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# Crystal structure of (*E*)-3-({6-[2-(4-chlorophenyl)-ethenyl]-3-oxo-2,3-dihydropyridazin-4-yl}methyl)-pyridin-1-ium chloride dihydrate

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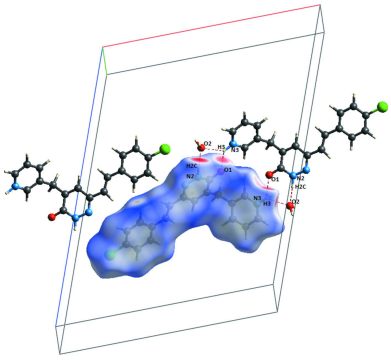
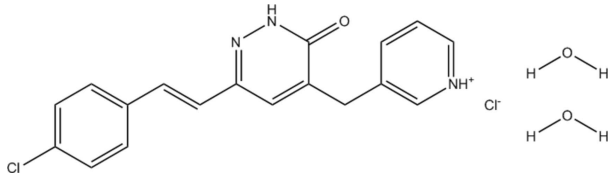
In the title compound, $C_{18}H_{15}ClN_3O^+\cdot Cl^-\cdot 2H_2O$, three intramolecular hydrogen bonds are observed, N—H···O, O—H···Cl and O—H···O. In the crystal, molecules are connected by C—H···Cl and N—H···O hydrogen bonds. Strong C—H···Cl, N—H···O, O—H···Cl and O—H···O hydrogen-bonding interactions are implied by the Hirshfeld surface analysis, which indicate that H···H contacts make the largest contribution to the overall crystal packing at 33.0%.

## 1. Chemical context

Pyridazine derivatives are an important class of heterocyclic chemicals that exhibit a wide range of biological actions. For example, their biological activity and antimicrobial properties have been researched extensively (Neumann *et al.*, 2018). As a result, the pyridazine ring can be found in a range of commercial medicinal compounds, including Cadralazine and Hydralazine, Minaprine, Pipofezine and others (Abu-Hashem *et al.*, 2020). Pyridazine derivatives can be found also in the backbones of several organic light-emitting diodes (OLEDs) (Liu *et al.*, 2017), organic solar cells (OSCs) (Knall *et al.*, 2021), chemosensors (Peng *et al.*, 2020), trifluoroacetic acid (TFA) sensors (Li *et al.*, 2018), bioconjugates (Bahou *et al.*, 2021), low carbon steel corrosion inhibitors (Khadiria *et al.*, 2016), and several other materials. They have also been used as starting materials in organic synthesis (Llona-Minguez *et al.*, 2017), acylating agents (Kung *et al.*, 2002), precursors for N-heterocyclic carbenes (NHCs) (Liu *et al.*, 2012) and metallocarbene precursors. An overview of arylglyoxal monohydrates-based one-pot multi-component synthesis of potentially biologically active pyridazines is given by Mousavi (2022).





## 2. Structural commentary

A perspective view of the title molecule is shown in Fig. 1. The pyridazine and pyridine rings subtend a dihedral angle of 57.27 (5)°. The other two rings, pyridazine and chlorobenzene,

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C10—H10···Cl2$^{i}$ | 0.93 | 2.72 | 3.6387 (19) | 168 |
| C18—H18···Cl2$^{ii}$ | 0.93 | 2.94 | 3.622 (2) | 132 |
| N3—H3···O2$^{iii}$ | 0.80 (3) | 2.35 (3) | 2.965 (2) | 135 (2) |
| N3—H3···O1$^{iii}$ | 0.80 (3) | 2.25 (3) | 2.855 (2) | 133 (3) |
| N2—H2*C*···O2 | 0.86 (2) | 1.97 (2) | 2.801 (2) | 161 (2) |
| O2—H2*A*···Cl2 | 0.83 (2) | 2.35 (2) | 3.170 (2) | 175 (3) |
| O2—H2*B*···O3 | 0.84 (2) | 1.92 (2) | 2.739 (3) | 167 (3) |

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

are almost planar, making an angle of 8.54 (11)°. The lengths of the C═C [1.349 (3) Å], C═N [1.313 (2) Å], N—N [1.351 (2) Å] and C=O [1.237 (2) Å] bonds are comparable with values published for other pyridazinones (see the *Database survey* section). Three intramolecular hydrogen bonds are observed, N2—H2*C*···O2, O2—H2*A*···Cl2 and O2—H2*B*···O3 (Table 1).

## 3. Supramolecular features

The water molecules and chloride anions are located in channels between the organic cations and are connected by O—H···O and O—H···Cl hydrogen bonds (Table 1) into chains, which are further connected *via* N—H···O and C—H···Cl hydrogen bonds into a three-dimensional supramolecular architecture. Fig. 2*a* shows a view of the hydrogen bonds along the *b*-axis direction. $\pi$–$\pi$ interactions are present (Fig. 2*b*) between the pyridazine rings [centroid–centroid distance = 3.4902 (12) Å], and also between the pyridine and benzene rings [3.7293 (13) and 3.8488 (13) Å], forming sheets.

