# research communications

# Crystal structure, Hirshfeld surface analysis and physicochemical characterization of bis[4-(dimethylamino)pyridinium] di-μ-chlorido-bis[dichloridomercurate(II)]

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The title molecular salt, $(C_7H_{11}N_2)_2[Hg_2Cl_6]$, crystallizes with two 4-(dimethylamino)pyridinium cations ($A$ and $B$) and two half hexachloridodimercurate(II) anions in the asymmetric unit. The organic cations exhibit essentially the same features with an almost planar pyridyl ring (r.m.s. deviations of 0.0028 and 0.0109 Å), which forms an inclined dihedral angle with the dimethyamino group [3.06 (1) and 1.61 (1)°, respectively]. The dimethylamino groups in the two cations are planar, and the C—N bond lengths are shorter than that in 4-(dimethylamino)pyridine. In the crystal, mixed cation–anion layers lying parallel to the (010) plane are formed through N—H···Cl hydrogen bonds and adjacent layers are linked by C—H···Cl hydrogen bonds, forming a three-dimensional network. The analyses of the calculated Hirshfeld surfaces confirm the relevance of the above intermolecular interactions, but also serve to further differentiate the weaker intermolecular interactions formed by the organic cations and inorganic anions, such as $\pi$–$\pi$ and Cl···Cl interactions. The powder XRD data confirms the phase purity of the crystalline sample. Furthermore, the vibrational absorption bands were identified by IR spectroscopy and the optical properties were studied by using optical UV–visible absorption spectroscopy.

## 1. Chemical context

Hybrid organic–inorganic materials have been widely studied in recent years for their promising applications in different fields, including catalysis, magnetism and optics and for their luminescence properties (Clément *et al.*, 1994; Rabu *et al.*, 2001; Hu *et al.*, 2003; Morris *et al.*, 2008). However, owing to the confinement of the inorganic layers, the organic cations have to possess the right ionic bond and steric hindrance, as well as hydrogen bonds, to fit the coordination environment provided by the inorganic framework for stabilization of these organic–inorganic hybrid systems.

Hybrids based on mercury have been synthesized and characterized with simple, different techniques, thanks to their self-assembling character (Mitzi *et al.*, 2001) and are very interesting both for fundamental physics exploration such as electronic confinement (Wei *et al.*, 2015) or as low-dimensional magnetic systems (Fersi *et al.*, 2015) and diversify the field of technological applications.

A number of chloromercurate(II) complexes have been shown to exhibit ferroelectric behaviour (Mitsui & Nakamura, 1990) and interest has focused on the mechanism of the
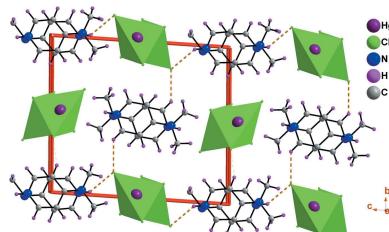
ferroelectric–paraelectric phase transition (White, 1963; Körfer *et al.*, 1988; Jiang *et al.*, 1995; Liesegang *et al.*, 1995) for which structural information is crucial. In addition, the ability of the anions in this class of compounds to exhibit a wide range of geometry, stoichiometry and connectivity has long been known (Grdenic, 1965). This flexibility is a result of the large volume and spherical charge distribution of the $Hg^{2+}$ ion, which are a consequence of the filled 4*f* and 5*d* electron shells. Moreover, organic–inorganic materials with pyridine and its derivatives as template agents have led to the preparation of some materials with interesting physical properties (Aakeröy *et al.*, 2000; Prince *et al.*, 2003) and biological activities (Bossert *et al.*, 1981; Wang *et al.*, 1989).
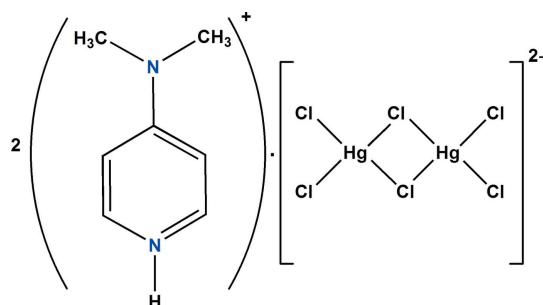
As part of our continuing investigation of new hybrid compounds containing an organic cation and an inorganic anion such as $CrO_4^{2-}$ (Chebbi *et al.*, 2000; Chebbi & Driss, 2001, 2002*a*,*b*, 2004), $Cr_2O_7^{2-}$ (Chebbi *et al.*, 2016, Ben Smail *et al.*, 2017), $NO_3^-$ (Chebbi *et al.*, 2014, 2018) and $ClO_4^-$ (Chebbi *et al.*, 2017; Ben Jomaa *et al.*, 2018), we report in this work the crystal structure, the Hirshfeld surface analysis and the physicochemical characterization of a new organic chloromercurate(II), $(C_7H_{11}N_2)_2[Hg_2Cl_6]$ (I).
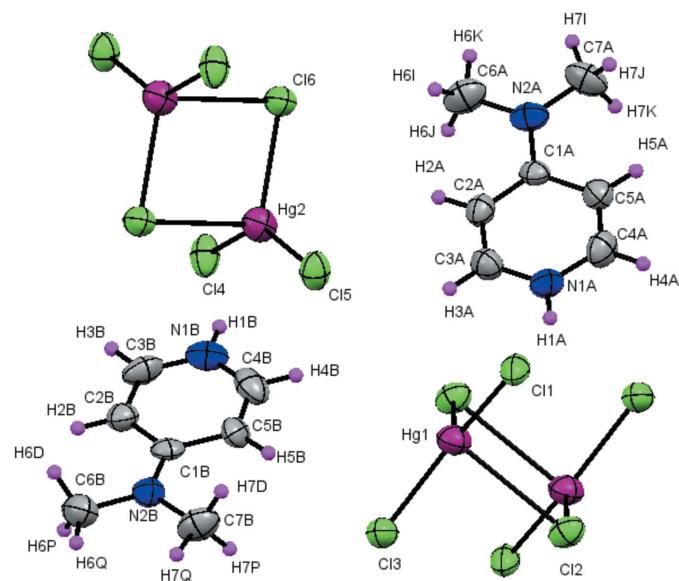
## 2. Structural commentary

