Synthesis and crystal structure of 1,3-bis(4-hydroxyphenyl)-1H-imidazol-3-ium chloride

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Synthesis and crystal structure of 1,3-bis(4-hydroxyphenyl)-1H-imidazol-3-ium chloride

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Imidazolium salts are common building blocks for functional materials and in the synthesis of N-heterocyclic carbene (NHC) as σ-donor ligands for stable metal complexes. The title salt, 1,3-bis(4-hydroxyphenyl)-1H-imidazol-3-ium chloride (IOH-Cl), C_{15}H_{13}N_{2}O_{2}^{+}Cl^{-}, is a new imidazolium salt with a hydroxy functionality. The synthesis of IOH-Cl was achieved in high yield via a two-step procedure involving a diazabutadiene precursor followed by ring closure using trimethylchlorosilane and paraformaldehyde. The structure of IOH-Cl consists of a central planar imidazolium ring (r.m.s. deviation = 0.0015 Å), with out-of-plane phenolic side arms. The dihedral angles between the 4-hydroxyphenyl substituents and the imidazole ring are 55.27 (7) and 48.85 (11)°. In the crystal, O−H⋯Cl hydrogen bonds connect the distal hydroxy groups and Cl− anions in adjacent asymmetric units, one related by inversion (−x + 1, −y + 1, −z + 1) and one by the n-glide (x − 1/2, −y + 1/2, z − 1/2), with donor–acceptor distances of 2.977 (2) and 3.0130 (18) Å, respectively. The phenolic rings are each π−π stacked with their respective inversion-related [(−x + 1, −y + 1, −z + 1) and (−x, −y + 1, −z + 1)] counterparts, with interplanar distances of 3.560 (3) and 3.778 (3) Å. The only other noteworthy intermolecular interaction is an O−O (not hydrogen bonded) close contact of 2.999 (3) Å between crystallographically different hydroxy O atoms on translationally adjacent molecules (x + 1, y, x + 1).

1. Chemical context

N-Heterocyclic carbenes (NHCs) represent a versatile class of ligand systems for metal-center activation or stabilization in modern organic synthesis (Arduengo et al., 1999; Benhamou et al., 2011). Chemically, carbenes are nucleophilic ‘phosphine mimics’ that are high in the order of the Tolman electronic and steric parameter scales, which influences their reactivity. Metal complexes bearing NHC ligands are found in many catalytic reactions (Flanigan et al., 2015; Hopkinson et al., 2014; Huynh, 2018; Marion & Nolan, 2008; Scholl et al., 1999; Velazquez & Verpoort, 2012; Wang et al., 2018), and recently have shown promise as cytotoxic agents (Garrison & Youngs, 2005; Lam et al., 2018; Liu & Gust, 2013; Mora et al., 2019; Rienert et al., 2014; Zou et al., 2018). Imidazolium salts, which are simple salts of the free carbene, are commonly used in many systems in preference to their free carbene counterparts due to their high stability. Unlike the free carbenes, which readily react with water or oxygen (Alder et al., 1995), imidazolium salts are indefinitely stable. Use of the imidazolium salt does not require Schlenk techniques and the corresponding ‘free’ carbene can be prepared in situ via deprotonation with a strong base (e.g. NaO'Bu and NaH) (Arduengo et al., 1991; McGuinness et al., 2001; Hauwert et al., 2008; Voutchkova et al., 2005). Expanding the functional diversity of NHC ligands
will broaden their utility. The synthesis of the novel imidazolium salt in this report offers a unique extension of previously reported imidazolium salts through the addition of phenolic groups, herein referred to as IOH·Cl, for functionalization (see Scheme). The hydroxyl functional group presents the possibility of tethering other chemical groups for varied applications, including catalysis, materials, and biomedicine. The synthesis of IOH·Cl (Fig. 1) does not require Schlenk techniques and the product is isolated as an air-stable solid that can be stored indefinitely without decomposition. The synthesis is part of a study to develop reaction methods for C–N bond formation from high-oxidation-state transition metals.