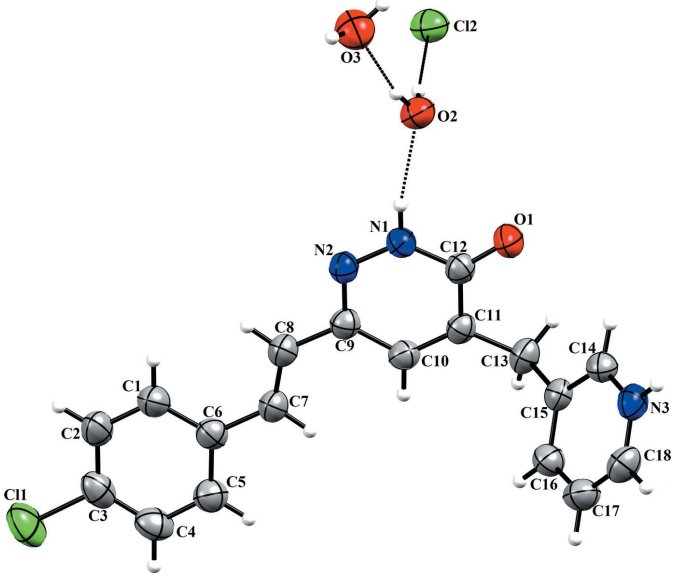



**Figure 1**
Perspective view and atom labelling of the molecule. Displacement ellipsoids are drawn at the 50% probability level.

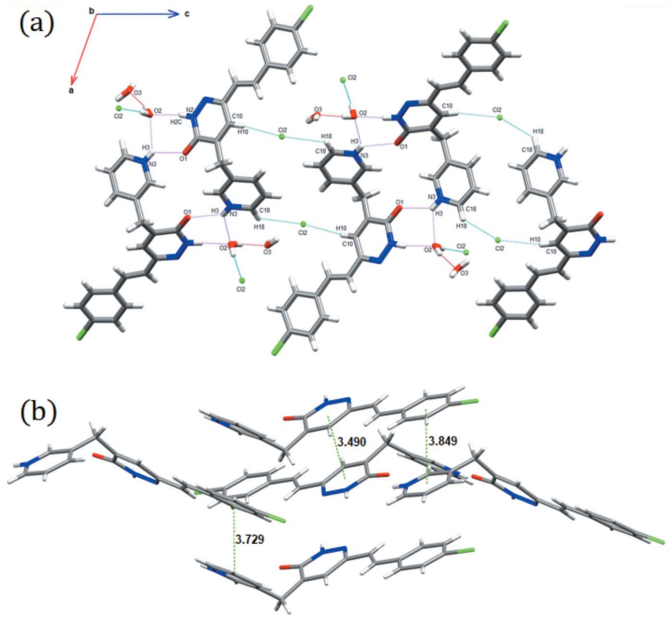



**Figure 2**
(*a*)View along the *b* axis of the unit cell showing the molecular sheets. (*b*) $\pi$–$\pi$ interactions.

## 4. Database survey

There are no direct precedents for the structure of the title compound in the crystallographic literature. A search of the Cambridge Structural Database (*ConQuest* version 2021.3.0; Groom *et al.*, 2016) for the 2,3-dihydropyridazin-4-yl moiety gave various hits, four of them for similar pyridazine compounds but with different substituents on the pyridazine ring: 5-(2-chlorobenzyl)-6-methyl-3(2*H*)pyridazinone (ZAYJIS; Moreau *et al.*, 1995), 2-{4-[(5-chloro- 1-benzofuran-2-yl)methyl]-3-methyl-6- oxo-1,6-dihydropyridazin-1-yl}acetate (XULSEE; Boukharsa *et al.*, 2015) , 4-[3-(trifluoromethyl)phenyl]-5,6,7,8-tetrahydrocinnolin-3(2*H*)-one (GISZAK; Wang *et al.*, 2008) and 5-(2-Chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazin-3(2*H*)-one (IJEMOZ; Abourichaa *et al.*, 2003). In ZAYJIS, the lengths of the C═C [1.343 (3) Å], C═N [1.301 (4) Å], N—N [1.357 (3) Å] and C═O [1.255 (3) Å] bonds in the pyridazinone ring are very similar to those in the title compound. In XULSEE, te Cl—C1 bond length is 1.742 (2) Å while in the pyridazine ring, the N1—N2 bond length is 1.365 (2) Å and O2═C2 is 1.228 (2) Å. In GISZAK, the N1—N2 bond is 1.343 (5) Å whereas the C8═O1 bond is 1.246 (5) Å. In IJEMOZ, the pyridazinone ring has a similar value for the N4—N5 bond of 1.367 (2) Å.

