



Crystal structure of tetrakis(1-oxidopyridin-2-yl)methane methanol tetrasolvate

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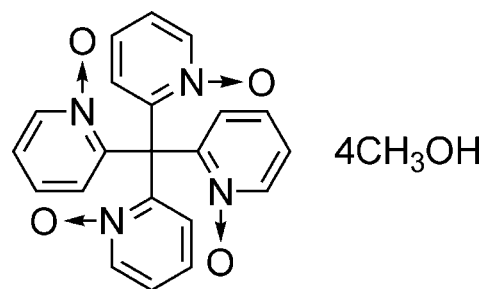
The asymmetric unit of the title compound, $C_{21}H_{16}N_4O_4 \cdot 4CH_3OH$, consists of a quarter molecule of tetrakis(1-oxidopyridin-2-yl)methane and one methanol solvent molecule. In the crystal, the pyridine *N*-oxide derivative is located about a fourfold rotoinversion axis and exhibits S_4 symmetry along the *c* axis. An intermolecular O—H...O hydrogen bond is observed between the O atom of the pyridine *N*-oxide and the OH group of the methanol. An intermolecular C—H...O bond is also observed between adjacent pyridine *N*-oxide rings.

Keywords: crystal structure; pyridine *N*-oxide; S_4 symmetry; hydrogen bonding.

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1. Related literature

For aspects of pyridine *N*-oxides, see: Katritzky & Lagowski (1971). For reviews of metal complexes of pyridine *N*-oxides, see: Orchin & Schmidt (1968); Carlin & De Jongh (1986). For the synthesis of the title compound, see: Matsumoto *et al.* (2003). For coordination polymers of pyridine *N*-oxides, see: Henkelis *et al.* (2012). For structures of related molecules, see: Betz *et al.* (2011); Matsumoto *et al.* (2014). For the effect of the formation of hydrogen bonds on the N—O bond length of pyridine *N*-oxides, see: Eichhorn (1987).



2. Experimental

2.1. Crystal data

$C_{21}H_{16}N_4O_4 \cdot 4CH_3O$
 $M_r = 516.54$
Tetragonal, $I4_1/a$
 $a = 14.4474$ (4) Å
 $c = 12.2965$ (5) Å
 $V = 2566.62$ (18) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 200$ K
 $0.2 \times 0.2 \times 0.1$ mm

2.2. Data collection

Rigaku R-Axis RAPID
diffractometer
12321 measured reflections

1470 independent reflections
1289 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.031$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.138$
 $S = 1.07$
1470 reflections

86 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 0.40$ e Å⁻³
 $\Delta\rho_{min} = -0.25$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------|-------|--------------|--------------|----------------|
| O2—H5...O1 | 0.84 | 1.90 | 2.7285 (15) | 169 |
| C4—H2...O1 ⁱ | 0.95 | 2.37 | 3.290 (2) | 163 |

Symmetry code: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Yadokari-XG 2009* (Wakita, 2001) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *Yadokari-XG 2009* and *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5417).

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supporting information

Acta Cryst. (2015). E71, o754–o755 [doi:10.1107/S2056989015016862]

Crystal structure of tetrakis(1-oxidopyridin-2-yl)methane methanol tetrasolvate

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S1. Comment

Pyridine *N*-oxides are one of the most common heterocyclic *N*-oxides and their physical and chemical properties are studied in detail (Katritzky & Lagowski, 1971). Pyridine *N*-oxides are the important compounds not only as the precursors of the substituted pyridine derivatives but also as the ligand molecules for the metal complexes (Orchin & Schmidt, 1968; Carlin & De Jongh, 1986). Recently, the bridging ligands containing more than two pyridine *N*-oxide groups were explored (Henkelis *et al.*, 2012). In the course of our investigation of tetrakis(pyridin-2-yl)methane (Matsumoto *et al.*, 2003), we are interested in the corresponding *N*-oxides as the bridging ligand and now we report the crystal structure of the title compound (Fig. 1). The bond lengths and angles of pyridine rings are similar to those of 2-methylpyridine *N*-oxide (Betz *et al.*, 2011). The C1—C2 bond length [1.5472 (11) Å] is similar to that of tetrakis-(pyridin-2-yl)methane [1.545 (2) Å] (Matsumoto *et al.*, 2014) and the prominent C1—C2 bond elongation by *N*-oxidation is not observed. The N—O bond length [1.3174 (14) Å] is also normal value in considering the formation of hydrogen bond with methanol molecule (Eichhorn, 1987). The interatomic distance of hydrogen bond is O1...H5 = 1.90 Å [O1...O2 = 2.7285 (15) Å]. An intermolecular C—H...O bond is also observed between the adjacent pyridine *N*-oxide rings [C4...H2 = 2.37 Å, O1...O2 = 3.290 (2) Å; Table 1].

