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N,N,N',N'-Tetrakis(2-pyridiniomethyl)-1,3-diaminopropane tetraperchlorate monohydrate

Takashi Fujihara,* Miki Saito and Akira Nagasawa

Department of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama 338-8570, Japan

Correspondence e-mail: fuji@chem.saitama-u.ac.jp

Key indicators

Single-crystal X-ray study

$T = 173$ K

Mean σ(C–C) = 0.004 Å

R factor = 0.066

wR factor = 0.183

Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The cation of the title compound, $H_4tptn^{4+} \cdot 4ClO_4^- \cdot H_2O$, where H_4tptn^{4+} is N,N,N',N'-tetrakis(2-pyridiniomethyl)-1,3-diaminopropane ($C_{27}H_{34}N_6^{4+}$), contains an intramolecular N—H···N hydrogen bond, and the average ring angle at the N atoms in the pyridinium rings is 123.6 (1)°. Intermolecular N—H···O and O—H···O hydrogen bonds are also found in the crystal structure.

Comment

As a part of systematic investigations for the syntheses of a class of multidentate ligands, tetrakis(2-pyridylmethyl)-alkanediamines have been prepared *via* reductive amination reactions (Fujihara *et al.*, 2004). We report here the crystal structure of the title compound, $H_4tptn^{4+} \cdot 4ClO_4^- \cdot H_2O$, (I).

(I)
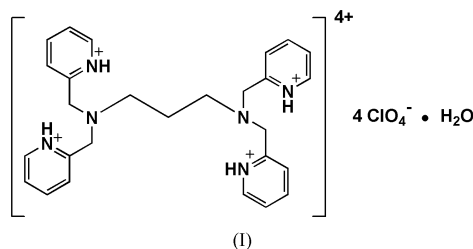
The molecular structure of (I) is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The average C—N—C bond angle of 123.6 (1)° in the protonated pyridine rings is similar to those of an analogous compound, $H_4tpen^{4+} \cdot 4ClO_4^-$ [H_4tpen^{4+} = N,N,N',N'-tetrakis(2-pyridinio-methyl)-1,2-diaminomethane; *ca* 123°; Gunatilleke & Norman, 2003]. The pyridine rings (N3/C5–C9, N4/C11–C15, N5/C17–C21 and N6/C23–C27) are planar, the largest deviation from the plane being that of atom C21 [0.011 (2) Å].

There are intramolecular and intermolecular N—H···O and intermolecular O—H···O hydrogen bonds (Table 2). The N atoms of the propanediamine backbone form intramolecular hydrogen bonds with the pyridinium H atoms [N1···N3 = 2.737 (3) Å and N2···N5 = 2.659 (3) Å]. The pyridinium N atoms (N3, N4 and N6) act as hydrogen-bond donors, forming intermolecular hydrogen bonds with water and perchlorate O atoms. Water atom O1 acts as a hydrogen-bond donor, forming intermolecular hydrogen bonds with perchlorate ions. These interactions play a role in the crystal packing (Fig. 2).

Experimental

To 1,2-dichloroethane (5 ml) in a flask were added 1,3-diamino-propane (0.39 g, 5.2 mmol) and 2-pyridinecarboxaldehyde (2.7 g, 25 mmol), and the mixture was stirred for 30 min at room temperature (293 K) under an argon atmosphere. A small amount of sodium
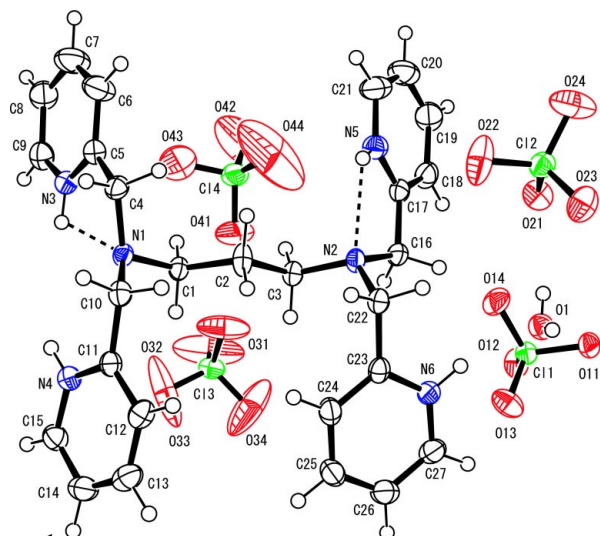
Figure 1
A view of (I), showing the intramolecular hydrogen bonds (dashed lines), with 50% probability displacement ellipsoids and the atom-numbering scheme.
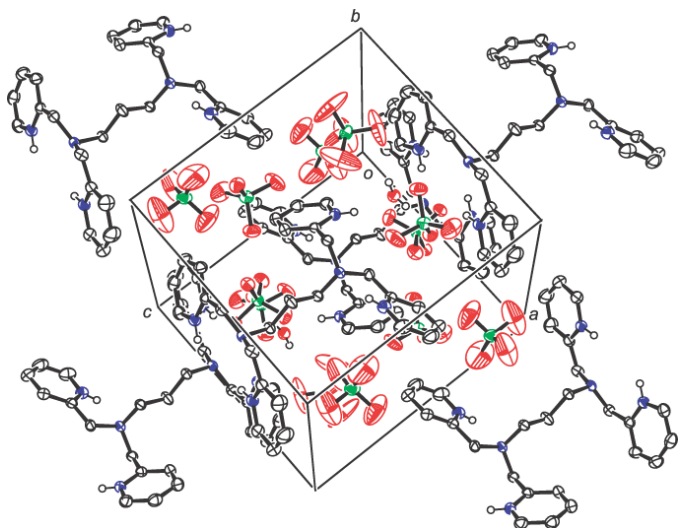