The asymmetric unit of the title compound comprises two 4-(dimethylamino)pyridinium cations (*A* and *B*), and two half $[Hg_2Cl_6]^{2-}$ anions (Fig. 1). The two independent $[Hg_2(1,2)Cl_6]^{2-}$ anions are found to adopt a centrosymmetric arrangement with terminal Cl1—Hg1—Cl3 and Cl4—Hg2—Cl5 angles of 141.4 (1)° and 141.7 (1)° respectively. Each anion appears to be a distorted edge-shared bitetrahedron, similar to that reported by Larock *et al.* (1987), with its center of mass coincident with a crystallographic center of symmetry. The two independent Hg···Cl bridging distances are 2.539 (2) and 2.542 (2) Å, leading to a slightly asymmetric bridging system as has been found in most structures containing the $[Hg_2Cl_6]^{2-}$ moiety (Linden *et al.*, 1999; Zabel *et al.*, 2008). In each anion, the two terminal Hg—Cl bonds are quite short [Hg1—Cl1 = 2.371 (2) and Hg1—Cl3 = 2.380 (2) Å, Hg2—Cl4 = 2.367 (3) and Hg2—Cl5 = 2.392 (2) Å] with a Cl1—Hg1—Cl2 and Cl4—Hg2—Cl6 angles of 112.01 (9) and 112.72 (10)°, respectively. Assessment of the organic geometrical features shows that they exhibit essentially the same features with an almost planar pyridyl ring (r.m.s. deviation = 0.0028 and 0.0109 Å for C1*A*–C5*A*/N1*A* and C1*B*–C5*B*/N1*B*, respectively), which forms an inclined dihedral angle with the dimethyamino group [3.06 (1) and 1.61 (1)°, respectively]. The dimethylamino groups in the two cations are planar and the C—N bond lengths [1.357 (11) Å for *A* and 1.326 (11) Å for *B*] are shorter than that in 4-dimethylaminopyridine [1.367 (2) Å; Ohms & Guth, 1984]. These findings indicate the presence of strong conjugation between the dimethylamino group and the pyridine ring. The C3*A*—N1*A*—C4*A* [121.2 (8)°] and C3*B*—N1*B*—C4*B* [119.8 (9)°] bond angles are wider than that in pyridine (116.94°; Sørensen *et al.*, 1974), which indicates that the pyridine ring N atom is protonated. Examination of the C—C(N) distances and C—C—C (N), C—N—C angles in the 4-(dimethylamino)pyridinium dications (*A* and *B*) shows no significant difference from those obtained in other organic materials associated with the same organic groups (Chao *et al.*, 1977; Mustaqim *et al.*, 2005).

The experimental powder X-ray diffraction pattern of the title compound, $(C_7H_{11}N_2)_2[Hg_2Cl_6]$ is in good agreement with that simulated (Fig. 2). This indicates the purity of the synthesized product and confirms the crystal data used.



**Figure 1**
The molecular structure of (I). Atomic displacement parameters for the non-H atoms are drawn at the 50% probability level. Unlabelled atoms are related to labelled ones by the symmetry operation −*x* + 1, −*y*, −*z* + 2.
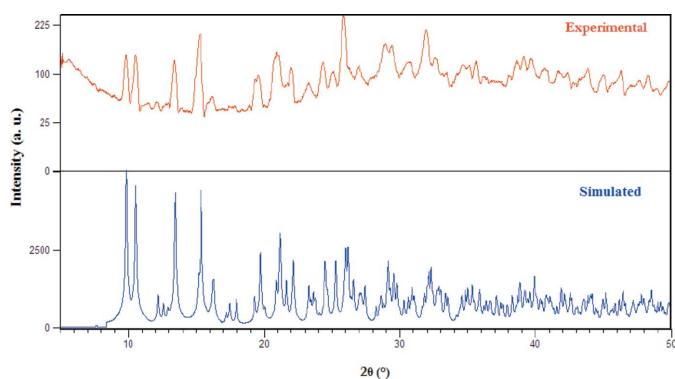


**Figure 2**
Experimental and simulated powder XRD patterns of (I).

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| N1A—H1A⋯Cl3 | 0.86 | 2.54 | 3.239 (8) | 140 |
| N1B—H1B⋯Cl5 | 0.86 | 2.46 | 3.195 (10) | 145 |
| C2B—H2B⋯Cl1i | 0.93 | 2.82 | 3.634 (11) | 147 |
| C3A—H3A⋯Cl5 | 0.93 | 2.75 | 3.485 (11) | 136 |

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

## 3. Supramolecular features

In the crystal structure, mixed cation–anion layers lying parallel to the (010) plane are formed through N—H⋯Cl hydrogen bonds and adjacent layers are linked by C—H⋯Cl hydrogen bonds, forming a three-dimensional network (Table 1, Fig. 3). A mixed layer is formed by alternating of organic and inorganic columns parallel to the [100] direction



**Figure 3**
Structure of (I) viewed along the *a* axis showing the succession of mixed layers parallel to the (010) plane. The orange dotted lines indicate hydrogen bonds.
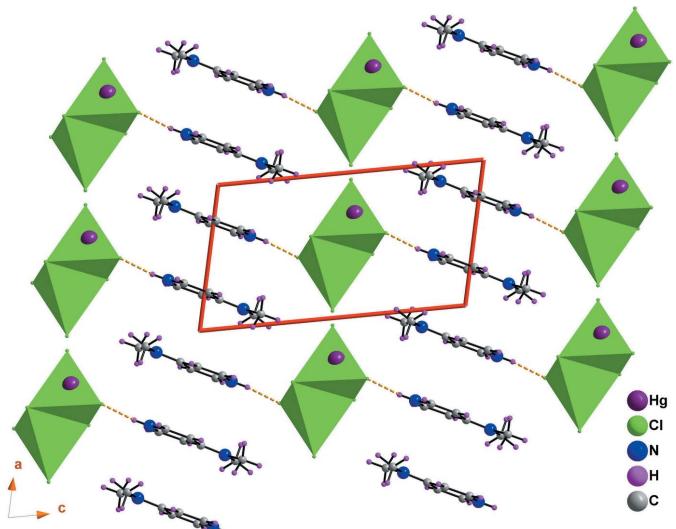


**Figure 4**
A view of the supramolecular mixed layer in the *ac* plane of (I), showing the alternating organic and inorganic columns parallel to the [100] direction. The orange dotted lines indicate N—H⋯Cl hydrogen bonds.