2. Structural commentary

In the structure of IOH·Cl (Fig. 2), there are no unusual bond lengths or angles. The organic cation consists of a central planar imidazolium ring (r.m.s. deviation = 0.0018 Å), with para-phenol substituents (C4–C9/O1 and C10–C16/O2) bonded to the imidazolium N atoms \( [N1–C4 = 1.442 (3) \text{ Å} \) and \( N2–C10 = 1.441 (3) \text{ Å} \). The phenol groups are out-of-plane, forming dihedral angles with the imidazolium ring of 55.27 (7) and 48.85 (11)° for rings C4–C9 and C10–C15, respectively. The hydroxy H-atom coordinates were refined freely and are slightly out-of-plane of their respective phenolic groups; the torsion angles are 9.1 (19)° for C6–C7–O1–H1O and 11 (2)° for C12–C13–O2–H2O.

3. Supramolecular features

The most prominent intermolecular interactions in the crystals of IOH·Cl are O–H⋯Cl hydrogen bonds. These link the Cl\(^{-}\) anion at \((x, y, z)\) to two different IOH·Cl molecules, one related by inversion and the other by the \( n \)-glide. These hydrogen bonds, viz. O1–H1O⋯Cl and O2\(^{-}\)–H2O⋯Cl\(^{-}\) [symmetry codes: (i) \(-x+1, -y+1, -z+1\); (ii) \(x, -y+1, -z+1\); (iii) \(-x, y+1, -z\); (iv) \(-x, -y+1, -z\); (v) \(-x+1, y+z+1\)], have donor–acceptor distances of 2.975 (2) and 3.012 (2) Å, respectively. Weaker bifurcated C–

![Figure 1](image1.png)

**Figure 1** Synthesis of IOH·Cl.

![Figure 2](image2.png)

**Figure 2** The molecular structure of IOH·Cl, with displacement ellipsoids drawn at the 50% probability level.

![Figure 3](image3.png)

**Figure 3** A plot of the O–H⋯Cl hydrogen bonds in crystals of IOH·Cl. These interactions, drawn as dashed solid lines, link molecules into head-to-tail zigzag chains that extend parallel to the \( b \) axis. The unlabelled molecule is related to its labelled counterpart by the crystallographic 2 \( \overline{1} \) screw axis \((-x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2})\).

### Table 1

Hydrogen-bond geometry (Å, °).

| \( D–H\cdots A \) | \( D–H \) | \( H\cdots A \) | \( D\cdots A \) | \( D–H\cdots A \) |
|-----------------|---------|-----------|-------------|----------------|
| O1–H1O⋯Cl\(^{-}\) | 0.93 (3) | 2.06 (3) | 2.975 (2) | 169 (3) |
| O2–H2O⋯Cl\(^{-}\) | 0.89 (3) | 2.13 (3) | 3.0118 (19) | 171 (3) |
| C1–H1⋯O1\(^{-}\) | 0.95 | 2.45 | 3.280 (3) | 145 |
| C1–H1⋯O2\(^{-}\) | 0.95 | 2.51 | 3.271 (3) | 137 |
| C2–H2⋯Cl\(^{-}\) | 0.95 | 2.80 | 3.647 (3) | 150 |
| C3–H3⋯Cl\(^{-}\) | 0.95 | 2.74 | 3.655 (3) | 163 |

Symmetry codes: (i) \(-x+1, -y+1, -z+1\); (ii) \(x, -y+1, -z+1\); (iii) \(-x, y+1, -z\); (iv) \(-x, -y+1, -z\); (v) \(-x+1, y+z+1\).
H···O interactions occur between imidazole ring atoms (C1—H1) and hydroxy O atoms (O1\(^1\) and O2\(^2\)) on molecules related by different inversion centres. These same hydroxy O atoms are in close contact with each other, i.e. O1\(^1\)···O2\(^2\) = 2.999 (3) Å [symmetry codes: (i) \(-x, -y + 1, -z\); (ii) \(-x + 1, -y + 1, -z + 1\)]. In addition to hydrogen bonding, there are offset \(\pi\)–\(\pi\) stacking interactions (Fig. 5). The perpendicular stacking distance between the C4–C9 benzene ring and an inversion-related equivalent at \((-x + 1, -y + 1, -z + 1)\) is 3.560 (3) Å. The overlap of the C10–C15 benzene ring C10–C15 with an inversion-related equivalent at \((-x, -y + 1, -z)\) is weaker, giving a perpendicular stacking distance of 3.777 (3) Å. All hydrogen-bond interactions are readily apparent in the Hirshfeld surface and fingerprint plots (McKinnon et al., 2007; Turner et al., 2017; Tan et al., 2019). In Fig. 6(a), the prominent deep-red ellipse-shaped regions represent the O—H···Cl hydrogen bonds, while the smaller pink regions correspond to the C—H···O bifurcated weak hydrogen bonds. In (b), the faint-pink regions in the upper middle of the diagram correspond to close contacts between imidazole-ring C—H groups and Cl\(^-\) anions.

