (15)	0.58974 (6)	0.47778 (12)	0.0166 (3)
H11	0.225318	0.553192	0.445582	0.020*
C10	0.34769 (14)	0.59482 (5)	0.58641 (12)	0.0152 (3)
C32	0.42195 (15)	0.54261 (5)	0.64432 (12)	0.0159 (3)
H32A	0.517729	0.533627	0.599484	0.019*
H32B	0.451059	0.550377	0.733507	0.019*
C18	0.37971 (14)	0.33659 (5)	0.63364 (11)	0.0147 (3)
C26	0.32646 (15)	0.28790 (5)	0.56690 (12)	0.0149 (3)
C25	0.33229 (16)	0.19127 (6)	0.54381 (13)	0.0202 (3)
H25	0.369287	0.155360	0.571115	0.024*
C24	0.22986 (16)	0.19316 (6)	0.43768 (13)	0.0201 (3)
H24	0.199022	0.159386	0.395561	0.024*
C23	0.17619 (15)	0.24426 (6)	0.39693 (12)	0.0184 (3)
H23	0.107461	0.246448	0.325589	0.022*
C22	0.22304 (14)	0.29418 (6)	0.46112 (12)	0.0155 (3)
C21	0.17602 (15)	0.34958 (6)	0.42809 (12)	0.0160 (3)
C20	0.22712 (15)	0.39587 (5)	0.49410 (12)	0.0158 (3)
H20	0.192449	0.432446	0.469409	0.019*
C19	0.33086 (14)	0.39000 (5)	0.59859 (12)	0.0149 (3)

C33	0.39747 (15)	0.44078 (5)	0.66884 (12)	0.0161 (3)
H33A	0.391454	0.433928	0.760515	0.019*
H33B	0.508195	0.444687	0.648964	0.019*
C31	0.17818 (19)	0.45064 (6)	1.03634 (14)	0.0275 (3)
H31	0.148197	0.416988	1.077902	0.033*
C30	0.2379 (2)	0.49411 (7)	1.10939 (15)	0.0319 (4)
H30	0.248406	0.490490	1.198317	0.038*
C29	0.2820 (2)	0.54326 (7)	1.04912 (15)	0.0336 (4)
H29	0.326388	0.573774	1.095767	0.040*
C28	0.26013 (19)	0.54709 (6)	0.91951 (14)	0.0275 (3)
H28	0.286291	0.580816	0.876508	0.033*
C27	0.19926 (16)	0.50086 (6)	0.85279 (14)	0.0194 (3)
C34	0.17597 (16)	0.50134 (6)	0.71084 (13)	0.0184 (3)
H34A	0.102144	0.470897	0.686968	0.022*
H34B	0.127431	0.537725	0.685943	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02415 (17)	0.01778 (18)	0.01801 (17)	−0.00480 (12)	−0.00494 (12)	0.00060 (11)
Cl2	0.02456 (17)	0.01686 (18)	0.01837 (17)	0.00323 (12)	−0.00578 (12)	0.00063 (11)
O3	0.0250 (5)	0.0100 (5)	0.0223 (5)	−0.0007 (4)	−0.0080 (4)	−0.0009 (4)