(Fig. 4). The cations (*A* or *B*) interact *via* offset face-to-face π–π stacking interactions, leading to two types of organic columns formed by the cations (*A* or *B*) with centroid-centroid distances of 3.698 (2) and 3.982 (2) Å, respectively (Fig. 5) (Janiak, 2000; Ben Moussa *et al.*, 2018). Similarly, the hexa-chloridodimercurate(II) anions are dispersed parallel to the *a* axis whose cohesion is ensured by Cl⋯Cl [3.652 (6) Å] and Hg⋯Cl [3.167 (7) Å] weak interactions (Sumanesh *et al.*, 2016; Ben Moussa *et al.*, 2019*a*,*b*; Fig. 6).

## 4. Vibrational study

The obtained FT–IR spectrum for the studied hexachlorido-dimercurate(II) salt is depicted in Fig. 7. Detailed assignment of all bands observed in the infrared spectrum of the 4-(di-methylamino)pyridinium cation in the title compound is based on the comparison with other compounds associated to the same cation (Koleva *et al.*, 2008; Hu *et al.*, 2012). In the region of high frequencies, the bands at 3243, 3130, 3100, 2959 cm$^{-1}$ are due to the stretching vibrations of the N—H and C—H bonds. The band at 1646 cm$^{-1}$ is assigned to the N—H bending mode. The bands at 1557 and 1445 cm$^{-1}$ are attributed to the C=C and C=N stretching modes of the pyridine ring. The absorption band located at 1212 cm$^{-1}$ corresponds to the $\nu$(C—N) and $\nu$(C—C) modes. The band at 1056 cm$^{-1}$ can be attributed to the $\delta$(C—C) mode. The remaining bands in the



**Figure 5**
π–π stacking interactions between the nearest aromatic organic cation neighbors into two types of organic columns (*A* or *B*).
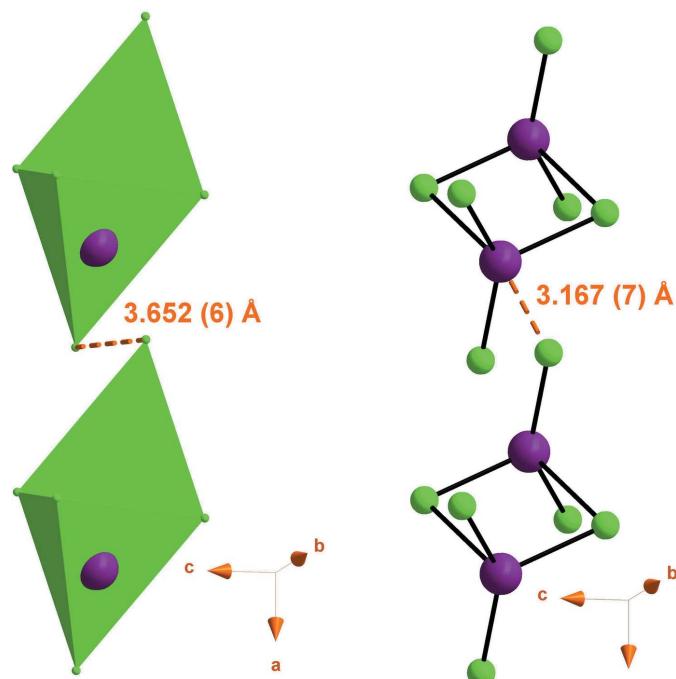
**Figure 6**
Cl···Cl and Hg···Cl interactions between hexachloridodimercurate(II) anions dispersed parallel to the *a* axis in the inorganic column.

range 1000 to 500 cm$^{-1}$ are assigned to $\gamma$(C—C), $\gamma$(C—H) and $\gamma$(C—N) out-of-plane bending modes.

## 5. Optical properties and frontier molecular orbitals

Optical absorption (OA) measurement of the title compound was performed at ambient temperature in an ethanol solution ($10^{-4}$ *M*). As shown in Fig. 8, the OA spectrum exhibits two distinct absorption bands around 213 and 278 nm assigned to the $\pi\rightarrow\pi*$ absorption bands of the 4-(dimethylamino)-pyridinium cations. Thus, the experimental band-gap energy obtained from the absorption edge wavelength is about 3.98 eV. This band-gap value indicates that the grown crystal
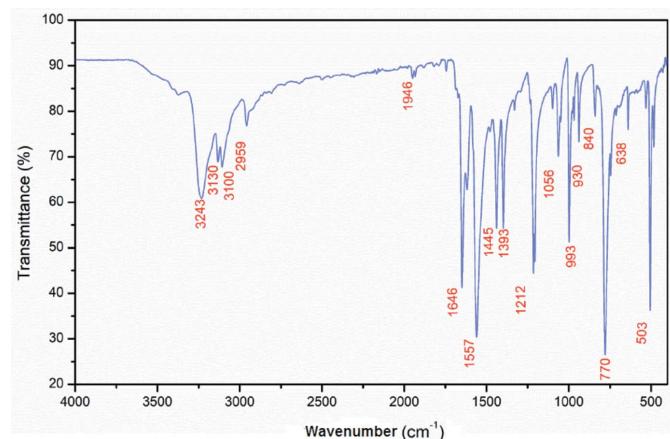