## 5. Hirshfeld surface analysis

To investigate the effect of the molecular interactions on the crystal packing, the Hirshfeld surface (Fig. 3) and fingerprint plots of the organic cation were analysed (Turner *et al.*, 2017). In Fig. 4*a*, the circular depressions (deep red) on the Hirshfeld surface imply strong hydrogen-bonding interactions of types C—H···Cl, N—H···O, O—H···Cl and O—H···O. In the

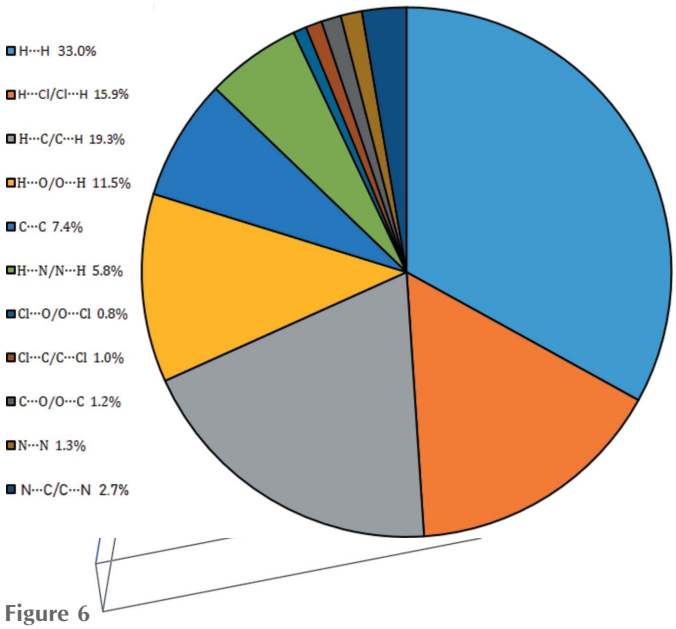



**Figure 6**
All interactions with percentage contributions.

shape-index map (Fig. 4*b*), the $\pi$–$\pi$ interactions are indicated by the red and blue triangles. Fig. 4*c* and Fig. 4*d* show $d_i$ and $d_e$ surfaces and Fig. 4*e* and 4*f* the curvedness and fragment path surfaces. Fig. 5*a* shows the overall two-dimensional fingerprint plot. The fingerprint plot delineated into H···H contacts (33.0% contribution, Fig. 5*b*) has a point with the tip at $d_e + d_i$ = 2.05 Å. The pair of wings in the fingerprint plot defined into H···C/C···H contacts (19.3 percent contribution to the HS), Fig.5*c*, has a pair of thin edges at $d_e + d_i$ ~2.99 Å while the pair of wings for the H···Cl/Cl···H contacts (15.9% contribution, Fig. 5*d*) are seen as two spikes with the points at $d_e + d_i$ = 2.97 Å and $d_e + d_i$ = 2.41 Å. The fingerprint plot for H···O/O···H contacts (11.5% contribution, Fig. 5*e*) has two spikes with the tips at $d_e + d_i$ = 2.11 Å and $d_e + d_i$ = 1.83 Å. As seen in Fig. 5*f* the C···C contacts (7.4%) have an arrow-shaped distribution of points with tips at $d_e + d_i$ = 3.37 Å. The contributions of the N···H/H···N contacts to the Hirshfeld surface (5.8%) are less important (Fig. 5*g*). Fig. 6 shows a pie chart of all interactions with their percentage contributions.

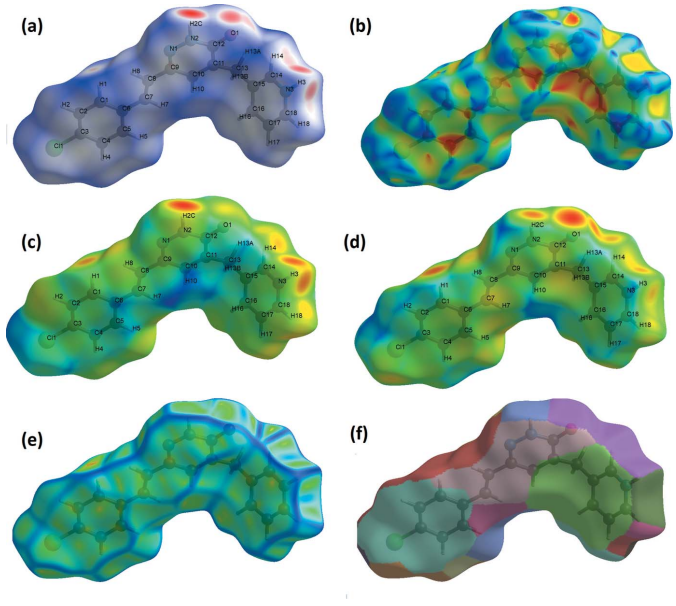



**Figure 4**
Graphical depictions of the molecular Hirshfeld surfaces; (*a*) $d_{norm}$, (*b*)shape-index, (*c*) $d_i$, (*d*) $d_e$,(*e*) curvedness and (*f*) fragment-path.

