

Crystal structure of a second polymorph of tetrakis(pyridin-2-yl)methane

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A second polymorph of the title compound, $C_{21}H_{16}N_4$, is reported. The original polymorph was solved by our group [Matsumoto *et al.* (2003). *Tetrahedron Lett.* **44**, 2861–2864] in the monoclinic space group $C2/c$ and refined to $R = 0.050$. Now the crystal structure of a tetragonal polymorph (space group $P4_21c$) has been solved and refined to $R = 0.036$. In the crystal, there are no strong intermolecular interactions. Reflecting the high symmetry of the molecular structure, the asymmetric unit is a quarter of the molecule, and the molecule exhibits S_4 symmetry along the c axis in the crystal.

Keywords: crystal structure; pyridine; bridging ligands; S_4 symmetry; polymorph.

CCDC reference: 1034349

1. Related literature

For a recent review on related bridging ligands, see: Sumbly (2011). For the synthesis of the title compound, see: Matsumoto *et al.* (2003); Abu-Shanab (2007). For transition metal complexes of the title compound, see: Matsumoto *et al.* (2004); Okazawa *et al.* (2004, 2005, 2006); Ishikawa *et al.* (2009); Hirosawa *et al.* (2012).

2. Experimental

2.1. Crystal data

$C_{21}H_{16}N_4$	$Z = 2$
$M_r = 324.38$	Mo $K\alpha$ radiation
Tetragonal, $P4_21c$	$\mu = 0.08 \text{ mm}^{-1}$
$a = 10.60 (1) \text{ \AA}$	$T = 200 \text{ K}$
$c = 7.03 (1) \text{ \AA}$	$0.5 \times 0.5 \times 0.4 \text{ mm}$
$V = 790 (2) \text{ \AA}^3$	

2.2. Data collection

Rigaku R-Axis RAPID imaging plate diffractometer	904 independent reflections
7257 measured reflections	858 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	57 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
904 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2012, 2014); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *Yadokari-XG 2009* (Wakita, 2001; Kabuto *et al.*, 2009) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *Yadokari-XG 2009* and *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: PK2537).

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supporting information

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Crystal structure of a second polymorph of tetrakis(pyridin-2-yl)methane

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S1. Comment

Bridging ligands that possess more than one coordination site have attracted considerable attention in relation to multinuclear metallosupramolecular assemblies and coordination polymers (Sumbly, 2011). The title compound (Fig. 1) is a typical tetrahedral bridging ligand when it binds to two metal ions in a two-fold bidentate fashion (Fig. 2*a*). The title compound was first synthesized by the reaction of tris(pyridin-2-yl)methyl anion with 2-chloropyridine (Matsumoto *et al.*, 2003). More recently, Abu-Shanab reported that the treatment of 2-picoline with excess of lithium diisopropylamide followed by 2-bromopyridine yielded the title compound as the main product (Abu-Shanab, 2007). The title compound takes on *S*₄ symmetry along the *c* axis in the crystal (Fig. 1), reflecting the highly symmetric molecular structure.