4. Database survey

A search of the Cambridge Structural Database (CSD; Version 5.40, November 2018; Groom et al., 2016) on the three-ring fragment of the title compound yielded over 600 examples of 1311–1315.

Figure 4
A plot showing the bifurcated C—H···O interactions (dashed solid lines) and O···O close contacts (dotted lines) in crystalline IOH-Cl. The unlabelled molecules are related to the partially labelled molecule by inversion [upper left: \((-x, -y + 1, -z)\); upper right: \((-x + 1, -y + 1, -z + 1)\)].

Figure 5
A plot highlighting the \(\pi\)–\(\pi\) stacking (open dashed lines) of benzene rings in crystals of IOH-Cl. Unlabelled molecules are related to the labelled molecule by inversion [lower right: \((-x + 1, -y + 1, -z + 1)\); lower left: \((-x, -y + 1, -z)\)].
hits, ranging from similar simple salts to metal complexes containing analogous NHC frameworks. A search with H atoms bonded to the three carbons of the imidazole ring gave 180 hits. Of these, 28 had mesityl substituents, including IHOQUS (IMes-Cl; Lorber & Vendier, 2009) and GAKCAZ (IMes-BF₄; Bethel et al., 2016), and 62 had 2,6-diisopropylphenyl groups, including KIDKUG (IPr-ClO₄; Minaker et al., 2018), OHURIU (IPr-PF₆; Rheingold et al., 2015), TAXLOW (IPr-SiF₆; Alić et al., 2017), and XANPEJ (IPr-I; Solovey et al., 2010). Structures most similar to IOH-Cl in the present work include the commonly used IMes-Cl (IHOQUS) and IPr-ClO₄ (KIDKUG), and the unsubstituted phenyl analog IPh-ClO₄ (DPIMPC; Luger & Ruban, 1975). A more restrictive search with only para substitution allowed on the phenyl rings gave 47 hits, of which 44 were carboxylates that formed extended polymeric structures with metal-containing species. The remaining three, BOGVAV (Wan et al., 2008), TUPYAF (Garden et al., 2010), and DAQKOW (Suisse et al., 2005), have –OMe, –Br, and –OC₂H₅ groups at the para position. One other structure with comparative functionalization is LEBMUC (Schedler et al., 2012), which bears bis-methoxy groups at the ortho-phenyl-ring positions.

5. Synthesis and crystallization

The overall reaction for the synthesis of the title compound is depicted in Fig. 1. Step 1, Synthesis of the precursor N,N'-bis(4-hydroxyphenyl)-1,4-diazabutadiene (1): to a round-bottomed flask charged with 15 ml of methanol, 4-phenolaniline (813 mg, 7 mmol) was added and stirred until fully dissolved. Glyoxal (174 mg, 3 mmol) was added to the reaction solution with stirring. Upon addition of glyoxal solution, 40 wt.% in H₂O, a brown precipitate formed and the solution turned orange. The reaction was further stirred at room temperature for 5 h and the solid was vacuum filtered and washed with cold methanol (612 mg, 85% yield). Step 2, Synthesis of IOH-Cl:

![Figure 7](image)

(a) The full 2D (two-dimensional) fingerprint plot for IOH-Cl, along with separate plots highlighting the five most important and abundant specific contacts: (b) H···H, (c) C-··H, (d) Cl-··H, (e) O-··H, and (f) C-··C.