S2. Experimental

To a solution of tetrakis(pyridin-2-yl)methane (100 mg, 0.3 mmol) in acetic acid (4.5 mL) was added 30% aqueous solution of hydrogen peroxide (66 mmol). The mixture was heated to 90 °C for 2.5 hours. After cooling to room temperature, acetone (20 mL) was added. When the mixture was stirred a few minutes, white precipitates appeared. Collection of the precipitate by filtration gave the title compound (120 mg, 46%) as colourless solid. The single crystals were prepared by slow evaporation of a solution of the title compound in methanol. The obtained single crystals were highly efflorescent and the exposure of the crystal to the air should be avoided.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms, and with O—H = 0.84 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ for hydroxyl H atoms.

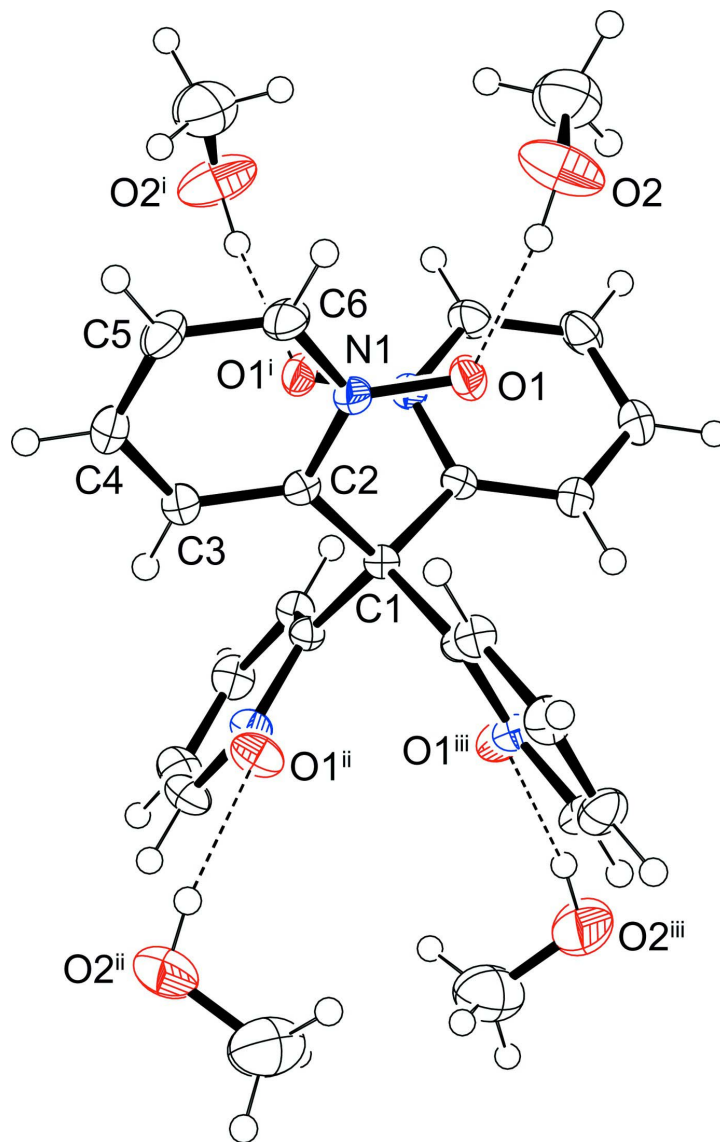


Figure 1

ORTEP drawing of the title compound (viewed along the *b* axis). Displacement ellipsoids are drawn at the 50% probability level. The hydrogen bonds are shown in the dashed lines. [Symmetry codes: (i) $-x, 1/2 - y, z$; (ii) $-1/4 + y, 1/4 - x, 5/4 - z$; (iii) $1/4 - y, 1/4 + x, 5/4 - z$.]