## 6. Synthesis and crystallization

The title compound was synthesized according to a previously published procedure (Daoui *et al.*, 2019, 2021). To a solution of (*E*)-6-(4-chlorostyryl)-4,5-dihydropyridazin-3(2*H*)-one

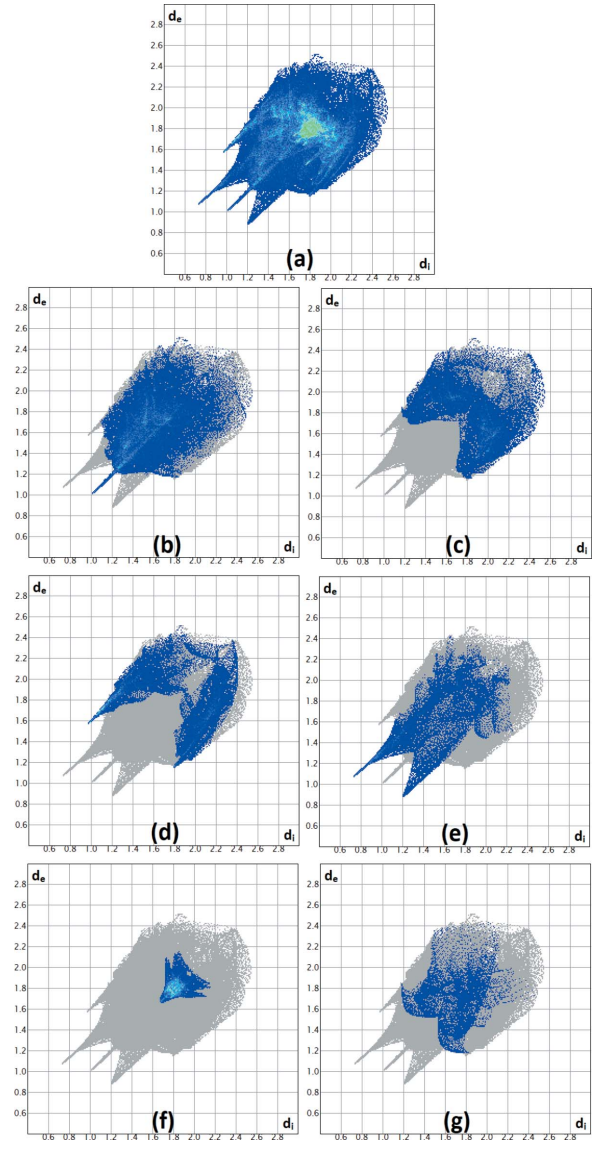



**Figure 5**
Fingerprint plots of the interactions involving the organic cation. (*a*) All contributions and decomposed into the main contributions: (*b*) H···H, (*c*) H···C/C···H, (*d*) H···Cl/Cl···H, (*e*) H···O/O···H, (*f*) C···C and (*g*) N···H/H···N interactions

(0.23 g, 1 mmol) and nicotinaldehyde (0.107 g, 1 mmol) in 30 ml of ethanol, sodium ethanoate (0.23 g, 2.8 mmol) was added. The mixture was refluxed for 3 h. The reaction mixture was cooled, diluted with cold water and acidified with concentrated hydrochloric acid. The precipitate was filtered, washed with water, dried and recrystallized from ethanol. White single crystals were obtained by slow evaporation at room temperature, yield 86%; m.p. 453 K; FT–IR (KBr): $\nu$ 3322 (NH), 1651 (C═O), 1584 cm$^{-1}$ (C═N); $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 13.20 (*s*, 1H, H-pyridyl) , 8.98 (*d*, *J* = 1.8 Hz, 1H, H-pyridyl), 8.83 (*d*, *J* = 5.6 Hz, 1H, H-pyridyl), 8.57 (*dt*, *J* = 8.1, 1.8 Hz, 1H, H-pyridyl), 8.05 (*s*, 1H, H-pyridazinone) 8.02 (*dd*, *J* = 8.1, 5.6 Hz, 1H, H-pyridyl), 7.65 (*d*, *J* = 8.4 Hz, 2H, H1, H-Ar), 7.45 (*d*, *J* = 8.4 Hz, 2H, H 4, H-Ar), 7.36 (*d*, *J* = 16.7 Hz, 1H, CH═CH), 7.08 (,*d J* = 16.7 Hz, 1H, CH=CH), 4.09 ppm (*s*, 2H, $CH_2$); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 160.43, 145.98, 143.89, 141.87, 140.05, 139.25, 137.97, 134.90, 132.84,130.85, 128.82, 128.62, 128.54, 126.80, 125.08, 32.33 ppm. ESI-MS: *m/z* = 324.08 $[M+H]^+$.

## 7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound H atoms were placed in calculated positions (C—H = 0.93–0.98 Å) and thereafter treated as riding. A torsional parameter was refined for the methyl group. The positions of N- and O-bound H atoms were refined freely (distances are in Table 1). For all H atoms, $U_{iso}$(H) = 1.2 $U_{eq}$(C,N,O).