O4	0.0214 (5)	0.0092 (5)	0.0218 (5)	0.0009 (4)	−0.0062 (4)	0.0010 (4)
N5	0.0197 (5)	0.0107 (5)	0.0202 (5)	−0.0005 (4)	−0.0009 (4)	−0.0006 (4)
N8	0.0166 (5)	0.0070 (5)	0.0229 (6)	−0.0006 (4)	−0.0004 (4)	0.0003 (4)
N6	0.0197 (5)	0.0100 (5)	0.0205 (5)	0.0008 (4)	−0.0013 (4)	0.0004 (4)
N7	0.0251 (6)	0.0165 (6)	0.0272 (6)	0.0012 (5)	0.0032 (5)	0.0048 (5)
C9	0.0161 (6)	0.0124 (6)	0.0165 (6)	−0.0012 (5)	0.0008 (5)	−0.0002 (5)
C17	0.0158 (6)	0.0120 (6)	0.0174 (6)	−0.0010 (5)	0.0018 (5)	−0.0001 (5)
C16	0.0245 (7)	0.0108 (6)	0.0265 (7)	0.0004 (5)	−0.0019 (5)	−0.0012 (5)
C15	0.0246 (7)	0.0130 (7)	0.0285 (7)	0.0020 (5)	−0.0050 (5)	0.0041 (5)
C14	0.0218 (6)	0.0161 (7)	0.0209 (6)	−0.0003 (5)	−0.0035 (5)	0.0031 (5)
C13	0.0163 (6)	0.0137 (6)	0.0183 (6)	−0.0011 (5)	0.0016 (5)	0.0015 (5)
C12	0.0172 (6)	0.0163 (6)	0.0155 (6)	−0.0024 (5)	−0.0014 (5)	0.0002 (5)
C11	0.0187 (6)	0.0124 (6)	0.0188 (6)	−0.0035 (5)	0.0015 (5)	−0.0020 (5)
C10	0.0163 (6)	0.0106 (6)	0.0188 (6)	−0.0006 (5)	0.0019 (5)	0.0007 (5)
C32	0.0176 (6)	0.0097 (6)	0.0203 (6)	−0.0017 (5)	−0.0005 (5)	−0.0002 (5)
C18	0.0157 (6)	0.0122 (6)	0.0162 (6)	−0.0002 (5)	0.0006 (5)	0.0008 (5)
C26	0.0167 (6)	0.0100 (6)	0.0179 (6)	0.0004 (5)	0.0019 (5)	0.0014 (5)
C25	0.0241 (7)	0.0103 (6)	0.0259 (7)	0.0014 (5)	−0.0023 (5)	0.0004 (5)
C24	0.0237 (7)	0.0130 (6)	0.0234 (7)	−0.0010 (5)	−0.0024 (5)	−0.0038 (5)
C23	0.0201 (6)	0.0153 (7)	0.0198 (6)	0.0000 (5)	−0.0017 (5)	−0.0013 (5)
C22	0.0153 (6)	0.0138 (6)	0.0175 (6)	0.0002 (5)	0.0021 (5)	−0.0002 (5)
C21	0.0165 (6)	0.0164 (6)	0.0153 (6)	0.0014 (5)	−0.0008 (5)	0.0011 (5)
C20	0.0181 (6)	0.0108 (6)	0.0185 (6)	0.0021 (5)	0.0015 (5)	0.0027 (5)
C19	0.0161 (6)	0.0108 (6)	0.0179 (6)	−0.0004 (5)	0.0023 (5)	0.0000 (5)
C33	0.0193 (6)	0.0089 (6)	0.0200 (6)	0.0013 (5)	−0.0022 (5)	0.0001 (5)
C31	0.0342 (8)	0.0202 (7)	0.0285 (7)	0.0053 (6)	0.0057 (6)	0.0063 (6)

