| | | | | |
|---|---|---|---|---|
| N1 | 0.0529 (4) | 0.1289 (8) | 0.2565 (3) | 0.0471 (9) |
| N3 | −0.2099 (5) | 0.2000 (8) | 0.1254 (4) | 0.0645 (12) |
| C2 | −0.0414 (6) | 0.1763 (9) | 0.1259 (4) | 0.0561 (13) |
| C4 | −0.2274 (6) | 0.1734 (9) | 0.2606 (5) | 0.0635 (13) |
| C5 | −0.0632 (7) | 0.1277 (9) | 0.3474 (4) | 0.0632 (13) |
| C6 | 0.2480 (6) | 0.0948 (11) | 0.3034 (6) | 0.089 (2) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| O4—C9 | 1.415 (4) | C9—C8 | 1.523 (6) |
| O3—C8 | 1.421 (5) | N1—C2 | 1.299 (5) |
| O1—C7 | 1.287 (5) | N1—C5 | 1.379 (5) |
| O5—C10 | 1.214 (4) | N1—C6 | 1.453 (6) |
| O6—C10 | 1.277 (4) | N3—C2 | 1.291 (6) |
| O2—C7 | 1.213 (4) | N3—C4 | 1.327 (6) |
| C7—C8 | 1.532 (5) | C4—C5 | 1.344 (7) |
| C10—C9 | 1.539 (5) | | |
| O2—C7—O1 | 126.4 (3) | O3—C8—C7 | 109.9 (3) |
| O2—C7—C8 | 119.8 (3) | C9—C8—C7 | 112.5 (3) |
| O1—C7—C8 | 113.8 (3) | C2—N1—C5 | 107.7 (3) |
| O5—C10—O6 | 127.2 (3) | C2—N1—C6 | 127.0 (4) |
| O5—C10—C9 | 119.0 (3) | C5—N1—C6 | 125.2 (4) |
| O6—C10—C9 | 113.7 (3) | C2—N3—C4 | 108.9 (4) |
| O4—C9—C8 | 110.2 (3) | N3—C2—N1 | 110.0 (4) |
| O4—C9—C10 | 111.5 (3) | N3—C4—C5 | 108.1 (4) |
| C8—C9—C10 | 110.0 (3) | C4—C5—N1 | 105.3 (3) |
| O3—C8—C9 | 109.6 (3) | | |

Table 3. *Contact distances* (Å)

| | | | |
|---|---|---|---|
| $O(1)\cdots O(6^{i})$ | 2.48 (1) | $C(5)\cdots O(1^{iv})$ | 3.27 (1) |
| $O(3)\cdots O(4^{ii})$ | 2.89 (1) | $C(4)\cdots O(5^{v})$ | 3.20 (1) |
| $O(4)\cdots O(2^{iii})$ | 2.89 (1) | $N(3)\cdots O(3^{vi})$ | 2.89 (1) |
| $C(2)\cdots O(2^{iii})$ | 3.14 (1) | | |

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

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

This work was supported by the Office of Scientific Research.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). C**51**, 1683–1687

# Mono- and Diprotonated 1,4-Dihydrazinophthalazine: $C_8H_{11}N_6^+.Cl^-$ and $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$

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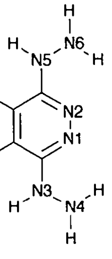
(*Received* 7 *September* 1994; *accepted* 3 *January* 1995)

## Abstract

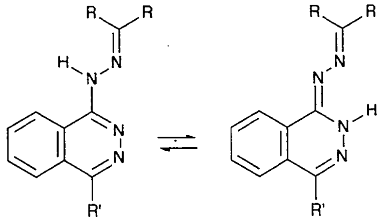
The crystal structures of 1,4-dihydrazinophthalazine monohydrochloride, $C_8H_{11}N_6^+.Cl^-$, and 1,4-dihydrazinophthalazine dihydrochloride dihydrate, $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$, have been determined. The protonation sites on the 1,4-dihydrazinophthalazine molecule were identified (*i.e.* 1,4-dihydrazinophthalazin-2-ium chloride and 4-hydrazinio-1-hydrazinophthalazin-2-ium dichloride dihydrate). A potentiometric study showed that in aqueous solution 1,4-dihydrazinophthalazine behaves as a diprotic base with $pK_{a1} = 4.24$ and $pK_{a2} = 8.13$.