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{18}H_{15}ClN_3O^+\cdot Cl^-\cdot 2H_2O$ |
| $M_r$ | 396.26 |
| Crystal system, space group | Monoclinic, *I*2/*a* |
| Temperature (K) | 296 |
| *a*, *b*, *c* (Å) | 19.6562 (14), 7.5587 (3), 26.4903 (16) |
| $\beta$ (°) | 109.762 (5) |
| *V* (Å$^3$) | 3704.0 (4) |
| *Z* | 8 |
| Radiation type | Mo *K*$\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.37 |
| Crystal size (mm) | 0.68 × 0.41 × 0.16 |
| | |
| Data collection | |
| Diffractometer | Stoe IPDS 2 |
| Absorption correction | Numerical (*X-RED32*; Stoe & Cie, 2002) |
| $T_{min}$, $T_{max}$ | 0.818, 0.961 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 13762, 5273, 3083 |
| $R_{int}$ | 0.064 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.702 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.050, 0.142, 0.98 |
| No. of reflections | 5273 |
| No. of parameters | 265 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.26, −0.43 |

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT2018/3* (Sheldrick, 2015*a*), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2020), *WinGX* (Farrugia, 2012), *SHELXL2018/3* (Sheldrick, 2015*b*), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).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# supporting information

*Acta Cryst.* (2022). E**78**, 458-462 [https://doi.org/10.1107/S2056989022003346]

# Crystal structure of (*E*)-3-({6-[2-(4-chlorophenyl)ethenyl]-3-oxo-2,3-dihydropyridazin-4-yl}methyl)pyridin-1-ium chloride dihydrate

**Said Daoui, Emine Berrin Çınar, Necmi Dege, Noureddine Benchat, Eiad Saif and Khalid Karrouchi**

## Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXT2018/3* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *SHELXL2018/3* (Sheldrick, 2015b), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

**(*E*)-3-({6-[2-(4-Chlorophenyl)ethenyl]-3-oxo-2,3-dihydropyridazin-4-yl}methyl)pyridin-1-ium chloride dihydrate**

*Crystal data*

$C_{18}H_{15}ClN_3O^+\cdot Cl^-\cdot 2H_2O$
$M_r$ = 396.26
Monoclinic, *I*2/*a*
*a* = 19.6562 (14) Å
*b* = 7.5587 (3) Å
*c* = 26.4903 (16) Å
*β* = 109.762 (5)°
*V* = 3704.0 (4) Å$^3$
*Z* = 8
*F*(000) = 1648
$D_x$ = 1.421 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 18653 reflections
*θ* = 1.6–30.3°
*μ* = 0.37 mm$^{-1}$
*T* = 296 K
Prism, colorless
0.68 × 0.41 × 0.16 mm

*Data collection*

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: numerical (X-RED32; Stoe & Cie, 2002)
$T_{min}$ = 0.818, $T_{max}$ = 0.961
13762 measured reflections
5273 independent reflections
3083 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.064
$\theta_{max}$ = 29.9°, $\theta_{min}$ = 1.6°
*h* = −21→27
*k* = −8→10
*l* = −36→36

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.142
*S* = 0.98
5273 reflections
265 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å$^{-3}$
$\Delta\rho_{min} = -0.43$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl2 | 0.43892 (4) | 0.44826 (8) | 0.29544 (2) | 0.06204 (18) |
| Cl1 | 0.16095 (4) | 0.93975 (11) | 0.67565 (3) | 0.0831 (2) |
| O2 | 0.51631 (9) | 0.7860 (3) | 0.36086 (6) | 0.0569 (4) |
| O1 | 0.63332 (8) | 0.6580 (2) | 0.47656 (6) | 0.0603 (4) |
| N2 | 0.52423 (9) | 0.7727 (2) | 0.46837 (7) | 0.0440 (4) |
| N1 | 0.46811 (9) | 0.8166 (2) | 0.48443 (6) | 0.0437 (4) |
| O3 | 0.47043 (12) | 1.0366 (3) | 0.28189 (9) | 0.0724 (5) |
| N3 | 0.83161 (10) | 0.6802 (3) | 0.61940 (8) | 0.0521 (4) |
| C11 | 0.58620 (10) | 0.6148 (3) | 0.54755 (7) | 0.0414 (4) |
| C9 | 0.47235 (10) | 0.7645 (3) | 0.53269 (7) | 0.0427 (4) |
| C12 | 0.58492 (10) | 0.6822 (3) | 0.49587 (7) | 0.0434 (4) |
| C15 | 0.71539 (10) | 0.5767 (3) | 0.61025 (7) | 0.0420 (4) |
| C6 | 0.34431 (11) | 0.8182 (3) | 0.61458 (8) | 0.0470 (5) |
| C10 | 0.53148 (11) | 0.6600 (3) | 0.56490 (7) | 0.0441 (4) |
| H10 | 0.5323 | 0.6223 | 0.5985 | 0.053* |
| C8 | 0.41189 (11) | 0.8140 (3) | 0.54971 (8) | 0.0477 (5) |
| H8 | 0.3747 | 0.8785 | 0.5256 | 0.057* |
| C7 | 0.40518 (11) | 0.7752 (3) | 0.59642 (8) | 0.0481 (5) |
| H7 | 0.4434 | 0.7136 | 0.6206 | 0.058* |
| C14 | 0.76951 (11) | 0.6075 (3) | 0.58944 (8) | 0.0479 (5) |
| H14 | 0.7626 | 0.5772 | 0.5540 | 0.057* |
| C13 | 0.64570 (11) | 0.4898 (3) | 0.57732 (8) | 0.0496 (5) |
| H13A | 0.6554 | 0.4116 | 0.5515 | 0.060* |
| H13B | 0.6288 | 0.4173 | 0.6009 | 0.060* |
| C5 | 0.34973 (12) | 0.7804 (3) | 0.66698 (9) | 0.0540 (5) |
| H5 | 0.3919 | 0.7288 | 0.6898 | 0.065* |
| C16 | 0.72876 (12) | 0.6223 (3) | 0.66349 (8) | 0.0514 (5) |
| H16 | 0.6936 | 0.6025 | 0.6792 | 0.062* |
| C18 | 0.84516 (12) | 0.7257 (3) | 0.67006 (9) | 0.0577 (5) |
| H18 | 0.8892 | 0.7768 | 0.6897 | 0.069* |
| C3 | 0.23208 (13) | 0.8927 (3) | 0.65221 (9) | 0.0566 (6) |
| C2 | 0.22442 (12) | 0.9330 (3) | 0.60014 (9) | 0.0583 (6) |
| H2 | 0.1820 | 0.9840 | 0.5776 | 0.070* |
| C1 | 0.28082 (12) | 0.8966 (3) | 0.58179 (9) | 0.0561 (5) |