**Figure 7**
Infrared spectrum of (I).
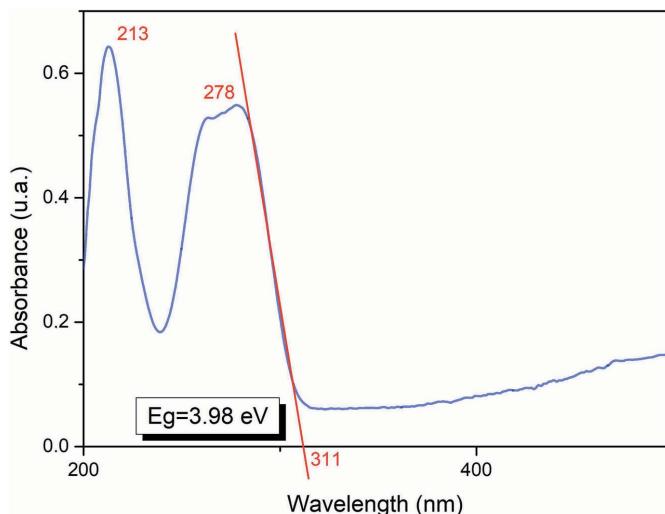


**Figure 8**
UV–vis spectrum of (I). The inset shows the experimental energy band gap obtained from the absorption edge wavelength.

exhibits semiconductor behavior (Rosencher & Vinter, 2002). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), known as frontier orbitals, obtained with a B3LYP/6-311G+(d,p) [H, C, N, Cl]–LANL2DZ [Hg] level calculation are illustrated in Fig. 9. The HOMO is mainly delocalized at the pyridine ring system. After excitation, the charge is localized on the hexa-chloridodimercurate(II) moieties, as depicted in the LUMO. The calculated HOMO–LUMO energy gap (4.26 eV) is shifted from the experimental value, which may be attributed to solvent effects, compared to the gas-phase calculation.
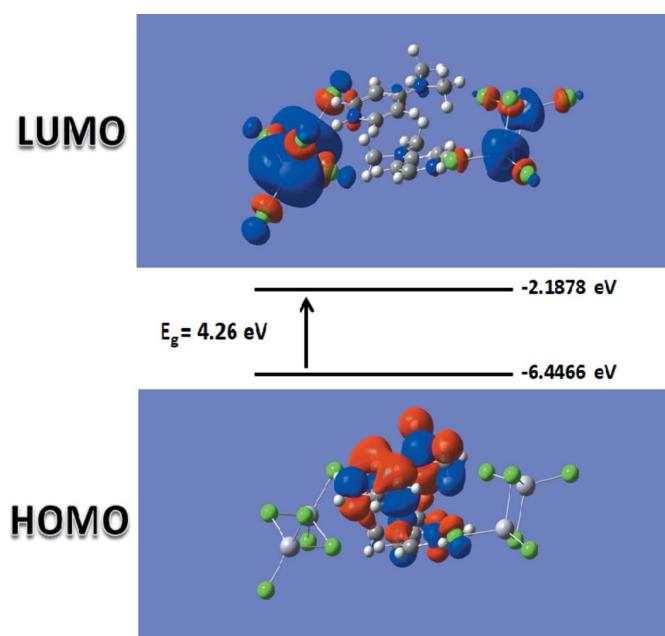


**Figure 9**
HOMO–LUMO molecular orbitals showing the ground to excited state electronic transitions for (I).

## 6. Hirshfeld surface analysis

A Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *CrystalExplorer17* (Turner *et al.*, 2017) to investigate the intermolecular interactions in the title compound. Fig. 10*a* illustrates the Hirshfeld surface mapped over $d_{norm}$, which was plotted with a colour scale of −0.211 to 1.132 a.u. with a standard (high) surface resolution. The red spots highlight the interatomic contacts including the N—H$\cdots$Cl and C—H$\cdots$Cl hydrogen bonds.

The shape-index of the Hirshfeld surface is a tool to visualize the $\pi$–$\pi$ stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no $\pi$–$\pi$ interactions. Fig.10*b* clearly suggests that $\pi$–$\pi$ interactions are present in the title hexachloridodimercurate(II) salt.
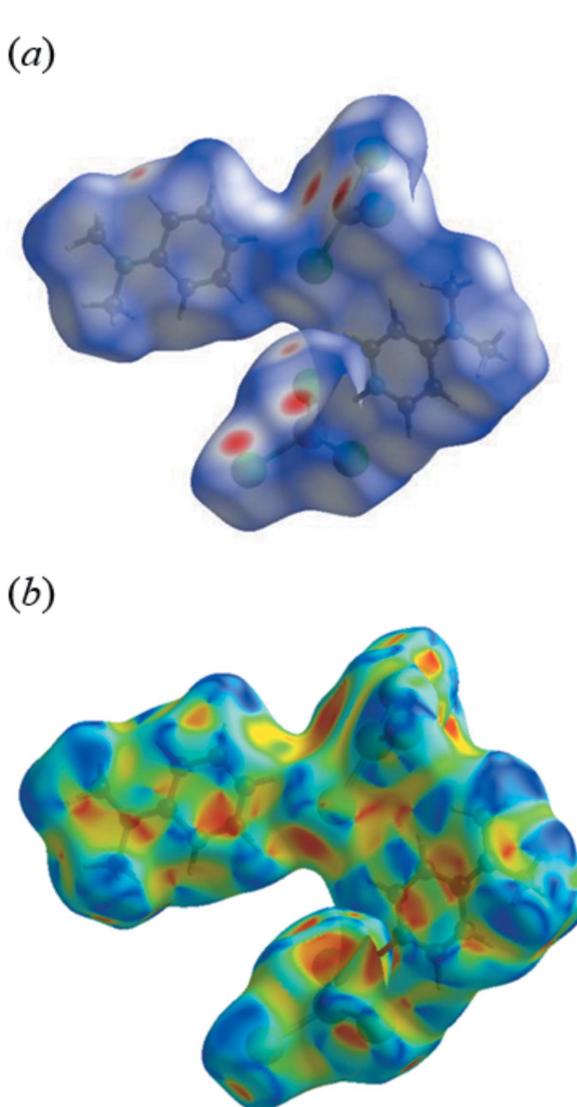