| Table 2 | Experimental details. |
|------------------|-----------------------|
| Crystal data     | C₁₉H₁₈N₂O₄⁺Cl⁻        |
| Chemical formula | Cl₃H₂N₃O₄⁺Cl⁻          |
| Mᵣ             | 268.72                 |
| Crystal system, space group | Monoclinic, P2₁/n |
| Temperature (K) | 90                     |
| a, b, c (Å)     | 8.1752 (6), 13.2684 (8), 12.7391 (10) |
| β (°)           | 100.105 (3)            |
| V (Å³)          | 1360.40 (17)           |
| Z                | 4                      |
| Radiation type  | Mo Ka                  |
| µ (mm⁻¹)        | 0.28                   |
| Crystal size (mm) | 0.24 x 0.03 x 0.03    |
| Data collection | Bruker D8 Venture dual source |
| Absorption correction | Multi-scan (SADABS; Krause et al., 2015) |
| T min, T max    | 0.821, 0.928           |
| No. of measured, independent and observed | 14925, 3109, 1869 |
| [I > 2σ(I)] reflections | 0.049, 0.083, 1.01 |
| R min (sin θ/λ)max (Å⁻¹) | 0.103 |
| R[F² > 2σ(F²)], wR(F²), S | 0.049, 0.083, 1.01 |
| No. of reflections | 3109 |
| No. of parameters | 187 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| ∆ρ max, ∆ρ min (e Å⁻³) | 0.34, –0.32 |

Computer programs: APEX3 (Bruker, 2016), SHELXT (Sheldrick, 2015a), XP in SHELXTL (Sheldrick, 2008), SHELX2018 (Sheldrick, 2015b) and CIFFIX (Parkin, 2013).
ethyl acetate (10 ml) was pre-heated to 343 K. To the hot solution was added (1) (200 mg, 1.2 mmol) and paraformaldehyde (36 mg, 1.2 mmol). The reaction mixture was stirred until all of the paraformaldehyde had dissolved. To this was added a solution of trimethylchlorosilane (TMSCl) (0.2 ml, 130 mg, 1.2 mmol) in ethyl acetate (0.15 ml) dropwise over 5 min while stirring. The solution was stirred for 2 h and then placed in a refrigerator (275 K) overnight. The precipitate was collected by vacuum filtration and washed with cold ethyl acetate and ether until the filtrate was colorless, yielding a dark-orange solid (yield 208 mg, 60%). Crystals were grown by slow evaporation of a concentrated solution in acetone.

6. Refinement

Crystal data, data collection, and structure refinement details are given in Table 2. All H atoms were found in difference Fourier maps. Hydroxy H-atom coordinates were refined freely, with $U_{	ext{iso}}$(H) = 1.5$U_{eq}$(O). Carbon-bound H atoms were included in calculated positions and refined using a standard riding model, with C—H = 0.95 Å and $U_{	ext{iso}}$(H) = 1.2$U_{eq}$(C). Refinement progress was checked using an R-tensor (Parkin, 2000), PLATON (Spek, 2009), and checkCIF (https://checkcif.iucr.org/).

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Computing details
Data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 (Bruker, 2016); data reduction: APEX3 (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL2018 (Sheldrick, 2015b) and CIFFIX (Parkin, 2013).

1,3-Bis(4-hydroxyphenyl)-1H-imidazol-3-ium chloride

Crystal data
C_{15}H_{13}N_2O_2^+·Cl^−

F(000) = 600
D_c = 1.410 Mg m\(^{-3}\)

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 1847 reflections
θ = 3.2–25.1°
μ = 0.28 mm\(^{-1}\)

T = 90 K
Needle, pale yellow

0.24 × 0.03 × 0.03 mm

Data collection
Bruker D8 Venture dual source diffractometer
Radiation source: microsource
Detector resolution: 7.41 pixels mm\(^{-1}\)
φ and ω scans
Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

T\(_{\text{min}}\) = 0.821, T\(_{\text{max}}\) = 0.928

14925 measured reflections
3109 independent reflections
1869 reflections with I > 2σ(I)

Refinement
Refinement on F\(^2\)
Least-squares matrix: full
R[F\(^2\) > 2σ(F\(^2\))] = 0.049
wR(F\(^2\)) = 0.083

S = 1.01
3109 reflections
187 parameters
0 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/[σ(F^2)\(^2\) + 0.9975P]
where P = (F^2 + 2F\(^c\)^2)/3

(Δρ\(_{\text{max}}\))\text{max} < 0.001
Δρ\(_{\text{max}}\) = 0.34 e Å\(^{-3}\)
Δρ\(_{\text{min}}\) = −0.32 e Å\(^{-3}\)
**Supporting Information**

*Experimental.* The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998). Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

**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 progress was checked using *Platon* (Spek, 2009) and by an R-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