C30	0.0424 (9)	0.0289 (9)	0.0247 (8)	0.0089 (7)	0.0054 (7)	−0.0020 (6)
C29	0.0458 (10)	0.0225 (8)	0.0329 (8)	0.0002 (7)	0.0061 (7)	−0.0107 (6)
C28	0.0365 (8)	0.0147 (7)	0.0318 (8)	0.0009 (6)	0.0086 (6)	−0.0026 (6)
C27	0.0183 (7)	0.0138 (6)	0.0265 (7)	0.0036 (5)	0.0042 (5)	0.0013 (5)
C34	0.0171 (6)	0.0119 (6)	0.0262 (7)	0.0009 (5)	0.0008 (5)	0.0031 (5)

Geometric parameters (Å, º)

Cl1—C12	1.7420 (13)	C32—H32A	0.9900
Cl2—C21	1.7476 (13)	C32—H32B	0.9900
O3—H3	0.80 (3)	C18—C26	1.4217 (17)
O3—C9	1.3512 (16)	C18—C19	1.3798 (18)
O4—H4	0.80 (2)	C26—C22	1.4222 (18)
O4—C18	1.3531 (15)	C25—H25	0.9500
N5—C17	1.3659 (17)	C25—C24	1.4128 (19)
N5—C16	1.3175 (17)	C24—H24	0.9500
N8—C32	1.4648 (16)	C24—C23	1.3607 (19)
N8—C33	1.4647 (16)	C23—H23	0.9500
N8—C34	1.4791 (17)	C23—C22	1.4166 (18)
N6—C26	1.3712 (16)	C22—C21	1.4133 (18)
N6—C25	1.3167 (17)	C21—C20	1.3665 (18)
N7—C31	1.3378 (19)	C20—H20	0.9500
N7—C27	1.3464 (18)	C20—C19	1.4124 (18)
C9—C17	1.4283 (18)	C19—C33	1.5184 (17)
C9—C10	1.3800 (18)	C33—H33A	0.9900
C17—C13	1.4204 (18)	C33—H33B	0.9900
C16—H16	0.9500	C31—H31	0.9500
C16—C15	1.4077 (19)	C31—C30	1.379 (2)
C15—H15	0.9500	C30—H30	0.9500
C15—C14	1.365 (2)	C30—C29	1.386 (2)
C14—H14	0.9500	C29—H29	0.9500
C14—C13	1.4125 (18)	C29—C28	1.387 (2)
C13—C12	1.4174 (18)	C28—H28	0.9500
C12—C11	1.3621 (19)	C28—C27	1.397 (2)
C11—H11	0.9500	C27—C34	1.515 (2)
C11—C10	1.4187 (18)	C34—H34A	0.9900
C10—C32	1.5138 (17)	C34—H34B	0.9900
C9—O3—H3	105.9 (17)	N6—C25—C24	124.08 (12)
C18—O4—H4	108.0 (16)	C24—C25—H25	118.0
C16—N5—C17	117.60 (11)	C25—C24—H24	120.6
C32—N8—C34	113.45 (10)	C23—C24—C25	118.77 (12)
C33—N8—C32	112.30 (10)	C23—C24—H24	120.6
C33—N8—C34	112.11 (10)	C24—C23—H23	120.1
C25—N6—C26	117.65 (11)	C24—C23—C22	119.85 (12)
C31—N7—C27	117.51 (13)	C22—C23—H23	120.1
O3—C9—C17	120.04 (11)	C23—C22—C26	117.19 (12)
O3—C9—C10	119.46 (12)	C21—C22—C26	117.51 (12)

C10—C9—C17	120.50 (12)	C21—C22—C23	125.29 (12)
N5—C17—C9	117.40 (11)	C22—C21—Cl2	118.64 (10)
N5—C17—C13	122.48 (12)	C20—C21—Cl2	119.37 (10)
C13—C17—C9	120.12 (12)	C20—C21—C22	121.99 (12)
N5—C16—H16	118.0	C21—C20—H20	119.6
N5—C16—C15	124.08 (12)	C21—C20—C19	120.80 (12)
C15—C16—H16	118.0	C19—C20—H20	119.6
C16—C15—H15	120.5	C18—C19—C20	118.94 (12)
C14—C15—C16	118.93 (12)	C18—C19—C33	118.92 (11)
C14—C15—H15	120.5	C20—C19—C33	122.05 (11)
C15—C14—H14	120.3	N8—C33—C19	113.46 (10)
C15—C14—C13	119.40 (12)	N8—C33—H33A	108.9
C13—C14—H14	120.3	N8—C33—H33B	108.9
C14—C13—C17	117.50 (12)	C19—C33—H33A	108.9
C14—C13—C12	124.77 (12)	C19—C33—H33B	108.9
C12—C13—C17	117.72 (12)	H33A—C33—H33B	107.7
C13—C12—Cl1	119.34 (10)	N7—C31—H31	117.8
C11—C12—Cl1	119.35 (10)	N7—C31—C30	124.44 (14)
C11—C12—C13	121.31 (12)	C30—C31—H31	117.8
C12—C11—H11	119.2	C31—C30—H30	121.0
C12—C11—C10	121.59 (12)	C31—C30—C29	117.97 (15)
C10—C11—H11	119.2	C29—C30—H30	121.0
C9—C10—C11	118.76 (12)	C30—C29—H29	120.6
C9—C10—C32	121.28 (11)	C30—C29—C28	118.82 (15)
C11—C10—C32	119.88 (11)	C28—C29—H29	120.6
N8—C32—C10	111.78 (10)	C29—C28—H28	120.3
N8—C32—H32A	109.3	C29—C28—C27	119.36 (14)
N8—C32—H32B	109.3	C27—C28—H28	120.3
C10—C32—H32A	109.3	N7—C27—C28	121.85 (14)
C10—C32—H32B	109.3	N7—C27—C34	115.75 (12)
H32A—C32—H32B	107.9	C28—C27—C34	122.39 (12)
O4—C18—C26	120.48 (11)	N8—C34—C27	115.70 (11)
O4—C18—C19	118.47 (11)	N8—C34—H34A	108.4
C19—C18—C26	121.03 (12)	N8—C34—H34B	108.4
N6—C26—C18	117.82 (11)	C27—C34—H34A	108.4
N6—C26—C22	122.46 (11)	C27—C34—H34B	108.4
C18—C26—C22	119.72 (11)	H34A—C34—H34B	107.4
N6—C25—H25	118.0		