**Figure 10**
View of the Hirshfeld surfaces for (I) mapped over (*a*) $d_{norm}$ and (*b*) shape-index, displaying the intermolecular interactions.
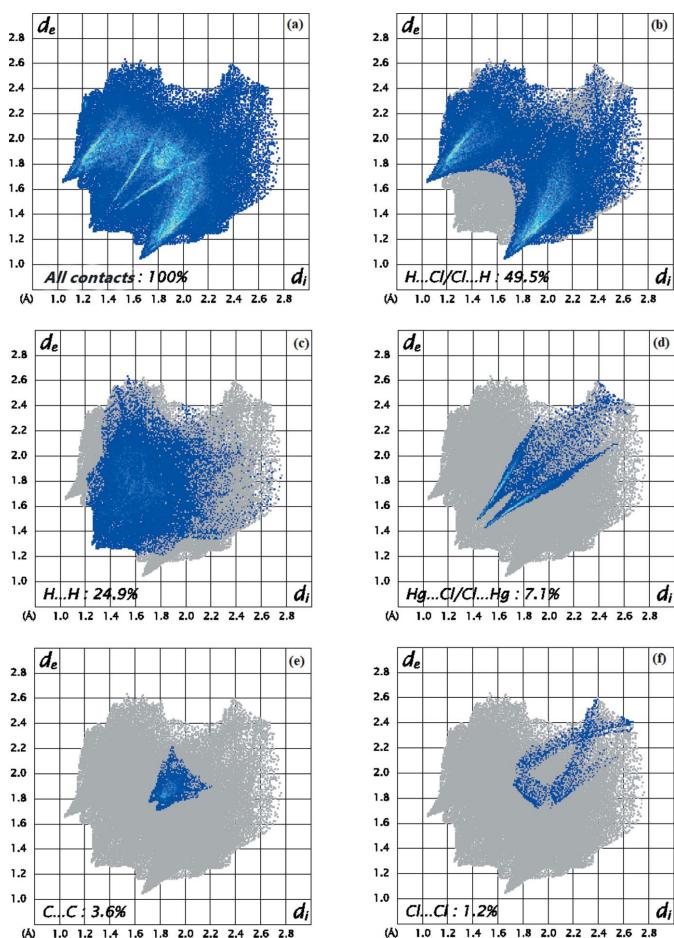


**Figure 11**
Full two-dimensional fingerprint plots for (I), showing (*a*) all interactions, and delineated into (*b*) H$\cdots$Cl/Cl$\cdots$H, (*c*) H$\cdots$H, (*d*) Hg$\cdots$Cl/Cl$\cdots$Hg, (*e*) C$\cdots$C and (*f*) Cl$\cdots$Cl interactions. The $d_i$ and $d_e$ values are the closest internal and external distances (in Å) from a given point on the Hirshfeld surface.

Fig. 11*a* shows the two-dimensional fingerprint of all contacts contributing to the Hirshfeld surface. In Fig. 11*b*, with two symmetrical wings on the left and right sides illustrate the H$\cdots$Cl/Cl$\cdots$H interactions with a contribution of 49.5%. Fig. 11*c* illustrates the two-dimensional fingerprint plot of ($d_i$, $d_e$) points related to H$\cdots$H contacts, which represent a 24.9% contribution. Furthermore, there are Hg$\cdots$Cl/Cl$\cdots$Hg
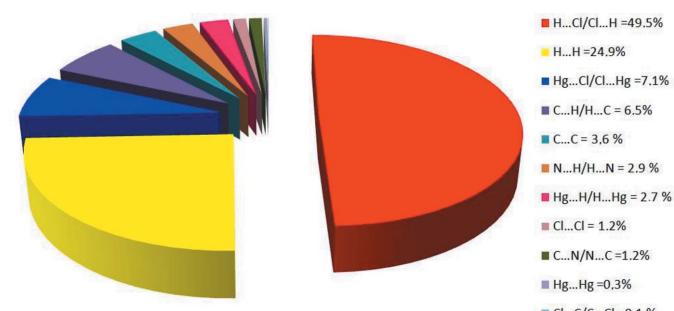


**Figure 12**
Relative contribution (%) of various intermolecular interactions to the Hirshfeld surface area.

**Table 2**
Experimental details.

| Crystal data | |
|---|---|
| Chemical formula | $(C_7H_{11}N_2)_2[Hg_2Cl_6]$ |
| $M_r$ | 860.23 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 293 |
| $a, b, c$ (Å) | 7.6558 (3), 11.8961 (5), 13.5853 (4) |
| $\alpha, \beta, \gamma$ (°) | 82.950 (3), 76.072 (3), 76.339 (4) |
| $V$ (Å$^3$) | 1164.07 (8) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 13.87 |
| Crystal size (mm) | $0.72 \times 0.24 \times 0.18$ |
| | |
| Data collection | |
| Diffractometer | Enraf–Nonius CAD-4 |
| Absorption correction | $\psi$ scan (North *et al.*, 1968) |
| $T_{min}$, $T_{max}$ | 0.53, 0.99 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 7139, 5875, 3913 |
| $R_{int}$ | 0.040 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.671 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.055, 0.153, 1.03 |
| No. of reflections | 5875 |
| No. of parameters | 236 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 3.41, −3.00 |

Computer programs: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992), *XCAD4* (Harms & Wocadlo, 1995), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2006), *Mercury* (Macrae *et al.*, 2006), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

(7.1%; Fig. 11d), C···C (3.6%; Fig. 11e) and Cl···Cl (1.2%; Fig. 11f) contacts. Fig. 12 shows the percentage contributions of the various contacts in the title structure.

## 7. Synthesis and crystallization

The title compound was synthesized by dissolving 2 mmol (241 mg) of 4-dimethylaminopyridine 98% (Sigma–Aldrich) in an HCl 36–38% (Sigma–Aldrich) aqueous solution and 1 mmol (273 mg) of mercury(II) chloride HgCl$_2$ (Merck) in ethanol in a molar ratio of 2:1. The mixture was then stirred for 2 h. The resulting aqueous solution was filtered and then evaporated at room temperature, which finally led to the growth of parallelepipedic colourless crystals after one day.

## 8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions, with N—H = 0.86 Å and C—H = 0.93 or 0.96 Å. $U_{iso}$(H) values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms, and $1.2U_{eq}$ for the remaining H atoms. The (111) and (121) reflections were omitted owing to bad disagreement.