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

|   | x       | y       | z       | Uiso* / Ueq |
|---|---------|---------|---------|-------------|
| Cl | 0.02919 (8) | 0.26975 (5) | 0.32981 (6) | 0.02188 (17) |
| N1 | 0.1115 (3) | 0.61456 (15) | 0.38285 (18) | 0.0172 (5) |
| N2 | −0.0616 (3) | 0.59391 (15) | 0.23466 (18) | 0.0177 (5) |
| O1 | 0.6632 (2) | 0.62630 (14) | 0.70648 (16) | 0.0267 (5) |
| H1O | 0.754 (4) | 0.658 (2) | 0.685 (2) | 0.040* |
| O2 | −0.3960 (2) | 0.45255 (13) | −0.15434 (15) | 0.0246 (5) |
| H2O | −0.407 (3) | 0.386 (2) | −0.155 (2) | 0.037* |
| C1 | 0.0899 (3) | 0.56926 (18) | 0.2872 (2) | 0.0196 (6) |
| H1 | 0.168035 | 0.527175 | 0.261384 | 0.023* |
| C2 | −0.0294 (3) | 0.66978 (18) | 0.3909 (2) | 0.0201 (6) |
| H2 | −0.047100 | 0.709198 | 0.450155 | 0.024* |
| C3 | −0.1369 (3) | 0.65700 (19) | 0.2986 (2) | 0.0209 (6) |
| H3 | −0.244440 | 0.685964 | 0.280713 | 0.025* |
| C4 | 0.2593 (3) | 0.61151 (18) | 0.4634 (2) | 0.0170 (6) |
| C5 | 0.4107 (3) | 0.64043 (18) | 0.4386 (2) | 0.0187 (6) |
| H5 | 0.420025 | 0.657846 | 0.367563 | 0.022* |
| C6 | 0.5480 (3) | 0.64350 (17) | 0.5191 (2) | 0.0187 (6) |
| H6 | 0.653195 | 0.661931 | 0.503157 | 0.022* |
| C7 | 0.5329 (3) | 0.61976 (18) | 0.6233 (2) | 0.0195 (6) |
| C8 | 0.3809 (3) | 0.58845 (18) | 0.6463 (2) | 0.0199 (6) |
| H8 | 0.371354 | 0.570419 | 0.717145 | 0.024* |
| C9 | 0.2436 (3) | 0.58362 (18) | 0.5658 (2) | 0.0204 (6) |
| H9 | 0.139637 | 0.561368 | 0.580702 | 0.024* |
| C10 | −0.1400 (3) | 0.55635 (18) | 0.1320 (2) | 0.0173 (6) |
| C11 | −0.1393 (3) | 0.45368 (19) | 0.1120 (2) | 0.0222 (7) |
| H11 | −0.082486 | 0.408543 | 0.163846 | 0.027* |
| C12 | −0.2225 (3) | 0.41836 (19) | 0.0158 (2) | 0.0231 (7) |
| H12 | −0.221456 | 0.348340 | 0.000365 | 0.028* |
| C13 | −0.3082 (3) | 0.48456 (19) | −0.0591 (2) | 0.0186 (6) |
| C14 | −0.3043 (3) | 0.58696 (19) | −0.0383 (2) | 0.0204 (6) |
| H14 | −0.359489 | 0.632414 | −0.090377 | 0.025* |
| C15 | −0.2207 (3) | 0.62337 (19) | 0.0576 (2) | 0.0201 (6) |
| H15 | −0.218569 | 0.693606 | 0.072208 | 0.024* |
### Atomic displacement parameters (Å²)