## Comment

1,4-Dihydrazinophthalazine, $C_8H_{10}N_6$, (I), derivatives have been studied because of their potential pharmaceutical applications as antihypertensive agents (Durey & Tripod, 1967). In addition, they have applications in coordination chemistry as binucleating ligands (Andrew, Ball & Blake, 1969; Andrew & Blake, 1969; Ball & Blake, 1969, 1974; Rosen, 1971; Sullivan & Palenik, 1977; Robichaud & Thompson, 1984; Attanasio, Dessy & Fares, 1985; Attanasio, Fares & Imperatori, 1986; Thompson, Mandal, Gabe & Charland, 1986; Wen, Thompson, Lee & Gabe, 1988; Thompson, Lee & Gabe, 1988; Bontchev *et al.*, 1989; Mandal, Thompson, Newlands, Charland & Gabe, 1990). Several such studies have shown the acidic H atoms of these molecules to be quite mobile, allowing tautomeric equilibria. For example, a detailed $^1$H NMR analysis (Thompson & Woon, 1986) of some hydrazone derivatives of 1,4-dihydrazinophthalazine showed that these molecules are present in solution as forms (II) and (III). It also revealed that the equilibrium between these tautomers is affected by complexation to metal ions, in particular diamagnetic copper(I). With regard to solid-state structures, Stadnicka & Lebioda (1979) and Herrnstadt, Mootz, Wunderlich & Mohrle (1979) reported the structure of the 1,4-dihydrazinophthalazine.$H_2SO_4$ salt in which the 1,4-dihydrazinophthalazine molecule is diprotonated, one proton being bonded to N2 and the other to N4. The crystal structure of 1-hydrazinophthalazine hydrochloride has also been determined (Stadnicka & Lebioda, 1978); in this case the protonation site is an N atom within the phthalazine ring.

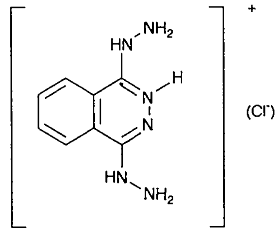


(I)

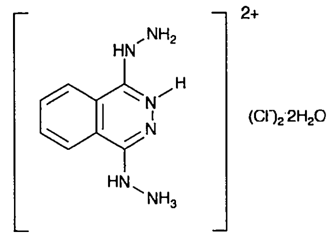


(II) (III)

As part of our study of the protonation of 1,4-dihydrazinophthalazine we report here the structures of 1,4-dihydrazinophthalazine monohydrochloride (I*a*) and dihydrochloride dihydrate (I*b*). The particular problem here is to determine which 1,4-dihydrazinophthalazine N atom is protonated first. A potentiometric study of the protonation equilibria of 1,4-dihydrazinophthalazine in water is also reported; this was undertaken in order to quantify the acidity of the protonation sites.



(I*a*)



(I*b*)

The structure of 1,4-dihydrazinophthalazine monohydrochloride shows the phthalazine atom N2 to be protonated (Fig. 1). There are two independent molecules in the asymmetric unit and an intramolecular N2—HN2···N6 hydrogen bond is formed (Table 3). Two independent molecules are connected by three hydrogen bonds (N2*A*—HN2*A*···N6$B^{i}$, N4*A*—HN4*A*1···N1$B^{i}$ and N2$B^{i}$—HN2$B^{i}$···N1*A*) and each pair of independent 1,4-dihydrazinophthalazine molecules is linked to another two pairs by N6$A^{ii}$—HN6*A*$1^{ii}$···N4*A* and N6$B^{iii}$—HN6*B*$1^{iii}$···N4$B^{i}$ hydrogen bonds, forming a sheet parallel to *b*. Adjacent sheets are connected by the two chloride anions present in the asymmetric unit (Fig. 2).