| | | | | |
|---|---|---|---|---|
| H1 | 0.2762 | 0.9252 | 0.5466 | 0.067* |
| C17 | 0.79392 (13) | 0.6969 (3) | 0.69313 (9) | 0.0593 (6) |
| H17 | 0.8029 | 0.7274 | 0.7288 | 0.071* |
| C4 | 0.29405 (13) | 0.8174 (3) | 0.68616 (9) | 0.0600 (6) |
| H4 | 0.2986 | 0.7917 | 0.7215 | 0.072* |
| H3 | 0.8616 (16) | 0.701 (4) | 0.6061 (11) | 0.070 (8)* |
| H2C | 0.5201 (13) | 0.802 (3) | 0.4362 (10) | 0.053 (6)* |
| H2A | 0.4937 (17) | 0.700 (3) | 0.3444 (12) | 0.094 (11)* |
| H2B | 0.5030 (16) | 0.874 (3) | 0.3409 (10) | 0.079 (9)* |
| H3A | 0.495 (3) | 1.018 (6) | 0.2630 (17) | 0.127 (16)* |
| H3B | 0.466 (2) | 1.141 (6) | 0.2847 (14) | 0.095 (13)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl2 | 0.0694 (4) | 0.0648 (4) | 0.0496 (3) | 0.0006 (3) | 0.0170 (2) | 0.0021 (2) |
| Cl1 | 0.0642 (4) | 0.1042 (6) | 0.0982 (5) | −0.0103 (4) | 0.0502 (4) | −0.0206 (4) |
| O2 | 0.0539 (9) | 0.0660 (12) | 0.0463 (8) | 0.0028 (9) | 0.0111 (7) | 0.0035 (8) |
| O1 | 0.0471 (8) | 0.0848 (12) | 0.0534 (8) | 0.0146 (8) | 0.0229 (7) | 0.0071 (8) |
| N2 | 0.0415 (8) | 0.0494 (10) | 0.0429 (8) | 0.0012 (8) | 0.0168 (7) | 0.0023 (7) |
| N1 | 0.0375 (8) | 0.0469 (10) | 0.0463 (8) | 0.0001 (7) | 0.0138 (7) | 0.0001 (7) |
| O3 | 0.0801 (14) | 0.0676 (14) | 0.0748 (12) | 0.0046 (11) | 0.0331 (10) | 0.0102 (10) |
| N3 | 0.0397 (9) | 0.0596 (12) | 0.0591 (10) | 0.0003 (9) | 0.0195 (8) | 0.0078 (8) |
| C11 | 0.0363 (9) | 0.0416 (10) | 0.0427 (9) | −0.0032 (8) | 0.0089 (7) | −0.0017 (7) |
| C9 | 0.0394 (9) | 0.0448 (11) | 0.0431 (9) | −0.0026 (9) | 0.0128 (7) | −0.0010 (8) |
| C12 | 0.0385 (9) | 0.0455 (11) | 0.0454 (9) | −0.0018 (8) | 0.0130 (8) | −0.0034 (8) |
| C15 | 0.0373 (9) | 0.0417 (11) | 0.0445 (9) | 0.0049 (8) | 0.0107 (7) | 0.0040 (7) |
| C6 | 0.0431 (10) | 0.0513 (12) | 0.0468 (10) | −0.0051 (9) | 0.0153 (8) | −0.0065 (8) |
| C10 | 0.0424 (10) | 0.0486 (12) | 0.0396 (9) | −0.0033 (9) | 0.0116 (8) | 0.0009 (8) |
| C8 | 0.0402 (10) | 0.0529 (12) | 0.0479 (10) | 0.0024 (9) | 0.0123 (8) | −0.0003 (8) |
| C7 | 0.0390 (10) | 0.0570 (13) | 0.0463 (10) | 0.0018 (9) | 0.0119 (8) | −0.0015 (8) |
| C14 | 0.0458 (11) | 0.0560 (12) | 0.0423 (9) | 0.0039 (10) | 0.0154 (8) | 0.0037 (8) |
| C13 | 0.0397 (10) | 0.0481 (12) | 0.0552 (10) | 0.0008 (9) | 0.0085 (9) | 0.0019 (9) |
| C5 | 0.0495 (11) | 0.0632 (14) | 0.0496 (11) | −0.0041 (11) | 0.0171 (9) | −0.0003 (9) |
| C16 | 0.0483 (11) | 0.0615 (13) | 0.0473 (10) | 0.0002 (10) | 0.0200 (9) | 0.0003 (9) |
| C18 | 0.0437 (11) | 0.0615 (14) | 0.0594 (12) | −0.0045 (10) | 0.0062 (9) | 0.0012 (10) |
| C3 | 0.0494 (11) | 0.0620 (14) | 0.0662 (13) | −0.0148 (11) | 0.0297 (10) | −0.0187 (10) |
| C2 | 0.0414 (11) | 0.0720 (16) | 0.0589 (12) | −0.0006 (11) | 0.0133 (9) | −0.0128 (11) |
| C1 | 0.0500 (11) | 0.0731 (15) | 0.0453 (10) | 0.0025 (11) | 0.0163 (9) | −0.0048 (10) |
| C17 | 0.0588 (13) | 0.0703 (16) | 0.0449 (10) | −0.0028 (12) | 0.0125 (10) | −0.0049 (10) |
| C4 | 0.0611 (14) | 0.0736 (16) | 0.0527 (12) | −0.0123 (12) | 0.0290 (11) | −0.0046 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C3 | 1.748 (2) | C6—C1 | 1.389 (3) |
| O2—H2A | 0.825 (18) | C6—C7 | 1.469 (3) |
| O2—H2B | 0.837 (18) | C10—H10 | 0.9300 |
| O1—C12 | 1.237 (2) | C8—C7 | 1.321 (3) |

