

## 2,8-Dihydroxy-1,3,7,9-tetramethyl-6,12-dihydrodipyrido[1,2-*a*:1',2'-*d*]-pyrazinediylum dichloride dihydrate

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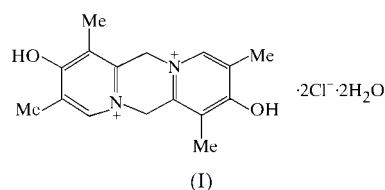
The 2,8-dihydroxy-1,3,7,9-tetramethyl-6,12-dihydrodipyrido[1,2-*a*:1',2'-*d*]pyrazinediylum dication possesses  $2/m$  symmetry and lies in the mirror plane together with a chloride anion and the water O atom. The dication also lies on an inversion centre, *i.e.*  $C_{16}H_{20}N_2O_2^{2+} \cdot 2Cl^- \cdot 2H_2O$ . Due to these symmetry constrictions the dication adopts an unexpected planar conformation. Molecules are linked by O—H...O and O—H...Cl hydrogen bonds to form chains, which are cross-connected by C—H...Cl attractive interactions forming a complex three-dimensional hydrogen-bond network.

### Comment

Condensed tricyclic molecules which incorporate the N atoms in the central ring have been synthesized with a wide variety of substituents (Bryce *et al.*, 1985; Eaves *et al.*, 1986). However, although many of the phenazine and acridine moieties have been structurally characterized, a search of the Cambridge Structural Database (1999; CSD) for the dipyrido[1,2-*a*:1',2'-*d*]pyrazinediylum cation retrieved only one hit, *i.e.* the structure of 6,12-dipyrido[1,2-*a*:1',2'-*d*]pyrazinediylum dibromide methanol solvate (Bryce *et al.*, 1985; CSD refcode: DEJGAA). In this structure, the core dipyrido[1,2-*a*:1',2'-*d*]pyrazinediylum dication has a crystallographic mirror plane bisecting the 1,2-*a* and 1',2'-*d* faces of the central pyrazine ring, as well as the analogous parallel faces of the outer pyrido rings. The bromide ions lie on these symmetry elements as does the C atom of the methanol solvate. The central pyrazine ring of the dication adopts an eclipsed boat conformation with the dihedral angle between the outer pyrido rings of 141°, similar to that found in the folded 9,10-dihydroanthracene systems (Herbstein *et al.*, 1986; Reboul *et al.*, 1987).

The title compound, (I), with the atomic numbering scheme is shown in Fig. 1. There are no significant differences between the bond lengths of the dication with bromide or chloride

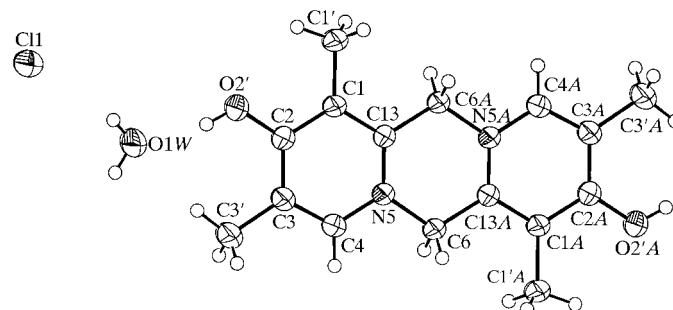
counter-ions. The value of the N5—C6 bond distance indicated its predominant single-bond character, while the N5—C13 and N5—C4 distances implied their aromatic nature (according to Allen *et al.*, 1987). In addition, the values of bond angles C13—N5—C6 and C4—N5—C6 have corroborated well with the existence of the dication and the  $sp^3$  hybridized C6 atom. Conformational properties of the title compound have confirmed its uniqueness compared to the bromine salt analogue, *i.e.* terminal 1,2,3-trisubstituted pyrido moieties are symmetrically related and therefore perfectly coplanar in (I), unlike the folded conformation of its unsubstituted bromine salt analogue.



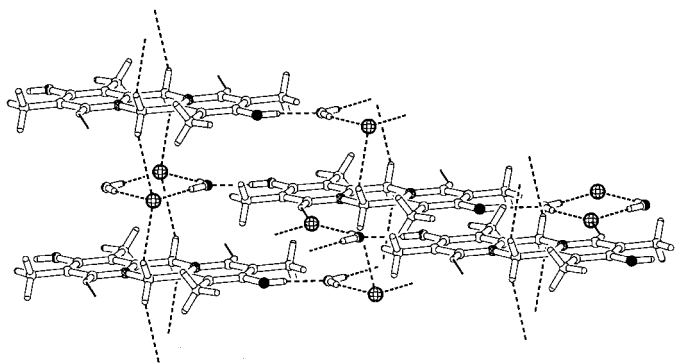
The dication possesses  $2/m$  symmetry with the mirror plane occupied by this dication together with a chloride anion and the water O atom. The dication also lies on an inversion centre, which is at the midpoint of the central pyrazine ring.