1,4-Dihydrazinophthalazine dihydrochloride dihydrate is protonated at the phthalazine N2 and the hydrazino N4 atoms (Fig. 3). Both protonations imply intramolecular hydrogen bonds (N2—HN2···N6

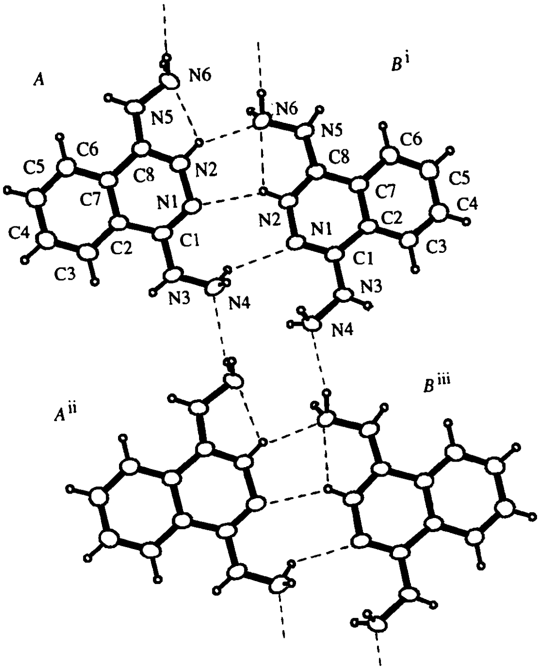


Fig. 1. View of 1,4-dihydrazinophthalazine monohydrochloride showing the atom-numbering scheme and the hydrogen-bond network. Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, y-1, z$; (iii) $1-x, -1-y, -z$.

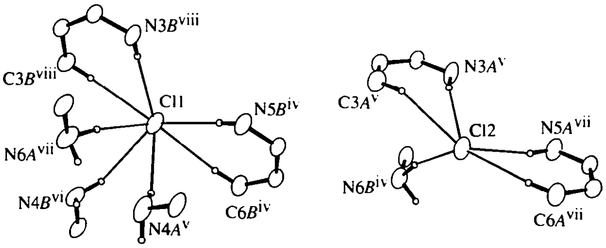


Fig. 2. Depiction of the first coordination sphere of the two independent chloride anions in the asymmetric unit of 1,4-dihydrazinophthalazine monohydrochloride (distances < 3.0 Å). Symmetry codes are given in Table 3.

and N4—HN4*B*···N1; Table 3). One of the two water molecules has a strong interaction with two 1,4-dihydrazinophthalazine molecules through N2—HN2···O1 and N4—HN4*B*···$O1^{ix}$ hydrogen bonds, forming a sort of dimer. Dimers are connected by the two chloride anions (Fig. 4). The two water molecules are hydrogen bonded (O1—HO1*B*···O2).

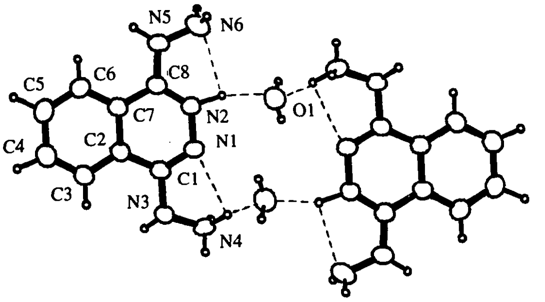


Fig. 3. View of 1,4-dihydrazinophthalazine dihydrochloride dihydrate showing the atom-numbering scheme and the hydrogen-bond network. The pseudo dimer is centrosymmetric.

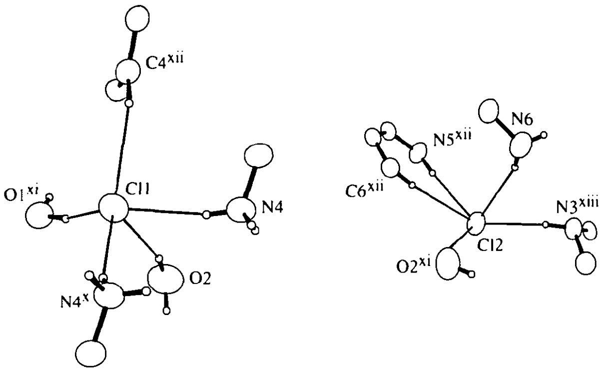
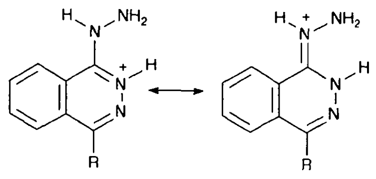


Fig. 4. Depiction of the first coordination sphere of the two chloride anions of 1,4-dihydrazinophthalazine dihydrochloride dihydrate (distances < 3.0 Å). Symmetry codes are given in Table 3.

