Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 4,4′-Trimethylenedipyridinium dinitrate

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Received 22 April 2003
Accepted 1 May 2003
Online 16 May 2003

**Key indicators**

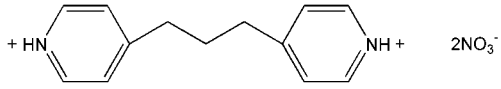
Single-crystal X-ray study
$T$ = 298 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.044
$wR$ factor = 0.048
Data-to-parameter ratio = 8.2

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

In the title compound, $C_{13}H_{16}N_2^{2+}\cdot 2NO_3^-$, the cation is the diprotonated form of 4,4′-trimethylenedipyridine. There are intermolecular hydrogen bonds and $\pi$–$\pi$ interactions between the pyridinium moieties of the cation and nitrate anions.

## Comment

4,4′-Trimethylenedipyridine (bpp) is a commonly employed bridging ligand in metal-organic coordination chemistry (Belcher *et al.*, 2002; Tong *et al.*, 2002). A salt of the monoprotonated form of bpp has been prepared and characterized (Wheatley *et al.*, 1999), but no structure of the diprotonated form ($bppH_2^{2+}$) has been reported. We report here the crystal structure of the nitrate salt of $bppH_2^{2+}$, (I), which was obtained as a by-product in the course of attempts to prepare a coordination polymer by reaction of bpp and $Cr(NO_3)_3\cdot 9H_2O$.




(I)

The structure determination of (I) reveals the presence of one $bppH_2^{2+}$ and two $NO_3^-$ ions. The $bppH_2^{2+}$ ion adopts approximately an *anti–anti* conformation for the trimethylene group (Fig. 1). This conformation is thermodynamically most favourable, since it minimizes intramolecular steric hindrance. The planes of the pyridine rings of the $bppH_2^{2+}$ ion are nearly orthogonal to the plane containing the trimethylene C atoms. The dihedral angles between the plane of the trimethylene group and those of the two pyridine rings are 89.8 (3) and 83.5 (3)°. This orthogonality increases the efficiency of stacking of $bppH_2^{2+}$ ions. $\pi$–$\pi$ interaction between the nitrate ions and the pyridine rings are observed. Both the $NO_3^-$ ions sit below and nearly parallel to the pyridine rings of the $bppH_2^{2+}$ ion. Nitrate atom N3 is under the N1-pyridine ring, with a dihedral angle of 5.2 (3)°. Similarly, nitrate atom N4 is under the N2-pyridine ring, making a dihedral angle of 2.2 (3)°. There are intermolecular hydrogen bonds between the pyridinium moieties of the $bppH_2^{2+}$ ion and $NO_3^-$ ions (Table 1 and Fig. 2).

## Experimental

In an attempt to prepare a coordination polymer, $Cr(NO_3)_3\cdot 9H_2O$ (0.429 g, 1.072 mmol) and bpp (0.071 g, 0.358 mmol) were dissolved in methanol (5 ml). By slow evaporation of the solution at room temperature, crystals of the title compound, (I), of considerable size (*ca* 0.5 mm) formed after six weeks.

*Crystal data*

$C_{13}H_{16}N_2^{2+}\cdot 2NO_3^-$
$M_r = 324.29$
Monoclinic, $P2_1/c$
$a = 7.894\ (6)$ Å
$b = 21.037\ (4)$ Å
$c = 9.879\ (6)$ Å
$\beta = 112.39\ (4)^\circ$
$V = 1516.9\ (16)$ Å$^3$
$Z = 4$
$D_x = 1.420$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.5$–$16.6^\circ$
$\mu = 0.11$ mm$^{-1}$
$T = 298\ (2)$ K
Block, yellow
0.28 × 0.19 × 0.15 mm

*Data collection*

AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2966 measured reflections
2761 independent reflections
1718 reflections with $I > 1.5\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.0^\circ$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 25$
$l = -11 \rightarrow 10$
3 standard reflections
every 250 reflections
intensity decay: 3.0%

*Refinement*

Refinement on $F$
$R = 0.044$
$wR = 0.048$
$S = 1.46$
1718 reflections
209 parameters
H-atom parameters constrained
$w = 1/[(\sigma)^2(F_o) + 0.00025(F_o)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.17$ e Å$^{-3}$
$\Delta\rho_{min} = -0.17$ e Å$^{-3}$
Extinction correction: Zachariasen type 2 Gaussian isotropic (Zachariasen, 1967)
Extinction coefficient: 16.860 (4)