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# supporting information

## Crystal structure, Hirshfeld surface analysis and physicochemical characterization of bis[4-(dimethylamino)pyridinium] di-*μ*-chlorido-bis-[dichloridomercurate(II)]

**Fatma Garci, Hela Ferjani, Hammouda Chebbi, Mariem Ben Jomaa and Mohamed Faouzi Zid**

**Computing details**

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS* (Duisenberg, 1992 ; Macíček & Yordanov, 1992); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

**Bis[4-(dimethylamino)pyridinium] di-*μ*-chlorido-bis[dichloridomercurate(II)]**

*Crystal data*

| | |
|---|---|
| $(C_7H_{11}N_2)_2[Hg_2Cl_6]$ | $Z = 2$ |
| $M_r = 860.23$ | $F(000) = 792$ |
| Triclinic, $P\bar{1}$ | $D_x = 2.454$ Mg m$^{-3}$ |
| $a = 7.6558$ (3) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 11.8961$ (5) Å | Cell parameters from 25 reflections |
| $c = 13.5853$ (4) Å | $\theta = 10$–$15°$ |
| $\alpha = 82.950$ (3)° | $\mu = 13.87$ mm$^{-1}$ |
| $\beta = 76.072$ (3)° | $T = 293$ K |
| $\gamma = 76.339$ (4)° | Parallelepiped, colorless |
| $V = 1164.07$ (8) Å$^3$ | $0.72 \times 0.24 \times 0.18$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 5875 independent reflections |
| Radiation source: fine-focus sealed tube | 3913 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.040$ |
| $\omega/2\theta$ scans | $\theta_{max} = 28.5°$, $\theta_{min} = 2.3°$ |
| Absorption correction: $\psi$ scan (North *et al.*, 1968) | $h = -10\rightarrow2$ |
| | $k = -15\rightarrow15$ |
| | $l = -18\rightarrow18$ |
| $T_{min} = 0.53$, $T_{max} = 0.99$ | 2 standard reflections every 120 reflections |
| 7139 measured reflections | intensity decay: 1% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $S = 1.03$ |
| Least-squares matrix: full | 5875 reflections |
| $R[F^2 > 2\sigma(F^2)] = 0.055$ | 236 parameters |
| $wR(F^2) = 0.153$ | 0 restraints |

Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0933P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 3.41$ e Å$^{-3}$
$\Delta\rho_{min} = -3.00$ e Å$^{-3}$
Extinction correction: SHELXL2018
   (Sheldrick, 2015b),
   Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$
Extinction coefficient: 0.0058 (5)

*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 (Å$^2$)*

|      | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|------|------|------|------|------|
| Hg1 | 0.73846 (6) | 0.52983 (3) | 0.96401 (3) | 0.04867 (15) |
| Hg2 | 0.70787 (6) | 0.02376 (3) | 0.53548 (3) | 0.05017 (16) |
| Cl3 | 0.7012 (4) | 0.6752 (2) | 0.82926 (18) | 0.0507 (6) |
| Cl5 | 0.5562 (4) | 0.1596 (2) | 0.66140 (18) | 0.0518 (6) |
| Cl2 | 0.4827 (3) | 0.5982 (2) | 1.11547 (17) | 0.0489 (6) |
| Cl6 | 0.5814 (4) | 0.1067 (2) | 0.37887 (17) | 0.0487 (5) |
| Cl1 | 0.9450 (4) | 0.3586 (2) | 1.0069 (2) | 0.0507 (6) |
| Cl4 | 0.9497 (4) | −0.1420 (2) | 0.5038 (2) | 0.0544 (6) |
| N1B | 0.3722 (13) | 0.0129 (9) | 0.8551 (6) | 0.055 (2) |
| H1B | 0.423341 | 0.022921 | 0.791911 | 0.067* |
| N1A | 0.6907 (12) | 0.5280 (8) | 0.6462 (6) | 0.047 (2) |
| H1A | 0.665775 | 0.537818 | 0.710142 | 0.056* |
| N2B | 0.1208 (12) | −0.0324 (7) | 1.1557 (6) | 0.0441 (18) |
| C1B | 0.2047 (12) | −0.0182 (8) | 1.0590 (6) | 0.0359 (19) |
| C5B | 0.2580 (14) | 0.0880 (8) | 1.0172 (8) | 0.043 (2) |
| H5B | 0.237846 | 0.149257 | 1.057848 | 0.051* |
| N2A | 0.8004 (12) | 0.4827 (8) | 0.3413 (6) | 0.047 (2) |
| C2A | 0.7198 (13) | 0.4105 (8) | 0.5161 (8) | 0.042 (2) |
| H2A | 0.712530 | 0.340021 | 0.496158 | 0.050* |
| C4B | 0.3388 (16) | 0.0977 (10) | 0.9166 (9) | 0.058 (3) |
| H4B | 0.372259 | 0.167244 | 0.889581 | 0.069* |
| C1A | 0.7683 (12) | 0.4958 (8) | 0.4424 (6) | 0.0352 (18) |
| C2B | 0.2482 (14) | −0.1070 (9) | 0.9916 (7) | 0.043 (2) |
| H2B | 0.223027 | −0.179339 | 1.015900 | 0.052* |
| C3B | 0.3261 (15) | −0.0884 (10) | 0.8918 (8) | 0.052 (3) |
| H3B | 0.347796 | −0.147079 | 0.848196 | 0.063* |
| C5A | 0.7751 (14) | 0.6032 (9) | 0.4768 (8) | 0.047 (2) |
| H5A | 0.805230 | 0.663582 | 0.430389 | 0.056* |
| C4A | 0.7372 (15) | 0.6156 (9) | 0.5779 (8) | 0.050 (2) |
| H4A | 0.742924 | 0.684838 | 0.600944 | 0.061* |
| C3A | 0.6831 (14) | 0.4271 (9) | 0.6157 (7) | 0.045 (2) |
| H3A | 0.652280 | 0.368100 | 0.663649 | 0.054* |
| C7B | 0.0765 (17) | 0.0644 (11) | 1.2239 (8) | 0.061 (3) |