Bond distances and angles within the 1,4-dihydrazinophthalazine molecules of both the mono- and diprotonated structures are comparable to literature values (Andrew & Blake, 1969; Herrnstadt, Mootz, Wunderlich & Mohrle, 1979; Stadnicka & Lebioda, 1979). The two independent 1,4-dihydrazinophthalazine molecules within the asymmetric unit of the monohydrochloride structure have statistically equivalent bond distances and angles. The positive charge resulting from the protonation of N2 is somewhat delocalized over the N2—C8—N5 fragment. The N2—C8 bond is longer than N1—C1 and N5—C8 is shorter than N3—C1. In the diprotonated structure also one positive charge is delocalized over the N2—C8—N5 moiety. The N2—C8 bond is longer than N1—C1 and N5—C8 is shorter than N3—C1. Both structures should therefore be represented by the mesomeric equilibrium between the limiting formulae (IV) and (V).



(IV) (V)

The 1,4-dihydrazinophthalazine molecule is not planar in either the mono- or diprotonated form. The fragment C2—C3—C4—C5—C6—C7 is planar within the e.s.d.'s and the deviations of the other atoms from this plane are similar in the two forms. All the pyridazine rings deviate slightly from planarity, adopting distorted boat conformations with the N2 and C2 atoms out of the plane (Cremer & Pople, 1975; Zefirov, Palyulin & Dashevskaya, 1990). The total puckering amplitudes are very small (0.035 and 0.028 Å, respectively, for molecules *A* and *B* of the monoprotonated structure and 0.030 Å for the diprotonated form) and the aromaticity indices $I_{6,6}$ (Bird, 1992) are quite high (73.8, 72.7 and 72.5, respectively) suggesting that the 1,4-dihydrazinophthalazines reported here are nearly aromatic.

A major difference between the monoprotonated and diprotonated structures is that the N1—C1 bond is shorter in the latter. The N3—C1 bond is also longer in this structure, which could imply that the N3—N4 hydrazino moiety is less involved in the overall electron delocalization in the diprotonated 1,4-dihydrazinophthalazine molecule, where the atom N4 has a positive charge.

The potentiometric results of the protonation equilibria involving 1,4-dihydrazinophthalazine have shown the following two protonation steps:

$$L + H^+ = [LH]^+ \qquad \log K = 8.13$$

$$[LH]^+ + H^+ = [LH_2]^{2+} \qquad \log K = 4.24$$

The potentiometric experiments revealed no evidence of dimerization.

## Experimental

1,4-Dihydrazinophthalazine dihydrochloride dihydrate was purchased from Aldrich and used without further purification. Crystals were grown by the slow concentration of a solution in ethanol at room temperature. Crystals of 1,4-dihydrazinophthalazine monohydrochloride were obtained by half-neutralization with aqueous NaOH of an ethanolic solution of the dihydrochloride and slow evaporation of the solvent at room temperature.

### Monoprotonated Compound

*Crystal data*

$C_8H_{11}N_6^+.Cl^-$ Cu *Kα* radiation
$M_r = 226.67$ $\lambda = 1.54184$ Å

Monoclinic
$P2_1/c$
$a = 19.100\,(2)$ Å
$b = 9.826\,(1)$ Å
$c = 13.411\,(1)$ Å
$\beta = 129.53\,(6)°$
$V = 1941.3\,(3)$ Å$^3$
$Z = 8$
$D_x = 1.55$ Mg m$^{-3}$

Cell parameters from 25 reflections
$\theta = 35–45°$
$\mu = 3.340$ mm$^{-1}$
$T = 293$ K
Prism
0.50 × 0.40 × 0.30 mm
Orange

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: $\psi$ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.79$, $T_{\max} = 0.99$
3991 measured reflections
3661 independent reflections

2636 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.021$
$\theta_{\max} = 70°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 11$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 7.9%

*Refinement*

Refinement on $F$
$R = 0.047$
$wR = 0.031$
$S = 0.899$
2636 reflections
359 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.17$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.18$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