Figure 2
A molecular packing diagram of (I). H atoms bonded to C atoms have been omitted for clarity.

triacetoxyborohydride (4.4 g, 21 mmol) and CH_2ClCH_2Cl (15 ml) were added to the solution, which was stirred for 24 h at room temperature under an argon atmosphere, producing a yellow solution. After neutralization by the addition of saturated aqueous $NaHCO_3$ (25 ml) to give a weakly alkaline solution, the product was extracted with $CHCl_3$ (3 × 20 ml), which was then dehydrated by adding anhydrous Na_2SO_4 (6 g). The crude product was purified by silica-gel column chromatography with a toluene–ethanol mixed eluant (16:1 v/v). A pale-yellow oily residue as a free tptn containing some toluene was available by the evaporation of the solvent under reduced pressure (yield: 1.38 g, 58%). Perchloric acid (60%) was added slowly to an aqueous solution of the free tptn until the pH became approximately 4. The crude product of (I) was obtained as a pale-yellow powder by adding ethanol to the acidic aqueous solution. Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution.

Spectroscopic analysis for (I): ^{1}H NMR (D_2O, TSP$_{int}$): δ 8.67 (4H, dd), 8.47 (4H, t), 7.95 (4H, d), 7.90 (4H, t), 4.28 (8H, s), 2.70 (4H, t),

1.84 (2H, q). Elemental analysis found: C 37.81, H 4.24, N 9.76%; calculated for $C_{27}H_{36}Cl_4N_6O_{17}$: C 37.78, H 4.23, N 9.79%.

Crystal data

$C_{27}H_{34}N_6^{4+}\cdot4ClO_4^-\cdot H_2O$	$Z = 2$
$M_r = 858.42$	$D_x = 1.577$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.6648$ (6) Å	Cell parameters from 8505
$b = 12.3882$ (6) Å	reflections
$c = 12.5333$ (6) Å	$\theta = 2.4$–27.9°
$\alpha = 92.168$ (1)°	$\mu = 0.41$ mm^{-1}
$\beta = 91.050$ (1)°	$T = 173$ (2) K
$\gamma = 92.252$ (1)°	Block, colourless
$V = 1808.09$ (15) Å^3	0.50 × 0.40 × 0.25 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	8519 independent reflections
	7487 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan	$\theta_{max} = 27.9°$
(SADABS; Sheldrick, 1996)	$h = -15 \rightarrow 13$
$T_{min} = 0.821$, $T_{max} = 0.904$	$k = -16 \rightarrow 15$
13 190 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0956P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.066$	$+ 2.858P]$
$wR(F^2) = 0.183$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
8519 reflections	$\Delta\rho_{max} = 1.25$ e Å^{-3}
512 parameters	$\Delta\rho_{min} = -1.19$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: SHELXTL-NT
	Extinction coefficient: 0.0043 (10)

Table 1
Selected geometric parameters (Å, °).

N1—C4	1.461 (3)	C1—C2	1.526 (3)
N1—C10	1.463 (3)	C3—C2	1.522 (4)
N1—C1	1.480 (3)	N6—C27	1.341 (4)
N2—C16	1.459 (3)	N6—C23	1.354 (4)
N2—C22	1.469 (3)	N5—C17	1.334 (4)
N2—C3	1.477 (3)	N5—C21	1.348 (4)
N4—C15	1.341 (4)	N3—C5	1.336 (4)
N4—C11	1.341 (3)	N3—C9	1.344 (4)
C15—N4—C11	123.3 (3)	C17—N5—C21	124.0 (3)
C27—N6—C23	123.5 (2)	C5—N3—C9	123.7 (3)
C4—N1—C1—C2	68.0 (3)	N1—C10—C11—N4	−42.1 (3)
C10—N1—C1—C2	−57.5 (3)	N2—C22—C23—N6	85.1 (3)
C16—N2—C3—C2	−161.5 (2)	N2—C3—C2—C1	175.3 (2)
C22—N2—C3—C2	66.1 (3)	N1—C1—C2—C3	−178.8 (2)
N1—C4—C5—N3	20.6 (3)	N5—C17—C16—N2	13.3 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3N$\cdots$O11^i	0.88 (4)	2.00 (4)	2.845 (3)	160 (4)
N3—H3N$\cdots$N1	0.88 (4)	2.38 (4)	2.737 (3)	105 (3)
N4—H4N$\cdots$O1^i	0.87 (4)	2.57 (4)	3.137 (3)	124 (3)
N5—H5N$\cdots$N2	0.78 (4)	2.23 (4)	2.659 (3)	115 (4)
N6—H6N$\cdots$O1	0.90 (4)	1.93 (4)	2.810 (3)	165 (3)
O1—H102$\cdots$O21	0.76 (4)	2.14 (4)	2.876 (3)	163 (4)
O1—H101$\cdots$O33^{ii}	0.77 (5)	2.41 (5)	3.088 (7)	147 (5)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, 1 - y, 1 - z$.

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The water and pyridinium H atoms were located in a difference Fourier map and refined isotropically. Other H atoms were placed in calculated positions, with C—H = 0.99 (for CH$_2$) or 0.95 Å (for the pyridine ring), and refined using a riding model, with U_{iso}(H) = $1.2U_{eq}$(parent). The highest difference map peak was 0.54 Å from atom O34 and the deepest hole was 0.26 Å from atom O34.

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SAINT-W2K/NT* (Bruker, 2003); data reduction: *SAINT-W2K/NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

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