| | | | |
|---|---|---|---|
| H7Q | 0.016344 | 0.039805 | 1.290807 | 0.091* |
| H7P | 0.188302 | 0.085789 | 1.227041 | 0.091* |
| H7D | −0.003486 | 0.129990 | 1.197662 | 0.091* |
| C6B | 0.0727 (16) | −0.1412 (10) | 1.1987 (8) | 0.058 (3) |
| H6Q | 0.013266 | −0.134628 | 1.269144 | 0.087* |
| H6D | −0.009493 | −0.159869 | 1.162861 | 0.087* |
| H6P | 0.182338 | −0.201411 | 1.192574 | 0.087* |
| C7A | 0.8505 (17) | 0.5720 (11) | 0.2661 (8) | 0.063 (3) |
| H7I | 0.867226 | 0.546304 | 0.199482 | 0.094* |
| H7J | 0.754609 | 0.640812 | 0.274933 | 0.094* |
| H7K | 0.963334 | 0.588643 | 0.273377 | 0.094* |
| C6A | 0.8007 (17) | 0.3711 (11) | 0.3057 (8) | 0.065 (3) |
| H6K | 0.825473 | 0.376560 | 0.232724 | 0.097* |
| H6I | 0.894286 | 0.311834 | 0.328549 | 0.097* |
| H6J | 0.682564 | 0.351849 | 0.332384 | 0.097* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Hg1 | 0.0531 (3) | 0.0467 (2) | 0.0452 (2) | −0.00220 (18) | −0.01806 (17) | −0.00119 (16) |
| Hg2 | 0.0507 (3) | 0.0470 (3) | 0.0479 (2) | −0.00196 (18) | −0.00822 (17) | −0.00665 (17) |
| Cl3 | 0.0702 (17) | 0.0420 (12) | 0.0451 (12) | −0.0111 (11) | −0.0240 (11) | −0.0015 (10) |
| Cl5 | 0.0602 (15) | 0.0440 (13) | 0.0483 (12) | −0.0159 (11) | 0.0017 (11) | −0.0101 (10) |
| Cl2 | 0.0486 (13) | 0.0604 (15) | 0.0393 (11) | −0.0136 (11) | −0.0069 (10) | −0.0111 (10) |
| Cl6 | 0.0551 (14) | 0.0543 (14) | 0.0414 (11) | −0.0190 (11) | −0.0166 (10) | 0.0044 (10) |
| Cl1 | 0.0547 (14) | 0.0363 (11) | 0.0709 (16) | −0.0105 (10) | −0.0348 (12) | 0.0018 (11) |
| Cl4 | 0.0431 (13) | 0.0373 (12) | 0.0800 (18) | −0.0075 (10) | −0.0079 (12) | −0.0065 (11) |
| N1B | 0.052 (5) | 0.072 (7) | 0.038 (4) | −0.005 (5) | −0.012 (4) | −0.002 (4) |
| N1A | 0.057 (5) | 0.053 (5) | 0.034 (4) | −0.016 (4) | −0.011 (4) | −0.006 (4) |
| N2B | 0.049 (5) | 0.048 (5) | 0.035 (4) | −0.012 (4) | −0.009 (3) | −0.004 (3) |
| C1B | 0.030 (4) | 0.043 (5) | 0.035 (4) | 0.002 (3) | −0.018 (3) | −0.002 (4) |
| C5B | 0.049 (5) | 0.028 (4) | 0.050 (5) | −0.001 (4) | −0.018 (4) | 0.000 (4) |
| N2A | 0.041 (4) | 0.067 (6) | 0.033 (4) | −0.011 (4) | −0.007 (3) | −0.005 (4) |
| C2A | 0.040 (5) | 0.035 (5) | 0.053 (5) | −0.006 (4) | −0.015 (4) | −0.007 (4) |
| C4B | 0.050 (6) | 0.047 (6) | 0.072 (7) | −0.005 (5) | −0.021 (5) | 0.017 (5) |
| C1A | 0.031 (4) | 0.042 (5) | 0.034 (4) | −0.007 (4) | −0.013 (3) | 0.001 (4) |
| C2B | 0.046 (5) | 0.044 (5) | 0.043 (5) | −0.006 (4) | −0.019 (4) | −0.004 (4) |
| C3B | 0.052 (6) | 0.061 (7) | 0.046 (5) | 0.004 (5) | −0.019 (5) | −0.026 (5) |
| C5A | 0.049 (6) | 0.043 (5) | 0.051 (6) | −0.013 (4) | −0.018 (5) | 0.003 (4) |
| C4A | 0.053 (6) | 0.038 (5) | 0.061 (6) | −0.004 (4) | −0.013 (5) | −0.014 (5) |
| C3A | 0.046 (5) | 0.048 (6) | 0.041 (5) | −0.013 (4) | −0.008 (4) | 0.004 (4) |
| C7B | 0.061 (7) | 0.080 (8) | 0.042 (5) | −0.014 (6) | −0.008 (5) | −0.019 (5) |
| C6B | 0.064 (7) | 0.063 (7) | 0.051 (6) | −0.019 (6) | −0.019 (5) | 0.005 (5) |
| C7A | 0.066 (7) | 0.074 (8) | 0.041 (5) | −0.013 (6) | −0.006 (5) | 0.013 (5) |
| C6A | 0.068 (8) | 0.081 (9) | 0.048 (6) | −0.014 (7) | −0.011 (5) | −0.020 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Hg1—Cl1 | 2.371 (2) | C2A—C3A | 1.344 (14) |
| Hg1—Cl3 | 2.380 (2) | C2A—C1A | 1.386 (13) |
| Hg1—Cl2 | 2.539 (2) | C2A—H2A | 0.9300 |
| Hg1—Cl2ⁱ | 2.975 (2) | C4B—H4B | 0.9300 |
| Hg2—Cl4 | 2.367 (3) | C1A—C5A | 1.429 (13) |
| Hg2—Cl5 | 2.392 (2) | C2B—C3B | 1.357 (15) |
| Hg2—Cl6 | 2.542 (2) | C2B—H2B | 0.9300 |
| Hg2—Cl6ⁱⁱ | 2.934 (3) | C3B—H3B | 0.9300 |
| N1B—C4B | 1.329 (15) | C5A—C4A | 1.352 (15) |
| N1B—C3B | 1.340 (15) | C5A—H5A | 0.9300 |
| N1B—H1B | 0.8600 | C4A—H4A | 0.9300 |
| N1A—C3A | 1.334 (13) | C3A—H3A | 0.9300 |
| N1A—C4A | 1.362 (14) | C7B—H7Q | 0.9600 |
| N1A—H1A | 0.8600 | C7B—H7P | 0.9600 |
| N2B—C1B | 1.326 (12) | C7B—H7D | 0.9600 |
| N2B—C6B | 1.445 (14) | C6B—H6Q | 0.9600 |
| N2B—C7B | 1.492 (13) | C6B—H6D | 0.9600 |
| C1B—C2B | 1.410 (13) | C6B—H6P | 0.9600 |
| C1B—C5B | 1.429 (14) | C7A—H7I | 0.9600 |
| C5B—C4B | 1.360 (15) | C7A—H7J | 0.9600 |
| C5B—H5B | 0.9300 | C7A—H7K | 0.9600 |
| N2A—C1A | 1.357 (11) | C6A—H6K | 0.9600 |
| N2A—C7A | 1.435 (14) | C6A—H6I | 0.9600 |
| N2A—C6A | 1.468 (15) | C6A—H6J | 0.9600 |
| | | | |
| Cl1—Hg1—Cl3 | 141.44 (10) | C2A—C1A—C5A | 117.1 (8) |
| Cl1—Hg1—Cl2 | 112.01 (9) | C3B—C2B—C1B | 121.0 (10) |
| Cl3—Hg1—Cl2 | 106.16 (9) | C3B—C2B—H2B | 119.5 |
| Cl1—Hg1—Cl2ⁱ | 93.63 (8) | C1B—C2B—H2B | 119.5 |
| Cl3—Hg1—Cl2ⁱ | 88.63 (8) | N1B—C3B—C2B | 121.1 (9) |
| Cl2—Hg1—Cl2ⁱ | 94.45 (7) | N1B—C3B—H3B | 119.4 |
| Cl4—Hg2—Cl5 | 141.70 (10) | C2B—C3B—H3B | 119.4 |
| Cl4—Hg2—Cl6 | 112.72 (10) | C4A—C5A—C1A | 119.1 (10) |
| Cl5—Hg2—Cl6 | 105.06 (9) | C4A—C5A—H5A | 120.5 |
| Cl4—Hg2—Cl6ⁱⁱ | 95.28 (8) | C1A—C5A—H5A | 120.5 |
| Cl5—Hg2—Cl6ⁱⁱ | 87.53 (8) | C5A—C4A—N1A | 120.7 (9) |
| Cl6—Hg2—Cl6ⁱⁱ | 94.73 (7) | C5A—C4A—H4A | 119.6 |
| Hg1—Cl2—Hg1ⁱ | 85.55 (7) | N1A—C4A—H4A | 119.6 |
| Hg2—Cl6—Hg2ⁱⁱ | 85.27 (7) | N1A—C3A—C2A | 120.3 (9) |
| C4B—N1B—C3B | 119.8 (9) | N1A—C3A—H3A | 119.9 |
| C4B—N1B—H1B | 120.1 | C2A—C3A—H3A | 119.9 |
| C3B—N1B—H1B | 120.1 | N2B—C7B—H7Q | 109.5 |
| C3A—N1A—C4A | 121.2 (8) | N2B—C7B—H7P | 109.5 |
| C3A—N1A—H1A | 119.4 | H7Q—C7B—H7P | 109.5 |
| C4A—N1A—H1A | 119.4 | N2B—C7B—H7D | 109.5 |
| C1B—N2B—C6B | 121.7 (9) | H7Q—C7B—H7D | 109.5 |