Tetrakis(1-oxidopyridin-2-yl)methane methanol tetrasolvate

Crystal data

$C_{21}H_{16}N_4O_4 \cdot 4CH_4O$

$M_r = 516.54$

Tetragonal, $I4_1/a$

$a = 14.4474(4) \text{ \AA}$

$c = 12.2965(5) \text{ \AA}$

$V = 2566.62(18) \text{ \AA}^3$

$Z = 4$

$F(000) = 1096$

$D_x = 1.337 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$

Cell parameters from 9662 reflections

$\theta = 3.6\text{--}27.4^\circ$

$\mu = 0.10 \text{ mm}^{-1}$

$T = 200 \text{ K}$

Prism, colourless

$0.2 \times 0.2 \times 0.1 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID
diffractometer

Detector resolution: 10.00 pixels mm⁻¹

ω scans

12321 measured reflections

1470 independent reflections

1289 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 27.4^\circ$, $\theta_{\text{min}} = 3.6^\circ$

$h = -18 \rightarrow 18$

$k = -18 \rightarrow 18$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.138$

$S = 1.07$

1470 reflections

86 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 1.7364P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.25 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement was performed using all reflections. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|---------------|--------------|--------------|----------------------------------|
| C1 | 0.0000 | 0.2500 | 0.6250 | 0.0172 (5) |
| C2 | -0.06345 (8) | 0.18960 (8) | 0.69738 (9) | 0.0181 (3) |
| C3 | -0.15822 (8) | 0.17917 (8) | 0.68249 (10) | 0.0218 (3) |
| H1 | -0.1873 | 0.2091 | 0.6228 | 0.026* |
| C4 | -0.21147 (9) | 0.12608 (9) | 0.75266 (11) | 0.0263 (3) |
| H2 | -0.2762 | 0.1198 | 0.7416 | 0.032* |
| C5 | -0.16814 (10) | 0.08235 (10) | 0.83934 (12) | 0.0299 (4) |
| H3 | -0.2030 | 0.0458 | 0.8887 | 0.036* |
| C6 | -0.07458 (9) | 0.09250 (10) | 0.85293 (11) | 0.0276 (3) |
| H4 | -0.0449 | 0.0623 | 0.9120 | 0.033* |
| C7 | 0.14412 (17) | 0.16009 (17) | 1.05514 (18) | 0.0626 (6) |
| H6 | 0.0822 | 0.1835 | 1.0727 | 0.094* |
| H7 | 0.1792 | 0.2082 | 1.0169 | 0.094* |
| H8 | 0.1764 | 0.1433 | 1.1224 | 0.094* |
| N1 | -0.02328 (7) | 0.14510 (7) | 0.78324 (8) | 0.0211 (3) |
| O1 | 0.06661 (6) | 0.15169 (7) | 0.79946 (8) | 0.0279 (3) |
| O2 | 0.13633 (12) | 0.08248 (11) | 0.98897 (12) | 0.0639 (5) |
| H5 | 0.1193 | 0.0987 | 0.9265 | 0.096* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.0179 (7) | 0.0179 (7) | 0.0159 (10) | 0.000 | 0.000 | 0.000 |
| C2 | 0.0194 (6) | 0.0181 (5) | 0.0167 (6) | 0.0004 (4) | 0.0014 (4) | 0.0005 (4) |
| C3 | 0.0202 (6) | 0.0224 (6) | 0.0230 (6) | 0.0003 (4) | -0.0006 (4) | -0.0001 (5) |
| C4 | 0.0195 (6) | 0.0286 (7) | 0.0308 (7) | -0.0018 (5) | 0.0037 (5) | -0.0003 (5) |
| C5 | 0.0275 (7) | 0.0321 (7) | 0.0300 (7) | -0.0014 (5) | 0.0095 (5) | 0.0067 (5) |
