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Tetraprotonated Tetra(2-pyridyl)pyrazine: Pyrazine-2,3,5,6-tetra(2-pyridinium) Tetrachloride Dihydrate

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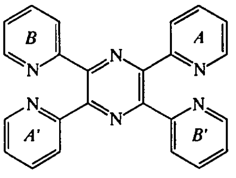
Abstract

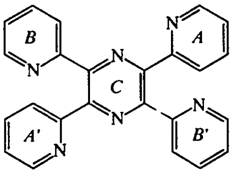
In the tetraprotonated form of tetra(2-pyridyl)pyrazine, $C_{24}H_{20}N_6^{4+}.4Cl^-.2H_2O$, all four pyridine groups are protonated. The structure possesses a crystallographic centre of symmetry. The four pyridinium-H atoms are hydrogen bonded to two Cl^- anions, forming NH···Cl···HN units. In the crystal, two more Cl^- anions and two water molecules of crystallization form a hydrogen-bonded chain that threads its way through the tetra-cations.

Comment

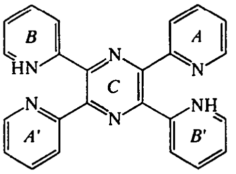
The ligand tetra(2-pyridyl)pyrazine (tppz) was first synthesized by Goodwin & Lions in 1959. The structures of two polymorphs have been reported previously. When recrystallized from $CHCl_3$ (Bock, Vaupel, Näther, Ruppert & Havlas, 1992) or CH_2Cl_2 (Greaves & Stoeckli-Evans, 1992), the monoclinic form tppz-I is normally obtained. A tetragonal form, tppz-II, has also been observed (Greaves & Stoeckli-Evans, 1992). Both forms possess C_i symmetry, the difference being in the orientation of the pyridine rings with respect to the pyrazine ring. A recent paper by Bailey, Grabarczyk, Hanks, Newton & Pennington (1996) describes the solid-state interconversion of polymorphs of tppz. We have been investigating the coordination chemistry of this ligand with first-row transition metals and have synthesized a number of mononuclear and binuclear complexes (Graf, Greaves & Stoeckli-Evans, 1993; Graf & Stoeckli-Evans, 1994; Graf, Stoeckli-Evans, Escuer & Vicente, 1996).



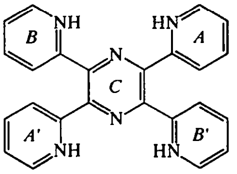
tppz-I



tppz-II



tppz-H2



tppz-H4

Bock and co-workers (Bock, Ruppert *et al.*, 1992) have shown that tppz exhibits proton-sponge properties, and that the reaction of tppz-I with 1*N* HCl leads to the formation of the diprotonated form, tppz-H2 (Bock, Vaupel *et al.*, 1992) in which two opposing pyridine rings (*B* and *B*′) were protonated and hydrogen bonded to two Cl^- anions. The orientation of the pyridine rings with respect to the pyrazine ring remains unchanged. They then studied the exchange of this preferred electron-rich proton-acceptor anion, Cl, for the phenyl-substituted tetraphenylborate. X-ray analysis revealed the formation of a second form of tppz-H2 in which intramolecular hydrogen bonds were formed. The two opposing protonated pyridine rings (*B* and *B*′) are now hydrogen bonded intramolecularly to the adjacent pyridine-N atoms of rings *A*′ and *A*, respectively.

The reaction of tppz-I with 2*N* HCl gave a white powder. When recrystallized from ethanol, very pale blue transparent crystals were produced but this material proved to be amorphous (no diffraction spots were observed). When recrystallized from water, large clear transparent blocks were formed. The structure analysis revealed a tetraprotonated form, tppz-H4 (Fig. 1). All four pyridine N atoms are protonated and the rings are rotated 180° from their original positions to hydrogen bond to two Cl^- anions (Cl1) situated above and below the plane of the pyrazine-N atoms (Fig. 2). Details of the hydrogen bonding are given in Table 3. The orientation of the pyridinium rings with respect to the central pyrazine ring is very different from that observed in the diprotonated form tppz-H2.2Cl (Bock, Vaupel *et al.*, 1992). In tppz-H2.2Cl, pyridine ring *A* has moved into the plane of the pyrazine ring and the dihedral angle between rings *A* and *C* is 16.6° compared with

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41.3 (1)° in tppz-H4. The dihedral angles of the pyridine rings with respect to the pyrazine ring in tppz-H4, tppz-H2.2Cl, tppz-I and tppz-II are compared in Table 4. In all four compounds, it is interesting to note that pyridine rings *A* and *B* (= *A'*/*B* = *A*/*B'*) are inclined to one another by *ca* 60°.