| | | | |
|---|---|---|---|
| C1B—N2B—C7B | 120.2 (9) | H7P—C7B—H7D | 109.5 |
| C6B—N2B—C7B | 118.1 (8) | N2B—C6B—H6Q | 109.5 |
| N2B—C1B—C2B | 122.2 (9) | N2B—C6B—H6D | 109.5 |
| N2B—C1B—C5B | 121.8 (9) | H6Q—C6B—H6D | 109.5 |
| C2B—C1B—C5B | 116.1 (9) | N2B—C6B—H6P | 109.5 |
| C4B—C5B—C1B | 118.6 (9) | H6Q—C6B—H6P | 109.5 |
| C4B—C5B—H5B | 120.7 | H6D—C6B—H6P | 109.5 |
| C1B—C5B—H5B | 120.7 | N2A—C7A—H7I | 109.5 |
| C1A—N2A—C7A | 122.1 (9) | N2A—C7A—H7J | 109.5 |
| C1A—N2A—C6A | 120.1 (9) | H7I—C7A—H7J | 109.5 |
| C7A—N2A—C6A | 117.6 (9) | N2A—C7A—H7K | 109.5 |
| C3A—C2A—C1A | 121.6 (9) | H7I—C7A—H7K | 109.5 |
| C3A—C2A—H2A | 119.2 | H7J—C7A—H7K | 109.5 |
| C1A—C2A—H2A | 119.2 | N2A—C6A—H6K | 109.5 |
| N1B—C4B—C5B | 123.3 (11) | N2A—C6A—H6I | 109.5 |
| N1B—C4B—H4B | 118.4 | H6K—C6A—H6I | 109.5 |
| C5B—C4B—H4B | 118.4 | N2A—C6A—H6J | 109.5 |
| N2A—C1A—C2A | 122.8 (9) | H6K—C6A—H6J | 109.5 |
| N2A—C1A—C5A | 120.0 (9) | H6I—C6A—H6J | 109.5 |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1*A*—H1*A*···Cl3 | 0.86 | 2.54 | 3.239 (8) | 140 |
| N1*B*—H1*B*···Cl5 | 0.86 | 2.46 | 3.195 (10) | 145 |
| C2*B*—H2*B*···Cl1ⁱⁱⁱ | 0.93 | 2.82 | 3.634 (11) | 147 |
| C3*A*—H3*A*···Cl5 | 0.93 | 2.75 | 3.485 (11) | 136 |

Symmetry code: (iii) −*x*+1, −*y*, −*z*+2.