|    | \(U_1^{11}\)   | \(U_2^{22}\)   | \(U_3^{33}\)   | \(U_{12}\)   | \(U_{13}\)   | \(U_{23}\)   |
|----|----------------|----------------|----------------|-------------|-------------|-------------|
| Cl1 | 0.0211 (3)     | 0.0216 (3)     | 0.0222 (4)     | 0.0002 (3)  | 0.0016 (3)  | 0.0014 (3)  |
| N1  | 0.0161 (12)    | 0.0175 (11)    | 0.0171 (13)    | 0.0012 (9)  | 0.0003 (10) | −0.001 (1)  |
| N2  | 0.0184 (13)    | 0.0184 (11)    | 0.0155 (13)    | 0.0004 (9)  | 0.0008 (10) | −0.0011 (9) |
| O1  | 0.0184 (11)    | 0.0370 (12)    | 0.0223 (12)    | −0.0078 (9) | −0.0031 (9) | 0.0074 (9)  |
| O2  | 0.0334 (12)    | 0.0194 (10)    | 0.0176 (12)    | −0.0022 (9) | −0.0044 (10)| −0.0014 (9) |
| C1  | 0.0202 (15)    | 0.0199 (14)    | 0.0180 (17)    | 0.0023 (11) | 0.0015 (13) | 0.0003 (12) |
| C2  | 0.0191 (15)    | 0.0226 (14)    | 0.0197 (17)    | 0.0058 (11) | 0.0062 (13) | −0.0025 (12)|
| C3  | 0.0180 (15)    | 0.0222 (14)    | 0.0222 (17)    | 0.0054 (12) | 0.0028 (13) | −0.0001 (12)|
| C4  | 0.0156 (14)    | 0.0183 (13)    | 0.0160 (16)    | −0.0002 (11)| 0.0000 (12) | −0.0012 (12)|
| C5  | 0.0222 (16)    | 0.0182 (14)    | 0.0158 (16)    | 0.0015 (11) | 0.0035 (13) | −0.0006 (11)|
| C6  | 0.0182 (15)    | 0.0181 (14)    | 0.0198 (16)    | −0.0012 (11)| 0.0035 (13) | 0.0017 (12) |
| C7  | 0.0200 (15)    | 0.0185 (13)    | 0.0179 (16)    | 0.0007 (11) | −0.0021 (13)| 0.0016 (12) |
| C8  | 0.0228 (16)    | 0.0238 (15)    | 0.0135 (16)    | −0.0018 (12)| 0.0041 (13) | 0.0053 (12) |
| C9  | 0.0189 (15)    | 0.0188 (14)    | 0.0229 (18)    | −0.0018 (11)| 0.0022 (13) | 0.0006 (12) |
| C10 | 0.0161 (15)    | 0.0196 (14)    | 0.0155 (16)    | −0.0014 (11)| 0.0005 (12) | −0.0026 (12)|
| C11 | 0.0227 (16)    | 0.0187 (14)    | 0.0233 (17)    | 0.0040 (12) | −0.0015 (13)| 0.0030 (12) |
| C12 | 0.0280 (17)    | 0.0178 (14)    | 0.0225 (18)    | −0.0012 (12)| 0.0015 (14) | 0.0001 (12) |
| C13 | 0.0182 (15)    | 0.0238 (14)    | 0.0138 (16)    | −0.0031 (11)| 0.0026 (12) | −0.0021 (12)|
| C14 | 0.0258 (16)    | 0.0188 (14)    | 0.0163 (16)    | 0.0027 (12) | 0.0027 (13) | 0.0022 (12) |
| C15 | 0.0235 (16)    | 0.0177 (14)    | 0.0185 (16)    | 0.0000 (11) | 0.0017 (13) | −0.0010 (12)|

### Geometric parameters (Å, °)

| Bond                 | Length (Å) | Angle (°)   |
|----------------------|------------|-------------|
| N1—C1               | 1.342 (3)  |             |
| N1—C2               | 1.384 (3)  |             |
| N1—C4               | 1.442 (3)  |             |
| N2—C1               | 1.341 (3)  |             |
| N2—C3               | 1.385 (3)  |             |
| N2—C10              | 1.441 (3)  |             |
| O1—C7               | 1.366 (3)  |             |
| O1—H10              | 0.93 (3)   |             |
| O2—C13              | 1.364 (3)  |             |
| O2—H2O              | 0.89 (3)   |             |
| C1—C2               | 1.350 (4)  |             |
| C2—H2               | 0.9500     |             |
| C3—H3               | 0.9500     |             |
| C4—C9               | 1.384 (3)  |             |
| C5—C6               | 1.381 (4)  |             |
| C1—N1—C2            | 109.0 (2)  |             |
| C1—N1—C4            | 126.4 (2)  |             |
| C2—N1—C4            | 124.5 (2)  |             |
| C1—N2—C3            | 108.7 (2)  |             |