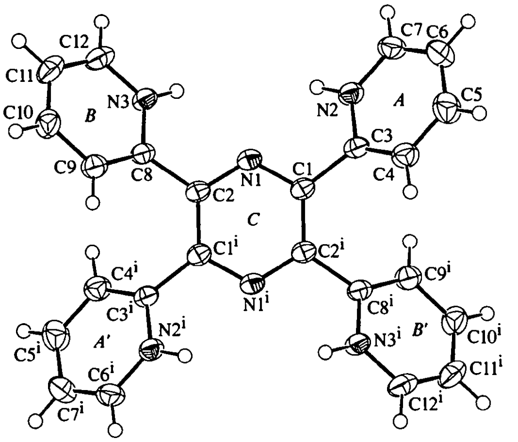

Fig. 1. Perspective view of tppz-H4 with displacement ellipsoids plotted at the 50% probability level.

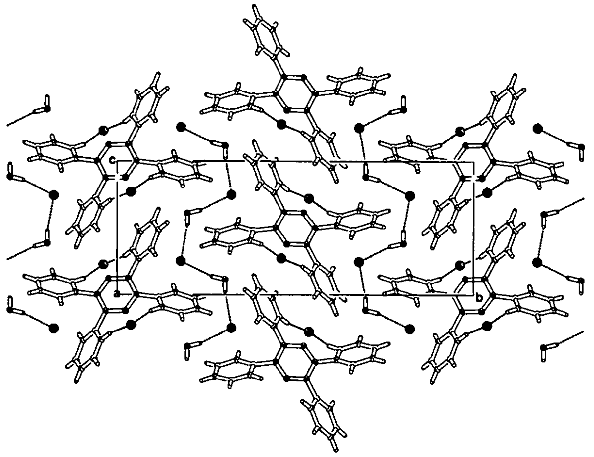

Fig. 2. Packing diagram of the title compound showing the intermolecular hydrogen bonds as dashed lines.

In the crystal of the title compound, the two remaining Cl anions (Cl2) form hydrogen bonds with the two water molecules of crystallization, resulting in chains extending in the **c** direction which thread through the tetra-cations (Fig. 2, Table 3).

Experimental

Tetra(2-pyridyl)pyrazine (tppz) was prepared according to the method described by Goodwin & Lions (1959). The title compound was prepared by dissolving 100 mg (0.26 mmol) of tppz in 20 ml of 2*N* HCl. The solution was stirred at room temperature for 30 min. It was then evaporated under reduced pressure and the white residue recrystallized from water. Analysis calculated for $C_{24}H_{24}Cl_4N_6O_2$: C 50.54, H 4.24, N 14.74%; found C 50.03, H 3.99, N 14.88%. IR (KBr cm^{-1}) 1612, 1543, 1461, 1379. ^{1}H NMR (D_2O/DSS): δ = 8.74 (*m*), 8.34 (*m*), 8.19 (*m*), 7.94 (*m*).

Crystal data

$C_{24}H_{20}N_6^{4+}.4Cl^-.2H_2O$
$M_r = 570.29$
Monoclinic
$P2_1/c$
$a = 6.284\,(1)$ Å
$b = 23.510\,(1)$ Å
$c = 9.033\,(1)$ Å
$\beta = 101.70\,(1)°$
$V = 1306.8\,(3)$ Å^3
$Z = 2$
$D_x = 1.449$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 14–19°$
$\mu = 0.488$ mm^{-1}
$T = 293\,(2)$ K
Plates
0.46 × 0.34 × 0.11 mm
Colourless

Data collection

Stoe AED-2 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2282 measured reflections
2282 independent reflections
1798 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 25.0°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 10$
2 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0323$
$wR(F^2) = 0.0800$
$S = 1.075$
2276 reflections
180 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.6839P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.061$
$\Delta\rho_{max} = 0.226$ e Å^{-3}
$\Delta\rho_{min} = -0.206$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0047 (11)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.0629 (3)	0.44447 (8)	0.5004 (2)	0.0252 (4)
C2	0.0125 (3)	0.53150 (9)	0.3770 (2)	0.0258 (4)
C3	0.1156 (3)	0.38310 (9)	0.4811 (2)	0.0271 (4)
C4	−0.0020 (4)	0.33720 (10)	0.5160 (3)	0.0352 (5)
C5	0.0448 (4)	0.28264 (10)	0.4701 (3)	0.0443 (6)
C6	0.2115 (4)	0.27447 (10)	0.3933 (3)	0.0435 (6)
C7	0.3293 (4)	0.32113 (10)	0.3645 (3)	0.0380 (5)
C8	0.0135 (3)	0.56046 (9)	0.2308 (2)	0.0274 (5)
C9	−0.1462 (4)	0.59671 (9)	0.1573 (2)	0.0338 (5)
C10	−0.1344 (4)	0.61678 (10)	0.0144 (3)	0.0397 (5)
C11	0.0390 (4)	0.60146 (10)	−0.0500 (2)	0.0409 (6)
C12	0.1932 (4)	0.56498 (10)	0.0267 (2)	0.0380 (5)