**Diprotonated Compound**

*Crystal data*

$C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$
$M_r = 299.16$
Monoclinic
$P2_1/c$
$a = 9.819\,(1)$ Å
$b = 21.581\,(2)$ Å
$c = 7.027\,(1)$ Å
$\beta = 113.88\,(6)°$
$V = 1361.6\,(3)$ Å$^3$
$Z = 4$
$D_x = 1.46$ Mg m$^{-3}$

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 35–45°$
$\mu = 4.443$ mm$^{-1}$
$T = 293$ K
Prism
0.20 × 0.20 × 0.10 mm
White

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: $\psi$ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.74$, $T_{\max} = 0.99$
2729 measured reflections
2341 independent reflections

1866 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.018$
$\theta_{\max} = 70°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 18$
$l = -7 \rightarrow 7$
3 standard reflections
frequency: 120 min
intensity decay: 0.2%

*Refinement*

Refinement on $F$
$R = 0.039$
$wR = 0.030$
$S = 0.935$
1866 reflections
227 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.15$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.14$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{\rm eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| $C_8H_{11}N_6^+.Cl^-$ | | | | |
| Cl1 | 0.10443 (5) | 0.13331 (8) | 0.69653 (6) | 3.83 (2) |
| Cl2 | 0.38667 (4) | 0.18299 (8) | 0.79150 (6) | 3.44 (2) |
| N1*A* | 0.6877 (1) | 0.2500 (3) | 0.0323 (2) | 2.81 (5) |
| N2*A* | 0.6894 (1) | 0.3906 (3) | 0.0451 (2) | 2.81 (5) |
| N3*A* | 0.6407 (2) | 0.0437 (3) | 0.0508 (2) | 3.42 (6) |
| N4*A* | 0.6856 (2) | −0.0249 (3) | 0.0130 (2) | 3.91 (6) |
| N5*A* | 0.6691 (1) | 0.5940 (3) | 0.1068 (2) | 3.22 (6) |
| N6*A* | 0.7150 (1) | 0.6570 (3) | 0.0670 (2) | 3.55 (6) |
| C1*A* | 0.6465 (2) | 0.1816 (3) | 0.0655 (2) | 2.64 (7) |
| C2*A* | 0.6040 (2) | 0.2457 (3) | 0.1134 (2) | 2.53 (6) |
| C3*A* | 0.5580 (2) | 0.1714 (3) | 0.1453 (3) | 3.24 (7) |
| C4*A* | 0.5202 (2) | 0.2382 (4) | 0.1923 (3) | 3.48 (7) |
| C5*A* | 0.5268 (2) | 0.3791 (4) | 0.2074 (3) | 3.58 (7) |
| C6*A* | 0.5721 (2) | 0.4544 (3) | 0.1759 (2) | 3.20 (7) |
| C7*A* | 0.6104 (2) | 0.3874 (3) | 0.1285 (2) | 2.51 (6) |
| C8*A* | 0.6574 (2) | 0.4607 (3) | 0.0932 (2) | 2.51 (6) |
| N1*B* | 0.1906 (1) | −0.0594 (2) | 0.0413 (2) | 2.83 (5) |
| N2*B* | 0.1968 (1) | −0.1999 (2) | 0.0559 (2) | 2.77 (5) |
| N3*B* | 0.1422 (1) | 0.1416 (3) | 0.0636 (2) | 3.18 (6) |
| N4*B* | 0.1741 (1) | 0.2129 (3) | 0.0071 (2) | 3.26 (6) |
| N5*B* | 0.1746 (1) | −0.4101 (3) | 0.1084 (2) | 3.19 (6) |
| N6*B* | 0.2199 (1) | −0.4735 (3) | 0.0676 (2) | 3.13 (5) |
| C1*B* | 0.1517 (2) | 0.0048 (3) | 0.0801 (2) | 2.51 (6) |
| C2*B* | 0.1162 (2) | −0.0640 (3) | 0.1361 (2) | 2.43 (6) |
| C3*B* | 0.0785 (2) | 0.0071 (3) | 0.1828 (2) | 2.91 (7) |
| C4*B* | 0.0465 (2) | −0.0641 (3) | 0.2362 (3) | 3.30 (7) |
| C5*B* | 0.0513 (2) | −0.2058 (3) | 0.2429 (3) | 3.33 (7) |
| C6*B* | 0.0884 (2) | −0.2776 (3) | 0.1977 (2) | 3.12 (7) |
| C7*B* | 0.1213 (2) | −0.2063 (3) | 0.1443 (2) | 2.53 (6) |
| C8*B* | 0.1648 (2) | −0.2754 (3) | 0.1008 (2) | 2.58 (6) |
| $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$ | | | | |
| Cl1 | 0.1304 (1) | 0.02895 (5) | 0.3133 (2) | 4.02 (2) |
| Cl2 | 0.8643 (1) | 0.17076 (5) | 0.4406 (2) | 4.25 (2) |
| O1 | 0.6448 (3) | 0.0055 (1) | 0.8771 (4) | 3.96 (7) |
| O2 | 0.3738 (4) | −0.0571 (2) | 0.6540 (6) | 6.0 (1) |
| N1 | 0.3954 (2) | 0.1015 (1) | 0.8387 (5) | 2.89 (7) |
| N2 | 0.5339 (3) | 0.1251 (1) | 0.8732 (5) | 2.92 (7) |
| N3 | 0.1553 (3) | 0.1166 (2) | 0.7993 (5) | 2.99 (7) |
| N4 | 0.1482 (3) | 0.0517 (2) | 0.7680 (5) | 3.27 (7) |
| N5 | 0.7044 (3) | 0.1999 (2) | 0.9007 (5) | 3.33 (7) |
| N6 | 0.8038 (4) | 0.1505 (2) | 0.9191 (6) | 4.36 (9) |
| C1 | 0.2932 (4) | 0.1419 (2) | 0.8208 (5) | 2.54 (8) |
| C2 | 0.3127 (4) | 0.2073 (2) | 0.8316 (5) | 2.48 (7) |
| C3 | 0.2004 (4) | 0.2501 (2) | 0.8151 (6) | 2.88 (8) |
| C4 | 0.2266 (4) | 0.3120 (2) | 0.8224 (6) | 3.24 (9) |
| C5 | 0.3672 (4) | 0.3347 (2) | 0.8475 (6) | 3.31 (9) |
| C6 | 0.4796 (4) | 0.2935 (2) | 0.8671 (5) | 2.96 (8) |
| C7 | 0.4546 (4) | 0.2304 (2) | 0.8589 (5) | 2.53 (7) |
| C8 | 0.5668 (4) | 0.1843 (2) | 0.8791 (5) | 2.60 (8) |