| | | | |
|---|---|---|---|
| N2—N1 | 1.351 (2) | C8—H8 | 0.9300 |
| N2—C12 | 1.354 (3) | C7—H7 | 0.9300 |
| N2—H2C | 0.86 (2) | C14—H14 | 0.9300 |
| N1—C9 | 1.313 (2) | C13—H13A | 0.9700 |
| O3—H3A | 0.81 (5) | C13—H13B | 0.9700 |
| O3—H3B | 0.80 (4) | C5—C4 | 1.382 (3) |
| N3—C18 | 1.322 (3) | C5—H5 | 0.9300 |
| N3—C14 | 1.329 (3) | C16—C17 | 1.376 (3) |
| N3—H3 | 0.80 (3) | C16—H16 | 0.9300 |
| C11—C10 | 1.349 (3) | C18—C17 | 1.361 (3) |
| C11—C12 | 1.453 (3) | C18—H18 | 0.9300 |
| C11—C13 | 1.503 (3) | C3—C4 | 1.369 (4) |
| C9—C10 | 1.426 (3) | C3—C2 | 1.370 (3) |
| C9—C8 | 1.455 (3) | C2—C1 | 1.380 (3) |
| C15—C14 | 1.373 (3) | C2—H2 | 0.9300 |
| C15—C16 | 1.388 (3) | C1—H1 | 0.9300 |
| C15—C13 | 1.504 (3) | C17—H17 | 0.9300 |
| C6—C5 | 1.386 (3) | C4—H4 | 0.9300 |