O1	0.3649 (5)	0.69750 (10)	−0.1139 (3)	0.0703 (7)
Cl1	0.54992 (9)	0.46160 (3)	0.27423 (7)	0.0419 (2)
Cl2	0.41012 (10)	0.67899 (3)	0.24778 (7)	0.0455 (2)
N1	0.0764 (3)	0.47686 (7)	0.3810 (2)	0.0262 (4)
N2	0.2776 (3)	0.37380 (8)	0.4059 (2)	0.0303 (4)
N3	0.1771 (3)	0.54476 (8)	0.1627 (2)	0.0301 (4)

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

C1—N1	1.337 (3)	C5—C6	1.382 (3)
C1—C2^{i}	1.408 (3)	C6—C7	1.378 (3)
C1—C3	1.498 (3)	C7—N2	1.352 (3)
C2—N1	1.344 (3)	C8—N3	1.352 (3)
C2—C1^{i}	1.408 (3)	C8—C9	1.380 (3)
C2—C8	1.487 (3)	C9—C10	1.391 (3)
C3—N2	1.351 (3)	C10—C11	1.383 (3)
C3—C4	1.380 (3)	C11—C12	1.372 (3)
C4—C5	1.398 (3)	C12—N3	1.340 (3)
N1—C1—C2^{i}	119.5 (2)	N2—C7—C6	120.6 (2)
N1—C1—C3	113.8 (2)	N3—C8—C9	119.7 (2)
C2^{i}—C1—C3	126.5 (2)	N3—C8—C2	114.8 (2)
N1—C2—C1^{i}	120.6 (2)	C9—C8—C2	125.2 (2)
N1—C2—C8	114.0 (2)	C8—C9—C10	119.1 (2)
C1^{i}—C2—C8	125.3 (2)	C11—C10—C9	119.8 (2)
N2—C3—C4	118.8 (2)	C12—C11—C10	119.1 (2)
N2—C3—C1	114.9 (2)	N3—C12—C11	120.5 (2)
C4—C3—C1	125.8 (2)	C1—N1—C2	119.9 (2)
C3—C4—C5	119.7 (2)	C3—N2—C7	122.3 (2)
C6—C5—C4	120.2 (2)	C12—N3—C8	121.7 (2)
C7—C6—C5	118.4 (2)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.94 (3)	2.15 (3)	3.071 (2)	165 (2)
N3—H3···Cl1	0.90 (3)	2.18 (3)	3.061 (2)	166 (2)
O1—H1A···Cl2	0.80 (4)	2.46 (4)	3.251 (3)	171 (3)
O1—H1B···Cl2^{i}	0.87 (4)	2.35 (4)	3.197 (3)	166 (4)

Symmetry code: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

Table 4. *Comparison of dihedral angles (°)*

	tppz-H4^{a}	tppz-H2^{b}	tppz-I^{b}	tppz-II^{c}
A^*B*	60.5(1)	60.0	62.4	60.4
A^*C*	41.3(1)	16.6	48.9	59.0
B^*C*	38.5(1)	59.6	51.7	46.4

References: (*a*) this work; (*b*) Bock, Vaupel *et al.* (1992); (*c*) Greaves & Stoeckli-Evans (1992).

The pyridinium and water H atoms were located from difference maps and refined isotropically. The aromatic H atoms were included in calculated positions as riding atoms with *SHELXL*93 default parameters (Sheldrick, 1993).

Data collection: *DIF*4 (Stoe & Cie, 1993*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON*, *PLATON* (Spek, 1993). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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γ-Aminobutyric Acid: a Novel Tetragonal Phase

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Abstract

In the tetragonal phase of γ-aminobutyric acid, $C_4H_9NO_2$, the single type of molecule adopts a partially folded zwitterionic form. Whereas in the previously characterized monoclinic phase the partially folded zwitterionic molecules exhibit a *gauche* conformation with respect to the C2—C3 bond, in this phase the molecules exhibit a *trans* conformation. The altered pattern of intramolecular N···O distances may be of significance with respect to the neurotransmission behavior of this substance. In addition to three strong hydrogen bonds involving the three H atoms bound to the N atom, as in the monoclinic phase, there is a fourth weaker one which results in a two-center bifurcated bond. There is also evidence suggestive of an intramolecular bridging