**Table 1**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1N···O1$^{i}$ | 0.87 | 2.58 | 3.182 (4) | 127 |
| N1—H1N···O2$^{i}$ | 0.87 | 1.93 | 2.730 (3) | 153 |
| N2—H2N···O5$^{ii}$ | 0.87 | 1.96 | 2.825 (4) | 170 |
| N2—H2N···O6$^{ii}$ | 0.87 | 2.43 | 3.084 (4) | 133 |
| C1—H1···O4$^{i}$ | 0.95 | 2.40 | 3.324 (4) | 164 |
| C4—H4···O6$^{iii}$ | 0.95 | 2.55 | 3.409 (4) | 151 |
| C5—H5···O5$^{iv}$ | 0.95 | 2.41 | 3.094 (4) | 129 |
| C5—H5···O1$^{i}$ | 0.95 | 2.59 | 3.200 (4) | 123 |
| C10—H10···O3$^{v}$ | 0.95 | 2.59 | 3.181 (4) | 120 |
| C11—H11···O3$^{v}$ | 0.95 | 2.51 | 3.142 (4) | 124 |
| C12—H12···O2$^{iii}$ | 0.95 | 2.54 | 3.225 (4) | 129 |

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

All H atoms were placed at geometrically calculated positions and refined as riding, with C—H = 0.95 Å and N—H = 0.87 Å, and with $U_{iso}(H) = 1.2U_{eq}$(carrier atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

We gratefully acknowledge financial support from the University of Hong Kong.

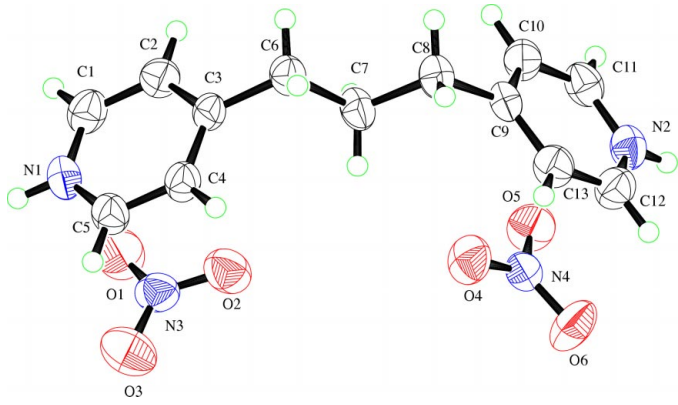



**Figure 1**
An *ORTEP*II (Johnson, 1976) drawing of the title compound, (I), with 50% probability ellipsoids, showing the crystallographic labeling scheme.

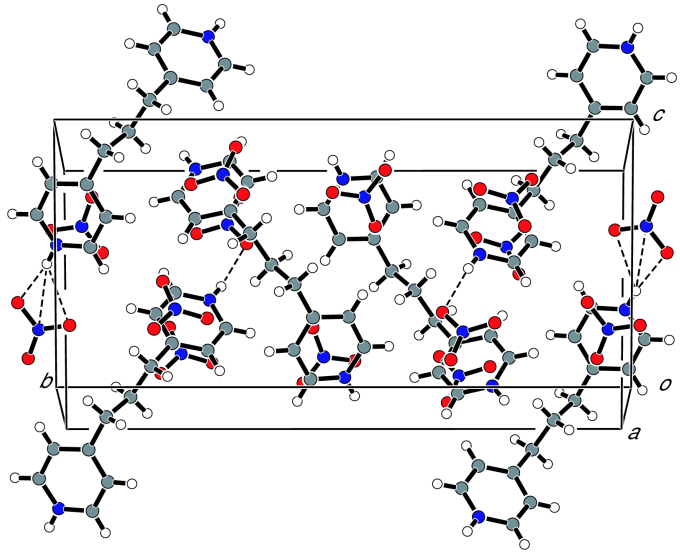



**Figure 2**
The packing diagram of (I), showing $\pi$–$\pi$ interactions and the hydrogen-bonding interactions (as dashed lines) between the nitrate ions and the pyridine rings.

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