

2-[[N-(Pyridinium-2-ylmethyl)-N-(pyridin-2-ylmethyl)amino]methyl]-1-(pyridin-2-ylmethyl)-pyridinium diperchlorate

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Key indicators

Single-crystal X-ray study

T = 100 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

Disorder in main residue

R factor = 0.073

wR factor = 0.161

Data-to-parameter ratio = 13.5

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

The cation of the title salt, $\text{C}_{24}\text{H}_{25}\text{N}_5^{2+} \cdot 2\text{ClO}_4^-$, contains a tris(2-pyridylmethyl)amine core in which one of the pyridine N atoms is protonated and a second pyridine N atom forms an additional C—N bond to another 2-pyridylmethyl group, resulting in a second pyridinium center. The protonated pyridinium hydrogen bonds to a pyridine ring of a neighboring dication. The hydrogen-bonded H atom is disordered between the two N atoms.

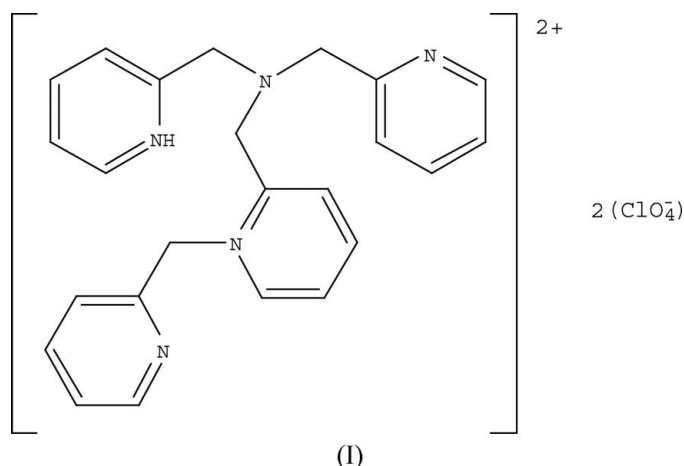
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Comment

During an attempt to prepare an Mn^{II} tpa complex [tpa is tris(2-pyridylmethyl)amine] by reacting manganese(II) chloride tetrahydrate with $\text{H}_3\text{tpa}(\text{ClO}_4)_3$ and triethylamine in methanol, the title compound was produced. The preparation of $[\text{Mn}(\text{tpa})\text{Cl}_2]$ has been reported (Allen *et al.*, 1995) under a nitrogen atmosphere, but the structure has not been reported. So far, our attempts to prepare the title compound, (I), under metal-free conditions by reaction of 2-picoly chloride hydrochloride with tpa [produced by *in situ* deprotonation of $\text{H}_3\text{tpa}(\text{ClO}_4)_3$] have been unsuccessful.



The structure of (I) consists of two perchlorate anions (which have typical distances and angles) and a dication, shown in Fig. 1. The dication contains a tpa core structure in which two of the pyridine N atoms share a proton and a third pyridine N atom forms an additional C—N bond to another 2-pyridylmethyl group, resulting in a second pyridinium center. There is a hydrogen bond between the partially protonated pyridinium N atom of one dication and the pyridine N atom of an adjacent molecule [the $\text{N}2 \cdots \text{N}3^{\text{I}}$ separation is $2.706(3) \text{ \AA}$; see Fig. 2; symmetry code as in Table 2]. The H atom is disordered across the hydrogen bond. Thus, in the tpa core,