Table 2. *Selected geometric parameters* (Å, °)

| | $C_8H_{11}N_6^+.Cl^-$ | | $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$ |
|---|---|---|---|
| | *A* | *B* | |
| N1—N2 | 1.390 (3) | 1.389 (3) | 1.379 (4) |
| N1—C1 | 1.311 (5) | 1.308 (5) | 1.296 (5) |
| N2—C8 | 1.329 (5) | 1.324 (5) | 1.313 (5) |
| N3—N4 | 1.414 (5) | 1.424 (5) | 1.415 (5) |
| N3—C1 | 1.364 (4) | 1.355 (4) | 1.410 (5) |
| N5—N6 | 1.428 (5) | 1.428 (5) | 1.415 (5) |
| N5—C8 | 1.321 (4) | 1.332 (4) | 1.340 (5) |

| | | | |
|---|---|---|---|
| C1—C2 | 1.458 (5) | 1.459 (5) | 1.421 (5) |
| C2—C3 | 1.404 (5) | 1.403 (5) | 1.407 (5) |
| C2—C7 | 1.401 (4) | 1.401 (4) | 1.418 (5) |
| C3—C4 | 1.389 (6) | 1.390 (5) | 1.357 (6) |
| C4—C5 | 1.393 (5) | 1.395 (5) | 1.408 (6) |
| C5—C6 | 1.393 (6) | 1.382 (6) | 1.380 (6) |
| C6—C7 | 1.402 (5) | 1.405 (5) | 1.381 (5) |
| C7—C8 | 1.447 (5) | 1.453 (5) | 1.448 (5) |
| N2—N1—C1 | 116.1 (3) | 116.2 (3) | 116.0 (3) |
| N1—N2—C8 | 126.4 (3) | 126.8 (3) | 125.2 (3) |
| N4—N3—C1 | 121.0 (3) | 121.1 (3) | 112.6 (3) |
| N6—N5—C8 | 117.8 (3) | 119.6 (3) | 116.6 (3) |
| N1—C1—N3 | 118.1 (3) | 117.7 (3) | 115.0 (3) |
| N1—C1—C2 | 123.4 (3) | 123.3 (3) | 125.4 (3) |
| N3—C1—C2 | 118.4 (3) | 119.0 (3) | 119.5 (3) |
| C1—C2—C3 | 122.8 (3) | 122.5 (3) | 124.3 (3) |
| C1—C2—C7 | 118.1 (3) | 118.1 (3) | 117.4 (3) |
| C3—C2—C7 | 119.1 (3) | 119.4 (3) | 118.3 (3) |
| C2—C3—C4 | 120.0 (3) | 119.8 (3) | 120.9 (4) |
| C3—C4—C5 | 120.8 (4) | 120.3 (4) | 120.5 (4) |
| C4—C5—C6 | 120.0 (4) | 120.7 (4) | 119.5 (4) |
| C5—C6—C7 | 119.5 (3) | 119.3 (3) | 120.7 (4) |
| C2—C7—C6 | 120.7 (3) | 120.4 (3) | 120.1 (3) |
| C2—C7—C8 | 117.5 (3) | 117.6 (3) | 116.1 (3) |
| C6—C7—C8 | 121.8 (3) | 121.9 (3) | 123.9 (3) |
| N2—C8—N5 | 119.5 (3) | 120.6 (3) | 118.1 (3) |
| N2—C8—C7 | 118.3 (3) | 117.9 (3) | 119.8 (3) |
| N5—C8—C7 | 122.2 (3) | 121.5 (3) | 122.1 (3) |

