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N,N,N′,N′-Tetrakis(2-pyridiniomethyl)ethylenediamine tetraperchlorate

Shamila S. Gunatilleke and Richard E. Norman*

Chemistry Department, CNSB-210, University of Louisiana at Monroe, Monroe, LA 71209, USA

Correspondence e-mail: rnorman@ulm.edu

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Key indicators

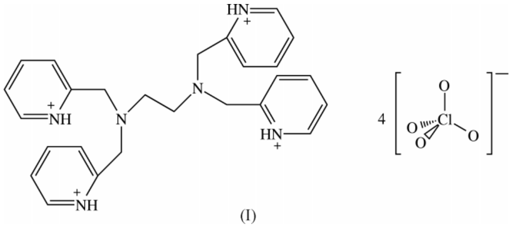
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.061
wR factor = 0.111
Data-to-parameter ratio = 11.3

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

The title compound, $(HpyCH_2)_2NCH_2CH_2N(CH_2PyH)_2(ClO_4)_4$ or $C_{26}H_{32}N_6^{4+}\cdot 4ClO_4^-$, is a salt of a centrosymmetric tetraprotonated tetrapyridine. As in many related compounds, the pyridyl N atoms are protonated while the tertiary amine N atoms are not.

Comment

During an attempted alternate synthesis of *N,N*-bis(2-pyridylmethyl)ethylenediamine (Matouzenko *et al.*, 1997), by the reaction of two equivalents of 2-picolyl chloride with one equivalent of ethylenediamine, the title compound, (I), was obtained.



(I)

The compound spans a center of symmetry and contains four perchlorate ions and a tetracation with only the pyridine N atoms protonated; the tertiary amine N atoms are not protonated. While this would seem to be unexpected (Gomes *et al.*, 2000; Kim *et al.*, 1995), based on the pK_a values of pyridine and triethylamine (5.2 and 11.0, respectively), the picolyl groups apparently have a profound inductive effect on the tertiary amine N atom, making it much less basic. The protonation constants of *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) were first reported (and the compound synthesized) in 1967 (Anderegg & Wenk, 1967). In that same article, the synthesis and protonation constants of a similar compound, tris(2-pyridylmethyl)amine (TPA), were also reported. The sites of protonation (the pyridine N atoms and not the tertiary amine N atoms) for TPEN and TPA were reported in 1977 (Anderegg *et al.*, 1977) and subsequently confirmed by ^{15}N NMR for TPA (Anderegg *et al.*, 1986). The structure of protonated TPA was first reported in 1991 (Britton *et al.*, 1991) and again in 1999 (Hazell *et al.*, 1999), with the pyridine N atom protonated.

Protonation of the pyridine N atoms in (I) results in a ring angle at nitrogen of about 123° [123.0 (2) and 123.1 (2)° at N2 and N3, respectively]. Similar angles are observed for other protonated pyridines (Britton *et al.*, 1991; Kim *et al.*, 1995; Hazell *et al.*, 1999; Gomes *et al.*, 2000), while neutral non-coordinated pyridines have smaller ring angles (for example, 119.6° in a pyridine macrocycle; Kim *et al.*, 1995). The pyridinium groups hydrogen bond to O3 [the N2···O3 and

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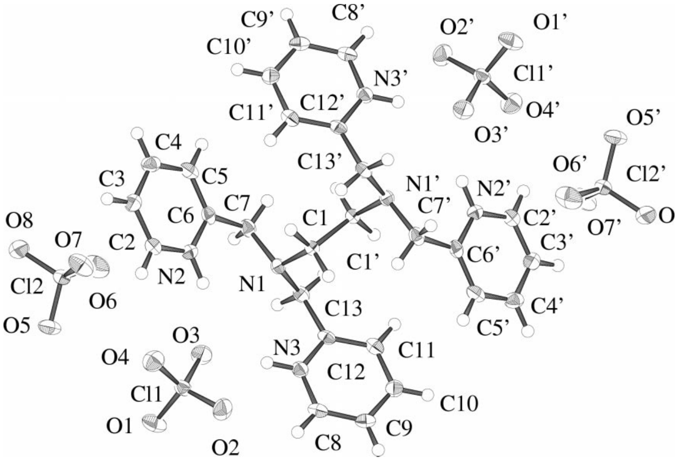

Figure 1
Perspective drawing of the title compound, with ellipsoids at the 50% probability level.