The complex three-dimensional hydrogen-bond networks (see Fig. 2) have been encoded *via* five different hydrogen bonds involving chloride anions and water molecules that link discrete cation moieties to each other. The cations are hydrogen bonded to water molecules *via* a  $D$  (notation according to graph-set analysis; Bernstein *et al.*, 1995) intermolecular  $O2'—H2' \cdots O1W$  hydrogen bond. Furthermore, the water molecules are hydrogen bonded *via* two additional  $D$  bonds, *i.e.*  $O1W—H2W \cdots Cl1$  and  $O1W—H1W \cdots Cl1^i$ . The water molecules and chloride anions are centrosymmetrically linked forming a pseudo-eight-membered ring, *i.e.*  $R_4^2(8)$  ring patterns. Also, by combining  $O2'—H2' \cdots O1W$  hydrogen bonds with a  $R_4^2(8)$  motif, chains along the  $[10\bar{1}]$  direction are formed giving  $C_4^3(17)$  chain patterns.

According to the criteria proposed by Taylor & Kennard (1982), there are two C—H...Cl attractive interactions (see Table 2) which join the dication to the anion. Namely, *via*  $D$   $C4—H4 \cdots Cl1^ii$  hydrogen bonds the second chain of molecules, *i.e.*  $C_2^1(9)$  chain patterns, have been formed. Thus, by linking designated patterns  $C_4^3(17)$  with  $C_2^1(9)$ , the sheets of molecules parallel with the (010) plane are generated.



**Figure 1**  
ORTEPII (Johnson, 1976) view of (I) with the atomic numbering scheme. Non-H atoms are drawn at the 50% probability level, while H atoms are drawn as spheres of arbitrary radii.



**Figure 2**  
The packing of (I). Cl ions are large and hatched, N atoms are small and hatched, O atoms are solid and hydrogen bonds are dashed lines.

The dications are stacked in the crystal along the [010] direction by the  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$  translation, which brings the central pyrazine ring about 5.5 Å above and below the centrosymmetric pseudo-eight-membered  $R_4^2(8)$  rings. In addition to stacking interactions,  $C6-H6 \cdots Cl1^{iii}$  *D* interactions have also been observed, which result in a third dication-anion chain, parallel to the [010] direction, *i.e.*  $C_2^1(4)$  chain patterns, thus completing the hydrogen-bond network.

Considering the  $sp^3$  hybridization of atom C6 and its symmetry-related atom C6A, the observed cation planarity was not expected. Nevertheless, it could be concluded that the described three-dimensional arrangement is formed due to symmetrically constrained dication planarity.

## Experimental

Crystals of (I) were obtained by slow evaporation of a mixture of ethanol and water in a 1:1 ratio at room temperature.

### Crystal data

$C_{16}H_{20}N_2O_2^{2+} \cdot 2Cl^- \cdot 2H_2O$   
 $M_r = 379.28$   
 Monoclinic,  $I2/m$   
 $a = 11.255$  (15) Å  
 $b = 6.8650$  (13) Å  
 $c = 11.9530$  (12) Å  
 $\beta = 104.15$  (2)°  
 $V = 895.5$  (12) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.407$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 10 reflections  
 $\theta = 6.38$ – $14.25$ °  
 $\mu = 0.385$  mm<sup>-1</sup>  
 $T = 293$  K  
 Prism, colourless  
 $0.50 \times 0.45 \times 0.40$  mm

### Data collection

Philips PW1100 diffractometer  
 upgraded by Stoe & Cie  
 $\omega$  scans  
 Absorption correction: numerical  
 (*X-RED*; Stoe & Cie, 1996)  
 $T_{min} = 0.801$ ,  $T_{max} = 0.888$   
 2776 measured reflections  
 1388 independent reflections  
 1146 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.021$   
 $\theta_{max} = 30$ °  
 $h = -15 \rightarrow 15$   
 $k = -9 \rightarrow 0$   
 $l = 0 \rightarrow 16$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 1.0%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.048$   
 $wR(F^2) = 0.169$   
 $S = 1.113$   
 1388 reflections  
 78 parameters

H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0895P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.33$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

N5—C13	1.333 (3)	N5—C6	1.474 (3)
N5—C4	1.359 (3)	O2'—C2	1.324 (3)
<hr/>			
C13—N5—C6	123.7 (2)	C4—N5—C6	114.5 (2)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O2'—H2' $\cdots$ O1 <i>W</i>	0.80 (3)	1.79 (3)	2.564 (4)	165 (2)
O1 <i>W</i> —H2 <i>W</i> $\cdots$ Cl1	0.71 (3)	2.44 (3)	3.133 (5)	165 (4)
O1 <i>W</i> —H1 <i>W</i> $\cdots$ Cl1 <sup>i</sup>	0.81 (3)	2.28 (3)	3.085 (5)	173 (2)
C4—H4 $\cdots$ Cl1 <sup>ii</sup>	0.93	2.81	3.675 (5)	156
C6—H6 <i>A</i> $\cdots$ Cl1 <sup>iii</sup>	0.97	2.74	3.588 (5)	147

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

The hydroxy-group and water-H atoms were located in difference Fourier maps, while all other H atoms were placed in geometrical positions (C—H 0.93–0.97 Å).

Data collection and cell refinement: *STADIA* (Stoe & Cie, 1996); *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON2000* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *PARST96* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1479). Services for accessing these data are described at the back of the journal.

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