Table 3. *Hydrogen-bonding geometry* (Å, °)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| $C_8H_{11}N_6^+.Cl^-$ | | | | |
| N2*A*—HN2*A*···N6*A* | 0.91 (5) | 2.20 (4) | 2.644 (4) | 110 (4) |
| N2*B*—HN2*B*···N6*B* | 0.88 (5) | 2.29 (4) | 2.713 (4) | 110 (4) |
| N2*A*—HN2*A*···N6*B*$^{\text{i}}$ | 0.91 (5) | 2.21 (5) | 3.045 (5) | 153 (4) |
| N4*A*—HN4*A*1···N1*B*$^{\text{i}}$ | 0.96 (4) | 2.54 (5) | 3.001 (5) | 110 (3) |
| N2*B*$^{\text{i}}$—HN2*B*$^{\text{i}}$···N1*A* | 0.88 (5) | 2.36 (5) | 3.136 (5) | 146 (4) |
| N6*A*$^{\text{ii}}$—HN6*A*1$^{\text{ii}}$···N4*A* | 0.86 (4) | 2.46 (5) | 3.177 (4) | 140 (3) |
| N6*B*$^{\text{iii}}$—HN6*B*1$^{\text{iii}}$···N4*B*$^{\text{i}}$ | 0.99 (4) | 2.30 (4) | 3.166 (4) | 147 (2) |
| N5*B*$^{\text{iv}}$—HN5*B*$^{\text{iv}}$···Cl1 | 0.86 (5) | 2.31 (5) | 3.165 (3) | 173 (2) |
| C6*B*$^{\text{iv}}$—H6*B*$^{\text{iv}}$···Cl1 | 0.97 (4) | 2.55 (4) | 3.510 (3) | 173 (4) |
| N4*A*$^{\text{v}}$—HN4*A*2$^{\text{v}}$···Cl1 | 0.96 (3) | 2.67 (3) | 3.537 (2) | 150 (4) |
| N4*B*$^{\text{vi}}$—HN4*B*1$^{\text{vi}}$···Cl1 | 1.02 (4) | 2.66 (5) | 3.559 (3) | 147 (4) |
| N6*A*$^{\text{vii}}$—HN6*A*2$^{\text{vii}}$···Cl1 | 1.08 (3) | 2.44 (3) | 3.504 (2) | 169 (4) |
| C3*B*$^{\text{viii}}$—H3*B*$^{\text{viii}}$···Cl1 | 0.95 (4) | 2.61 (4) | 3.557 (3) | 169 (3) |
| N3*B*$^{\text{viii}}$—HN3*B*$^{\text{viii}}$···Cl1 | 0.85 (5) | 2.39 (5) | 3.198 (3) | 160 (3) |
| N5*A*$^{\text{vii}}$—HN5*A*$^{\text{vii}}$···Cl2 | 0.90 (5) | 2.24 (5) | 3.106 (3) | 160 (4) |
| C6*A*$^{\text{vii}}$—H6*A*$^{\text{vii}}$···Cl2 | 0.95 (4) | 2.68 (4) | 3.615 (3) | 170 (4) |
| N6*B*$^{\text{iv}}$—HN6*B*2$^{\text{iv}}$···Cl2 | 1.09 (3) | 2.29 (4) | 3.351 (2) | 165 (3) |
| C3*A*$^{\text{v}}$—H3*A*$^{\text{v}}$···Cl2 | 0.97 (4) | 2.69 (4) | 3.580 (3) | 154 (2) |
| N3*A*$^{\text{v}}$—HN3*A*$^{\text{v}}$···Cl2 | 0.89 (5) | 2.50 (5) | 3.334 (3) | 156 (3) |
| $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$ | | | | |
| N2—HN2···N6 | 1.07 (5) | 2.37 (5) | 2.595 (5) | 90 (3) |