| C6 | 0.0287 (7) | 0.0315 (7) | 0.0225 (6) | 0.0021 (5) | 0.0039 (5) | 0.0091 (5) |
| C7 | 0.0630 (13) | 0.0783 (15) | 0.0464 (11) | -0.0129 (11) | -0.0033 (9) | -0.0051 (10) |
| N1 | 0.0194 (5) | 0.0251 (5) | 0.0186 (5) | 0.0015 (4) | 0.0009 (4) | 0.0029 (4) |
| O1 | 0.0183 (5) | 0.0382 (6) | 0.0271 (5) | 0.0004 (4) | -0.0033 (3) | 0.0090 (4) |
| O2 | 0.0954 (12) | 0.0553 (9) | 0.0411 (8) | 0.0033 (7) | -0.0273 (7) | 0.0119 (6) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--|--------------|-------------|--------------|
| C1—C2 | 1.5472 (11) | C5—C6 | 1.3698 (19) |
| C1—C2 ⁱ | 1.5472 (11) | C5—H3 | 0.9500 |
| C1—C2 ⁱⁱ | 1.5472 (11) | C6—N1 | 1.3643 (16) |
| C1—C2 ⁱⁱⁱ | 1.5472 (11) | C6—H4 | 0.9500 |
| C2—N1 | 1.3656 (16) | C7—O2 | 1.390 (3) |
| C2—C3 | 1.3895 (16) | C7—H6 | 0.9800 |
| C3—C4 | 1.3874 (18) | C7—H7 | 0.9800 |
| C3—H1 | 0.9500 | C7—H8 | 0.9800 |
| C4—C5 | 1.3881 (19) | N1—O1 | 1.3174 (14) |
| C4—H2 | 0.9500 | O2—H5 | 0.8400 |
| C2—C1—C2 ⁱ | 109.77 (9) | C6—C5—H3 | 120.3 |
| C2—C1—C2 ⁱⁱ | 109.32 (4) | C4—C5—H3 | 120.3 |
| C2 ⁱ —C1—C2 ⁱⁱ | 109.32 (4) | N1—C6—C5 | 121.26 (12) |
| C2—C1—C2 ⁱⁱⁱ | 109.32 (4) | N1—C6—H4 | 119.4 |
| C2 ⁱ —C1—C2 ⁱⁱⁱ | 109.32 (4) | C5—C6—H4 | 119.4 |
| C2 ⁱⁱ —C1—C2 ⁱⁱⁱ | 109.77 (9) | O2—C7—H6 | 109.5 |
| N1—C2—C3 | 118.00 (11) | O2—C7—H7 | 109.5 |
| N1—C2—C1 | 117.29 (9) | H6—C7—H7 | 109.5 |
| C3—C2—C1 | 124.69 (10) | O2—C7—H8 | 109.5 |
| C4—C3—C2 | 121.63 (11) | H6—C7—H8 | 109.5 |
| C4—C3—H1 | 119.2 | H7—C7—H8 | 109.5 |
| C2—C3—H1 | 119.2 | O1—N1—C6 | 118.73 (10) |
| C3—C4—C5 | 118.62 (12) | O1—N1—C2 | 120.13 (10) |
| C3—C4—H2 | 120.7 | C6—N1—C2 | 121.13 (11) |
| C5—C4—H2 | 120.7 | C7—O2—H5 | 109.5 |
| C6—C5—C4 | 119.34 (12) | | |
| C2 ⁱ —C1—C2—N1 | -45.51 (8) | C3—C4—C5—C6 | -0.2 (2) |
| C2 ⁱⁱ —C1—C2—N1 | 74.40 (6) | C4—C5—C6—N1 | 0.3 (2) |
| C2 ⁱⁱⁱ —C1—C2—N1 | -165.42 (10) | C5—C6—N1—O1 | -179.29 (12) |
| C2 ⁱ —C1—C2—C3 | 133.05 (13) | C5—C6—N1—C2 | 0.0 (2) |

| | | | |
|-----------------------------|--------------|-------------|-------------|
| C2 ⁱⁱ —C1—C2—C3 | -107.04 (14) | C3—C2—N1—O1 | 178.83 (10) |
| C2 ⁱⁱⁱ —C1—C2—C3 | 13.14 (11) | C1—C2—N1—O1 | -2.51 (15) |
| N1—C2—C3—C4 | 0.59 (18) | C3—C2—N1—C6 | -0.48 (18) |
| C1—C2—C3—C4 | -177.96 (10) | C1—C2—N1—C6 | 178.18 (10) |
| C2—C3—C4—C5 | -0.2 (2) | | |

Symmetry codes: (i) $-x, -y+1/2, z$; (ii) $-y+1/4, x+1/4, -z+5/4$; (iii) $y-1/4, -x+1/4, -z+5/4$.

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|--------------------------|------------|--------------|--------------|----------------|
| O2—H5...O1 | 0.84 | 1.90 | 2.7285 (15) | 169 |
| C4—H2...O1 ^{iv} | 0.95 | 2.37 | 3.290 (2) | 163 |

Symmetry code: (iv) $x-1/2, y, -z+3/2$.