N3···O3 separations are 2.917 (3) and 2.847 (3) Å, respectively]. The metrical parameters of the perchlorate ions are unremarkable.

Experimental

2-Picolyl chloride hydrochloride (60.96 mmol, 10.00 g) was added, with cooling, to 26.67 ml of deionized water in a 500 ml three-neck round-bottomed flask equipped with a separatory funnel. Aqueous NaOH (61 mmol, 11.3 ml of a 5.4 *M* solution) was added dropwise, producing a light-red emulsion. Ethylenediamine (30.48 mmol, 1.832 g, 2.038 ml) was slowly added dropwise through the separatory funnel. The resultant mixture was stirred for 5 h at ambient temperature. Two layers were observed. The top layer was carefully removed. Perchloric acid (70 wt%) was added dropwise to the remaining red-brown layer until the pH was approximately 3, resulting in crystallization. Recrystallization from deionized water gave brown crystals (2.96 g, 3.58 mmol).

Crystal data

$C_{26}H_{32}N_6^{4+}\cdot 4ClO_4^-$
$M_r = 826.38$
Triclinic, $P\overline{1}$
$a = 8.4278\ (2)$ Å
$b = 9.2848\ (2)$ Å
$c = 11.3490\ (3)$ Å
$\alpha = 100.2225\ (9)^\circ$
$\beta = 105.5358\ (10)^\circ$
$\gamma = 94.4063\ (13)^\circ$
$V = 834.76\ (4)$ Å^3
$Z = 1$
$D_x = 1.64$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 3927 reflections
$\theta = 2.5$–30.0°
$\mu = 0.44$ mm^{-1}
$T = 100$ K
Irregular fragment, gold
0.25 × 0.25 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
ω scans with κ offsets
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.891$, $T_{\max} = 0.957$
16863 measured reflections
4500 independent reflections
2656 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 29.5^\circ$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.111$
$S = 1.05$
2656 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.0014|F_o|^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.20 (4)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.483 (3)	C3—C4	1.395 (4)
N1—C7	1.465 (3)	C4—C5	1.389 (4)
N1—C13	1.466 (3)	C5—C6	1.372 (4)
N2—C2	1.340 (3)	C6—C7	1.502 (4)
N2—C6	1.352 (3)	C8—C9	1.366 (4)
N3—C8	1.341 (3)	C9—C10	1.384 (4)
N3—C12	1.354 (3)	C10—C11	1.390 (4)
C1—C1$^{\rm i}$	1.542 (5)	C11—C12	1.376 (4)
C2—C3	1.356 (4)	C12—C13	1.504 (4)
C1—N1—C7	112.1 (2)	N2—C6—C7	116.1 (2)
C1—N1—C13	113.7 (2)	C5—C6—C7	125.6 (2)
C7—N1—C13	111.8 (2)	N1—C7—C6	110.8 (2)
C2—N2—C6	123.0 (2)	N3—C8—C9	119.9 (2)
C8—N3—C12	123.1 (2)	C8—C9—C10	119.1 (2)
N1—C1—C1$^{\rm i}$	115.3 (2)	C9—C10—C11	119.7 (3)
N2—C2—C3	120.3 (2)	C10—C11—C12	120.0 (2)
C2—C3—C4	118.9 (3)	N3—C12—C11	118.1 (2)
C3—C4—C5	119.4 (3)	N3—C12—C13	117.3 (2)
C4—C5—C6	120.0 (2)	C11—C12—C13	124.6 (2)
N2—C6—C5	118.2 (3)	N1—C13—C12	111.6 (2)

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

The H atoms bound to C1 (H1 and H2) were found in difference maps, were refined for several cycles and were then fixed. All other H atoms were placed in calculated positions and refined using a riding model.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK*; data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997–1999); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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