| N4—HN4*B*···N1 | 0.99 (4) | 2.34 (5) | 2.514 (4) | 88 (3) |
| N2—HN2···O1 | 1.07 (5) | 1.77 (5) | 2.797 (4) | 158 (2) |
| N4—HN4*B*···O1$^{\text{ix}}$ | 0.99 (4) | 1.83 (4) | 2.789 (4) | 163 (5) |
| O1—HO1*B*···O2 | 0.76 (5) | 2.08 (5) | 2.826 (4) | 167 (5) |
| O2—HO2*B*···Cl1 | 0.80 (5) | 2.43 (5) | 3.203 (3) | 162 (5) |
| N4—HN4*A*···Cl1 | 0.88 (5) | 2.32 (5) | 3.167 (4) | 162 (4) |
| N4$^{\text{x}}$—HN4*C*$^{\text{x}}$···Cl1 | 0.81 (4) | 2.34 (4) | 3.095 (3) | 155 (4) |
| O1$^{\text{xi}}$—HO1*A*$^{\text{xi}}$···Cl1 | 0.89 (6) | 2.26 (6) | 3.099 (4) | 157 (4) |
| C4$^{\text{xii}}$—H4$^{\text{xii}}$···Cl1 | 1.05 (5) | 2.65 (4) | 3.553 (4) | 144 (3) |
| N6—HN6*A*···Cl2 | 0.95 (8) | 2.75 (8) | 3.670 (5) | 163 (5) |
| N3$^{\text{xiii}}$—HN3$^{\text{xiii}}$···Cl2 | 0.91 (3) | 2.27 (5) | 3.171 (3) | 172 (2) |
| O2$^{\text{xi}}$—HO2*A*$^{\text{xi}}$···Cl2 | 0.89 (5) | 2.44 (5) | 3.267 (4) | 155 (4) |
| C6$^{\text{xii}}$—H6$^{\text{xii}}$···Cl2 | 0.91 (4) | 2.79 (4) | 3.681 (4) | 167 (3) |
| N5$^{\text{xii}}$—HN5$^{\text{xii}}$···Cl2 | 0.96 (4) | 2.24 (4) | 3.159 (4) | 161 (3) |

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, y-1, z$; (iii) $1-x, -1-y, -z$; (iv) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (v) $1-x, -y, 1-z$; (vi) $x, y, 1+z$; (vii) $1-x, 1-y, 1-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $1-x, -y, 2-z$; (x) $-x, -y, 1-z$; (xi) $1-x, -y, 1-z$; (xii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (xiii) $1+x, y, z$.

Data were collected using graphite-monochromated radiation with the detector at 368 mm and the beam tunnel flushed with helium between crystal and detector.

Calculations were performed with *SDP* (Enraf–Nonius, 1985) and *MolEN* (Fair, 1990) on a MicroVAX 3100. Potentiometric measurements and p$K_a$ determinations were carried out according to Hay, Govan, Perotti & Carugo (1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: NA1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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