Cl1—C12—C11—C10	178.85 (10)	C10—C9—C17—N5	−179.81 (11)
Cl2—C21—C20—C19	−179.29 (9)	C10—C9—C17—C13	−0.20 (18)
O3—C9—C17—N5	−0.20 (18)	C32—N8—C33—C19	−147.94 (11)
O3—C9—C17—C13	179.41 (11)	C32—N8—C34—C27	−70.42 (14)
O3—C9—C10—C11	−179.85 (11)	C18—C26—C22—C23	178.85 (11)
O3—C9—C10—C32	−3.14 (18)	C18—C26—C22—C21	−0.80 (18)
O4—C18—C26—N6	1.97 (18)	C18—C19—C33—N8	−170.06 (11)
O4—C18—C26—C22	−177.20 (11)	C26—N6—C25—C24	−0.3 (2)
O4—C18—C19—C20	177.77 (11)	C26—C18—C19—C20	−0.42 (18)

O4—C18—C19—C33	1.26 (17)	C26—C18—C19—C33	−176.94 (11)
N5—C17—C13—C14	−0.56 (19)	C26—C22—C21—Cl2	179.83 (9)
N5—C17—C13—C12	179.70 (11)	C26—C22—C21—C20	0.14 (19)
N5—C16—C15—C14	−0.7 (2)	C25—N6—C26—C18	−178.81 (12)
N6—C26—C22—C23	−0.28 (18)	C25—N6—C26—C22	0.34 (18)
N6—C26—C22—C21	−179.93 (11)	C25—C24—C23—C22	−0.2 (2)
N6—C25—C24—C23	0.3 (2)	C24—C23—C22—C26	0.20 (19)
N7—C31—C30—C29	−0.1 (3)	C24—C23—C22—C21	179.82 (13)
N7—C27—C34—N8	−102.50 (14)	C23—C22—C21—Cl2	0.21 (18)
C9—C17—C13—C14	179.85 (12)	C23—C22—C21—C20	−179.49 (12)
C9—C17—C13—C12	0.11 (18)	C22—C21—C20—C19	0.40 (19)
C9—C10—C32—N8	146.40 (12)	C21—C20—C19—C18	−0.26 (19)
C17—N5—C16—C15	−0.3 (2)	C21—C20—C19—C33	176.14 (12)
C17—C9—C10—C11	−0.24 (18)	C20—C19—C33—N8	13.54 (17)
C17—C9—C10—C32	176.48 (11)	C19—C18—C26—N6	−179.87 (11)
C17—C13—C12—Cl1	−179.32 (9)	C19—C18—C26—C22	0.96 (18)
C17—C13—C12—C11	0.45 (19)	C33—N8—C32—C10	168.06 (10)
C16—N5—C17—C9	−179.45 (12)	C33—N8—C34—C27	58.09 (14)
C16—N5—C17—C13	0.95 (19)	C31—N7—C27—C28	1.1 (2)
C16—C15—C14—C13	1.0 (2)	C31—N7—C27—C34	−179.83 (13)
C15—C14—C13—C17	−0.47 (19)	C31—C30—C29—C28	1.8 (3)
C15—C14—C13—C12	179.26 (13)	C30—C29—C28—C27	−2.1 (2)
C14—C13—C12—Cl1	0.96 (18)	C29—C28—C27—N7	0.6 (2)
C14—C13—C12—C11	−179.27 (13)	C29—C28—C27—C34	−178.39 (14)
C13—C12—C11—C10	−0.9 (2)	C28—C27—C34—N8	76.56 (17)
C12—C11—C10—C9	0.81 (19)	C27—N7—C31—C30	−1.4 (2)
C12—C11—C10—C32	−175.96 (12)	C34—N8—C32—C10	−63.52 (14)
C11—C10—C32—N8	−36.92 (16)	C34—N8—C33—C19	82.95 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···N5	0.80 (3)	2.24 (2)	2.7337 (15)	121 (2)
O3—H3···N6^{i}	0.80 (3)	2.25 (2)	2.8362 (15)	131 (2)
O4—H4···N6	0.80 (2)	2.29 (2)	2.7485 (15)	117 (2)
O4—H4···N5^{ii}	0.80 (2)	2.22 (2)	2.8456 (15)	136 (2)
C34—H34*A*···Cl1^{iii}	0.99	2.78	3.7082 (15)	157

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+3/2; (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) −*x*, −*y*+1, −*z*+1.