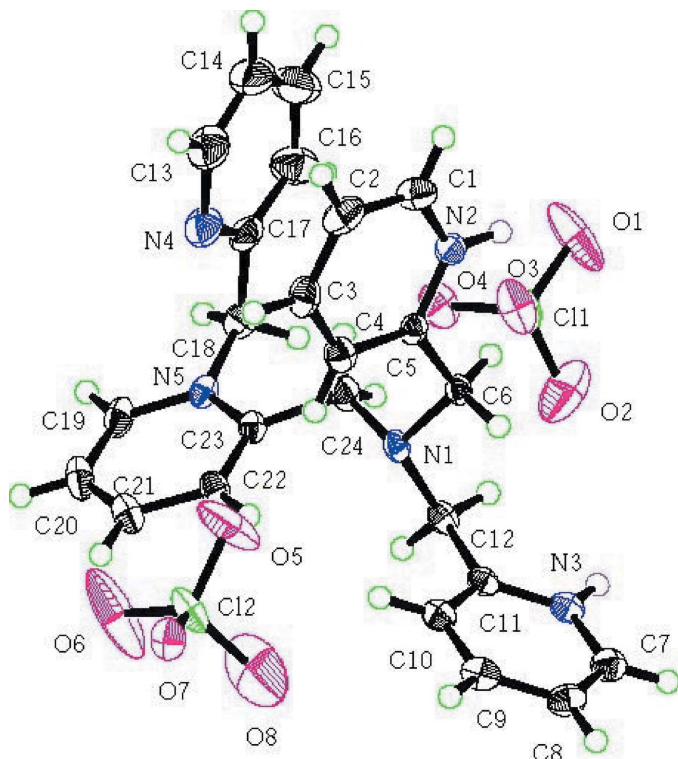


Figure 1
A view of (I), with displacement ellipsoids drawn at the 50% probability level. Both N2 and N3 are shown protonated, although the proton is shared by them.

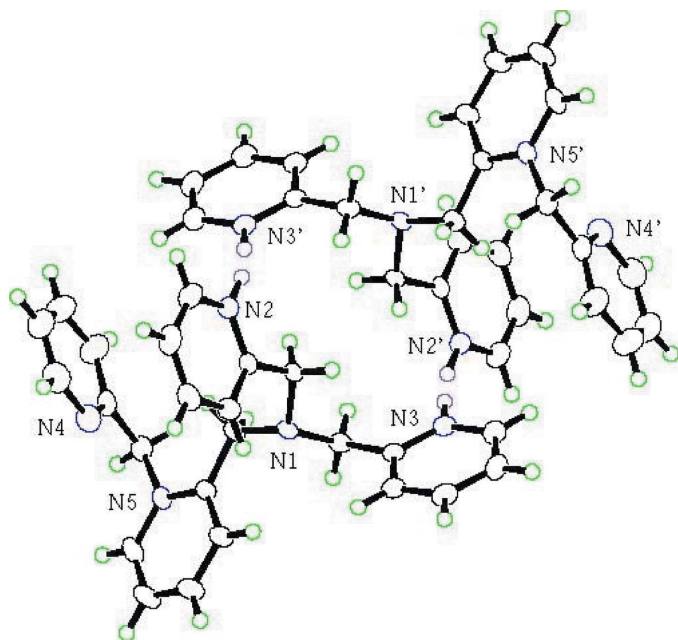


Figure 2
A view of two dications of (I), showing the hydrogen bonding. The disordered H atoms, bound to N2 and N3, are shown in violet. The prime corresponds to symmetry code (i) in Table 2.

two of the pyridine rings are half protonated and the third is alkylated.

There are no obvious trends in the distances and angles of the various pyridine rings in (I), and the values are typical of

other tpa structures (e.g. Britton *et al.*, 1991; Hazell *et al.*, 1999). The distances and angles of the 'extra' 2-pyridylmethyl group are also typical.

Experimental

Triethylamine (0.1513 g, 1.495 mmol) and $H_3tpa(ClO_4)_3$ (0.2956 g, 0.4995 mmol) were dissolved in methanol (20 ml). Manganese(II) chloride tetrahydrate (0.0989 g, 0.500 mmol) was added with stirring, producing a clear yellow solution. Colorless crystals formed after a few days. M.p. 445–449 K. 1H NMR (300 MHz, D_2O): 4.07 (6H), 5.91 (2H), 7.22 (*d*, 1H), 7.34 (*t*, 1H), 7.47 (*t*, 2H), 7.54 (*d*, 2H), 7.81 (*t*, 1H), 7.89 (*t*, 1H), 7.97 (*t*, 2H), 8.19 (*d*, 1H), 8.24 (*d*, 1H), 8.44 (*d*, 2H), 8.48 (*d*, 1H), 8.70 (*d*, 1H).

