

4,4'-(*m*-Phenylenedioxydimethylene)dipyridinium
dinitrate trihydrateJin-Sheng Gao,* Ying Liu,
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In the title compound, $C_{18}H_{18}N_2O_2^{2+} \cdot 2NO_3^- \cdot 3H_2O$, all bond lengths and angles in the diprotonated 1,3-bis(4-pyridylmethoxy)benzene cation are normal. The molecular skeleton of the cation is approximately planar; the central benzene ring makes dihedral angles of 8.98 (11) and 1.30 (12)° with the two outer pyridine rings. In the crystal structure, an extensive network of intermolecular of $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds stabilizes the packing.

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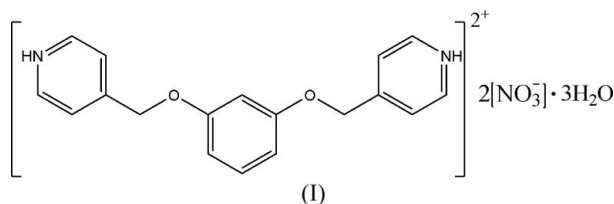
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.003$ Å
 R factor = 0.047
 wR factor = 0.153
Data-to-parameter ratio = 16.1

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

Comment

The 4,4'-bipyridine heterocyclic ring system is often used for bridging metal atoms in complexes. In contrast to the extensively studied 4,4'-bipyridine, the bis(4-pyridylmethoxy)benzene ligand has received less attention. The recent report of Hartshorn *et al.* (1998) described the formation of the palladium complex with the 1,4-bis(2-pyridylmethoxy)benzene ligand, which self-assembles into an M_2L_2 26-membered macrocycle. In our attempt to synthesize the bismuth complex with this ligand, we unexpectedly obtained the title compound, (I). We report its crystal structure here.



In the cation of (I), all bond lengths and angles are normal (Allen *et al.*, 1987). The benzene ring ($C7-C12$, A) and two pyridyl rings, ($N1/C1-C5$, B , and $N2/C14-C18$, C), make the following dihedral angles: A/B 8.98 (11)°, A/C 1.30 (12)° and B/C 10.27 (11)°. In the crystal structure, an extensive network of intermolecular $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds involving the water molecules and nitrate anions (Table 1) stabilizes the packing (Fig. 2).

Experimental

1,3-Bis(4-pyridylmethoxy)benzene was prepared by the reaction of *m*-benzenediol and 4-(chloromethyl)pyridine hydrochloric salt under alkaline condition (Gao *et al.*, 2004). All other chemicals were of analytical grade and were used without further purification. 1,3-Bis(4-pyridylmethoxy)benzene (1.46 g, 5 mmol) and bismuth trinitrate pentahydrate (2.41 g, 5 mmol) were dissolved in hot water (10 ml). The resulting solution was filtered, and the filtrate was allowed to stand in a desiccator at room temperature for several days. Colourless crystals of (I) were obtained. Unexpectedly, bismuth trinitrate

pentahydrate was hydrolysed to produce bismuth hydroxide and nitric acid; the nitric acid then formed a salt with 1,3-bis(4-pyridylmethoxy)benzene.

Crystal data

$C_{18}H_{18}N_2O_2^{2+} \cdot 2NO_3^- \cdot 3H_2O$
 $M_r = 472.41$
 Triclinic, $P\bar{1}$
 $a = 7.1509 (14) \text{ \AA}$
 $b = 10.821 (2) \text{ \AA}$
 $c = 15.214 (3) \text{ \AA}$
 $\alpha = 110.25 (3)^\circ$
 $\beta = 90.70 (3)^\circ$
 $\gamma = 90.09 (3)^\circ$
 $V = 1104.4 (4) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.421 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Block, colourless
 $0.38 \times 0.22 \times 0.22 \text{ mm}$

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.957, T_{\max} = 0.974$
 10880 measured reflections
 4958 independent reflections
 3347 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
 $R_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.153$
 $S = 1.09$
 4958 reflections
 307 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0784P)^2 + 0.1778P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.012 (3)

Table 1
 Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O11–H23 \cdots O6 ⁱ	0.85	2.07	2.901 (3)	166
O11–H24 \cdots O9 ⁱⁱ	0.85	1.92	2.767 (3)	173
O9–H19 \cdots O5	0.85	2.01	2.849 (3)	170
O9–H20 \cdots O10	0.85	1.99	2.835 (3)	174
O10–H21 \cdots O11 ⁱⁱⁱ	0.85	2.08	2.917 (3)	168
O10–H22 \cdots O11	0.85	2.05	2.896 (4)	173
N2–H16 \cdots O3	0.91 (4)	1.81 (4)	2.712 (3)	169 (3)
N1–H5 \cdots O7	0.97 (3)	1.77 (3)	2.741 (3)	176 (3)

Symmetry codes: (i) $-x + 2, -y + 2, -z + 2$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y + 1, -z$.

The C-bound H atoms were placed in calculated positions and treated as riding on their parent atoms, with C–H = 0.93 (aromatic) or 0.97 \AA (methylene) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atoms were located in a difference Fourier map and treated as riding on their parent atoms, with O–H = 0.85 \AA and $H \cdots H = 1.39 \text{ \AA}$, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The N-bound H atoms were located in a difference Fourier map and refined isotropically. The ADDSYM option of PLATON (Spek, 2003) detects pseudosymmetry in (I), which can be approximated by the monoclinic space group $C2/c$, but with the α and γ angles deviating from the exact monoclinic angles, at $90.09 (3)$ and $89.42 (3)^\circ$, respectively.

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MSK, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick,

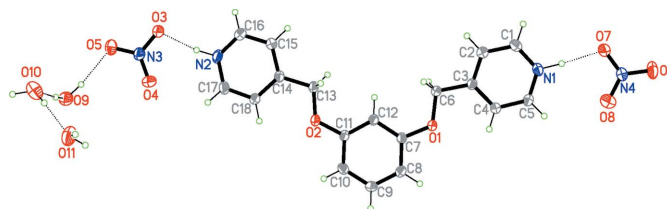


Figure 1
 The asymmetric unit of (I), showing the atom-labelling scheme and displacement ellipsoids drawn at the 30% probability level. Dashed lines indicate the hydrogen bonds.

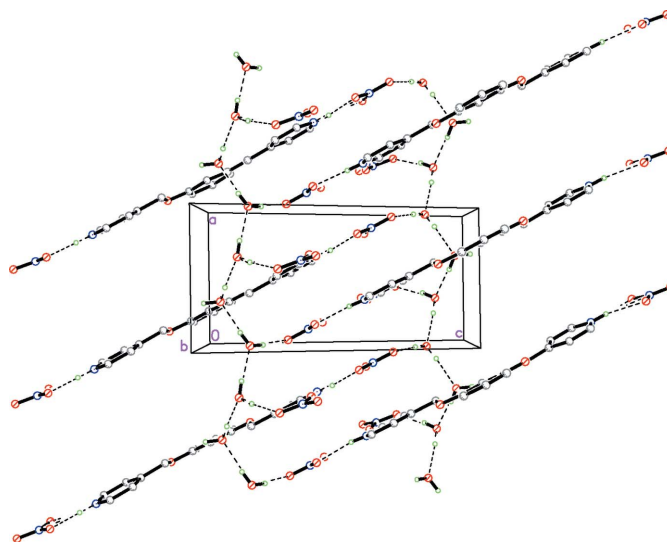


Figure 2
 The packing, viewed down the b axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXL97.

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