| | | | |
|---|---|---|---|
| H2A—O2—H2B | 107 (3) | N3—C14—C15 | 120.65 (18) |
| N1—N2—C12 | 128.25 (16) | N3—C14—H14 | 119.7 |
| N1—N2—H2C | 116.0 (16) | C15—C14—H14 | 119.7 |
| C12—N2—H2C | 115.7 (16) | C11—C13—C15 | 115.12 (17) |
| C9—N1—N2 | 116.31 (16) | C11—C13—H13A | 108.5 |
| H3A—O3—H3B | 109 (4) | C15—C13—H13A | 108.5 |
| C18—N3—C14 | 122.87 (19) | C11—C13—H13B | 108.5 |
| C18—N3—H3 | 118 (2) | C15—C13—H13B | 108.5 |
| C14—N3—H3 | 119 (2) | H13A—C13—H13B | 107.5 |
| C10—C11—C12 | 118.06 (18) | C4—C5—C6 | 121.6 (2) |
| C10—C11—C13 | 123.32 (18) | C4—C5—H5 | 119.2 |
| C12—C11—C13 | 118.51 (17) | C6—C5—H5 | 119.2 |
| N1—C9—C10 | 121.28 (17) | C17—C16—C15 | 120.08 (19) |
| N1—C9—C8 | 115.79 (17) | C17—C16—H16 | 120.0 |
| C10—C9—C8 | 122.88 (17) | C15—C16—H16 | 120.0 |
| O1—C12—N2 | 120.86 (17) | N3—C18—C17 | 119.2 (2) |
| O1—C12—C11 | 124.57 (18) | N3—C18—H18 | 120.4 |
| N2—C12—C11 | 114.55 (16) | C17—C18—H18 | 120.4 |
| C14—C15—C16 | 117.37 (19) | C4—C3—C2 | 121.6 (2) |
| C14—C15—C13 | 121.23 (17) | C4—C3—Cl1 | 119.49 (17) |
| C16—C15—C13 | 121.36 (18) | C2—C3—Cl1 | 118.91 (19) |
| C5—C6—C1 | 117.58 (18) | C3—C2—C1 | 118.8 (2) |
| C5—C6—C7 | 119.16 (19) | C3—C2—H2 | 120.6 |
| C1—C6—C7 | 123.26 (18) | C1—C2—H2 | 120.6 |
| C11—C10—C9 | 121.28 (17) | C2—C1—C6 | 121.6 (2) |
| C11—C10—H10 | 119.4 | C2—C1—H1 | 119.2 |
| C9—C10—H10 | 119.4 | C6—C1—H1 | 119.2 |
| C7—C8—C9 | 125.74 (19) | C18—C17—C16 | 119.8 (2) |
| C7—C8—H8 | 117.1 | C18—C17—H17 | 120.1 |

| | | | |
|---|---|---|---|
| C9—C8—H8 | 117.1 | C16—C17—H17 | 120.1 |
| C8—C7—C6 | 127.5 (2) | C3—C4—C5 | 118.8 (2) |
| C8—C7—H7 | 116.3 | C3—C4—H4 | 120.6 |
| C6—C7—H7 | 116.3 | C5—C4—H4 | 120.6 |
| | | | |
| C12—N2—N1—C9 | −0.4 (3) | C13—C15—C14—N3 | −178.22 (19) |
| N2—N1—C9—C10 | −3.0 (3) | C10—C11—C13—C15 | −100.2 (2) |
| N2—N1—C9—C8 | 179.47 (17) | C12—C11—C13—C15 | 83.7 (2) |
| N1—N2—C12—O1 | −177.03 (19) | C14—C15—C13—C11 | −92.5 (2) |
| N1—N2—C12—C11 | 4.6 (3) | C16—C15—C13—C11 | 90.2 (2) |
| C10—C11—C12—O1 | 176.3 (2) | C1—C6—C5—C4 | 0.5 (3) |
| C13—C11—C12—O1 | −7.4 (3) | C7—C6—C5—C4 | −179.8 (2) |
| C10—C11—C12—N2 | −5.4 (3) | C14—C15—C16—C17 | 0.6 (3) |
| C13—C11—C12—N2 | 170.88 (18) | C13—C15—C16—C17 | 178.0 (2) |
| C12—C11—C10—C9 | 2.6 (3) | C14—N3—C18—C17 | 0.3 (4) |
| C13—C11—C10—C9 | −173.49 (19) | C4—C3—C2—C1 | 0.0 (4) |
| N1—C9—C10—C11 | 1.8 (3) | Cl1—C3—C2—C1 | 179.66 (18) |
| C8—C9—C10—C11 | 179.15 (19) | C3—C2—C1—C6 | 0.9 (4) |
| N1—C9—C8—C7 | 179.9 (2) | C5—C6—C1—C2 | −1.1 (3) |
| C10—C9—C8—C7 | 2.5 (3) | C7—C6—C1—C2 | 179.2 (2) |
| C9—C8—C7—C6 | −178.2 (2) | N3—C18—C17—C16 | −0.5 (4) |
| C5—C6—C7—C8 | −174.2 (2) | C15—C16—C17—C18 | 0.0 (4) |
| C1—C6—C7—C8 | 5.4 (4) | C2—C3—C4—C5 | −0.5 (4) |
| C18—N3—C14—C15 | 0.3 (3) | Cl1—C3—C4—C5 | 179.77 (19) |
| C16—C15—C14—N3 | −0.8 (3) | C6—C5—C4—C3 | 0.3 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C10—H10···Cl2$^{i}$ | 0.93 | 2.72 | 3.6387 (19) | 168 |
| C18—H18···Cl2$^{ii}$ | 0.93 | 2.94 | 3.622 (2) | 132 |
| N3—H3···O2$^{iii}$ | 0.80 (3) | 2.35 (3) | 2.965 (2) | 135 (2) |
| N3—H3···O1$^{iii}$ | 0.80 (3) | 2.25 (3) | 2.855 (2) | 133 (3) |
| N2—H2*C*···O2 | 0.86 (2) | 1.97 (2) | 2.801 (2) | 161 (2) |
| O2—H2*A*···Cl2 | 0.83 (2) | 2.35 (2) | 3.170 (2) | 175 (3) |
| O2—H2*B*···O3 | 0.84 (2) | 1.92 (2) | 2.739 (3) | 167 (3) |

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