Crystal data

$C_{24}H_{25}N_5^{2+} \cdot 2ClO_4^-$
 $M_r = 582.40$
 Monoclinic, $P2_1/c$
 $a = 13.9313$ (2) Å
 $b = 10.9888$ (2) Å
 $c = 18.1280$ (4) Å
 $\beta = 108.0650$ (8)°
 $V = 2638.38$ (8) Å³
 $Z = 4$

$D_x = 1.466$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8603 reflections
 $\theta = 2.5$ – 32.0°
 $\mu = 0.30$ mm⁻¹
 $T = 100$ K
 Prism, colorless
 0.20 × 0.12 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans with κ offsets
 Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor 1997)
 $T_{min} = 0.869$, $T_{max} = 0.955$
 48722 measured reflections

9091 independent reflections
 4740 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.055$
 $\theta_{max} = 32.1^\circ$
 $h = -20 \rightarrow 20$
 $k = -16 \rightarrow 13$
 $l = -26 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.073$
 $wR(F^2) = 0.161$
 $S = 0.94$
 4740 reflections
 352 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o) + 0.003025|F_o|^2]$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.77$ e Å⁻³
 $\Delta\rho_{min} = -0.56$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1–C6	1.462 (3)	N3–C11	1.351 (3)
N1–C12	1.472 (3)	N4–C13	1.360 (4)
N1–C24	1.462 (3)	N4–C17	1.338 (4)
N2–C1	1.339 (4)	N5–C18	1.480 (4)
N2–C5	1.349 (4)	N5–C19	1.360 (3)
N3–C7	1.350 (4)	N5–C23	1.351 (3)
C6–N1–C12	111.1 (2)	N3–C7–C8	121.1 (3)
C6–N1–C24	110.2 (2)	N3–C11–C10	119.1 (2)
C12–N1–C24	110.0 (2)	N3–C11–C12	117.3 (2)
C1–N2–C5	119.1 (2)	N1–C12–C11	111.2 (2)
C7–N3–C11	121.6 (2)	N4–C13–C14	123.8 (4)
C13–N4–C17	116.3 (3)	N4–C17–C16	123.8 (3)
C18–N5–C19	118.2 (2)	N4–C17–C18	117.3 (3)
C18–N5–C23	121.1 (2)	N5–C18–C17	112.1 (2)
C19–N5–C23	120.7 (2)	N5–C19–C20	121.3 (3)
N2–C1–C2	122.0 (3)	N5–C23–C22	119.4 (2)
N2–C5–C4	121.4 (2)	N5–C23–C24	117.3 (2)
N2–C5–C6	116.2 (2)	N1–C24–C23	112.8 (2)
N1–C6–C5	112.7 (2)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H1\cdots N3^i$	0.95	1.79	2.706 (3)	162

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

Atom H1, the H atom associated with N2, was found in a difference map, and then placed in a calculated position. During subsequent refinement, atom H26, the H atom associated with N3, was observed in a difference map. Atoms N2 and N3 are the hydrogen-bonded pair of N atoms. Consequently, both H atoms were placed in calculated positions with half occupancy, and assigned displacement parameters 0.6 times those of N2 and N3 ($N-H = 0.95$ Å). All of the other H atoms were assigned displacement parameters 1.2 times those of the atoms to which they are bound and were treated as riding in idealized positions ($C-H = 0.95$ Å). The perchlorate anions are probably disordered, as reflected by the large displacement parameters. Attempts were made to model this disorder with various O atoms with partial occupancy, but the resulting models produced unreasonable distances and angles. The current model is reasonably well behaved and the Cl–O distances fall in the range 1.427 (3)–1.429 (3) Å for Cl1, and 1.391 (3)–1.444 (4) Å for Cl2.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction:

SCALEPACK and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN for Windows*.

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