C1—N2—C10 126.4 (2)  C7—C8—H8  120.1
C3—N2—C10 124.7 (2)  C8—C9—C4  119.3 (3)
C7—O1—H1O 110.7 (19) C8—C9—H9  120.3
C13—O2—H2O 111.0 (19) C4—C9—H9  120.3
N2—C1—N1 107.9 (2)  C15—C10—C11  121.6 (3)
N2—C1—H1 126.1  C15—C10—N2  118.9 (2)
N1—C1—H1 126.1  C11—C10—N2  119.4 (2)
C3—C2—N1 107.0 (2)  C15—C10—C11  118.7 (2)
C3—C2—H2 126.5  C12—C11—H11  120.6
N1—C2—H2 126.5  C8—C9—H9  120.3
C2—C3—N2 126.5  C4—C9—H9  119.8
N2—C3—C2 126.3  C11—C12—C13  120.4 (2)
N1—C3—C2 126.3  C10—C11—H11  120.6
C2—C3—H3 126.3  N2—C10—C15—C14  119.8
N1—C3—H3 126.3  C14—C13—C12  119.8
C9—C4—C5 121.6 (3)  C14—C13—H12  120.5
C9—C4—N1 118.3 (2)  C13—C12—C11  119.5
C5—C4—N1 120.1 (2)  C12—C11—H11  120.6
C6—C5—C4 118.8 (3)  C11—C10—C15—C14  117.4 (3)
C6—C5—H5 120.6  C14—C13—C12  119.8
C4—C5—H5 120.6  C10—C11—C12—C13  120.4 (2)
C5—C6—C7 120.4 (3)  C11—C12—C13—O2  120.5
C5—C6—H6 119.8  C3—N2—C10—C15  49.3 (4)
C4—C5—H6 119.8  C10—N2—C15—C14  176.1 (2)
C6—C5—H6 119.8  O2—C13—C14—C15  178.5 (3)
O1—C7—C8 117.4 (3)  C15—C10—C11—C12  176.8 (2)
C3—N2—C1—N1 0.4 (3)  C6—C7—C8—C9  177.9 (2)
C10—N2—C1—N1 −175.5 (2)  C7—C8—C9—C4  175.5 (2)
C2—N1—C1—N2 −0.3 (3)  C5—C4—C9—C8  121.8 (3)
C4—N1—C1—N2 −177.5 (2)  C1—C2—C3—N2  55.0 (4)
C1—N1—C2—C3 0.1 (3)  C1—N1—C2—C3  55.3 (3)
C4—N1—C2—C3 177.3 (2)  C1—N1—C2—C3  177.3 (2)
C1—N2—C3—C2 0.2 (3)  C1—N2—C3—C2  0.4 (3)
C1—N2—C3—C2 −0.4 (3)  C3—N2—C1—N1  175.7 (2)
C10—N2—C3—C2 175.7 (2)  C15—C10—C11—C12  175.7 (2)
C1—N1—C4—C9 −127.9 (3)  N2—C10—C11—C12  176.5 (3)
C2—N1—C4—C9 55.3 (3)  C10—C11—C12—C13  176.5 (3)
C1—N1—C4—C5 55.0 (4)  C11—C12—C13—O2  178.2 (3)
C2—N1—C4—C5 −121.8 (3)  C11—C12—C13—C14  2.5 (4)
C9—C4—C5—C6 −1.5 (4)  O2—C13—C14—C15  178.5 (3)
N1—C4—C5—C6 175.5 (2)  C12—C13—C14—C15  2.2 (4)
C4—C5—C6—C7 −1.2 (4)  C13—C14—C15—C10  0.5 (4)
C5—C6—C7—O1 −176.8 (2)  C11—C10—C15—C14  0.9 (4)
C5—C6—C7—C8 2.8 (4)  N2—C10—C15—C14  −176.1 (2)
O1—C7—C8—C9 177.9 (2)

Hydrogen-bond geometry (Å, °)

| D—H···A    | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| O1—H1O···Cl1 | 0.93 (3) 2.06 (3) 2.975 (2) 169 (3) |
|          |          |          |          |          |
|----------|----------|----------|----------|----------|
| O2—H2O···Cl1<sup>ii</sup> | 0.89 (3) | 2.13 (3) | 3.0118 (19) | 171 (3)  |
| C1—H1···O1<sup>i</sup> | 0.95     | 2.45     | 3.280 (3)  | 145      |
| C1—H1···O2<sup>ii</sup> | 0.95     | 2.51     | 3.271 (3)  | 137      |
| C2—H2···Cl1<sup>iv</sup> | 0.95     | 2.80     | 3.647 (3)  | 150      |
| C3—H3···Cl1<sup>v</sup> | 0.95     | 2.74     | 3.655 (3)  | 163      |

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