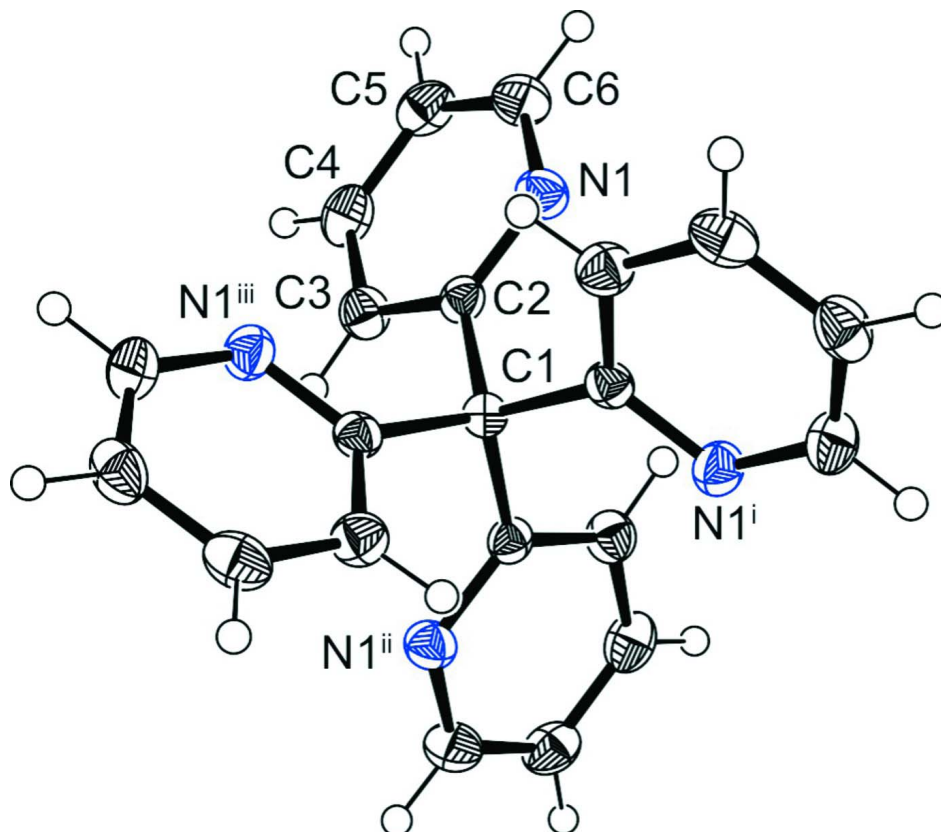
The silver complex of the title compound forms a one-dimensional coordination polymer in which the title compound acts as a two-fold bidentate bridging ligand (Matsumoto *et al.*, 2004). This coordination pattern was also observed in a dinuclear Mn(II) complex (Okazawa *et al.*, 2004) and dinuclear Ni(II) complex (Okazawa *et al.*, 2006). On the other hand, the title compound often takes bidentate (Fig. 2*b*) or tripodal coordination patterns (Fig. 2*c*) to bind only one metal ion. The bidentate coordination pattern was observed in the Cu(II) complexes of the title compound (Matsumoto *et al.*, 2004; Okazawa *et al.*, 2005) and tripodal coordination patterns were observed in Cu(II), Fe(II), and Co(II) complexes (Matsumoto *et al.*, 2004; Ishikawa *et al.*, 2009; Hirosawa *et al.*, 2012).

S2. Experimental

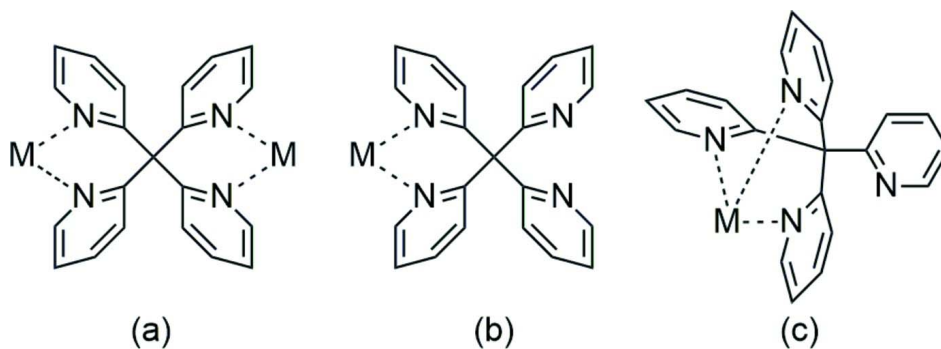
The title compound was synthesized by the reported procedure (Matsumoto *et al.*, 2003). Crystallization from methanol/chloroform (1/1) gave colorless crystals, which were used for X-ray analysis.

S3. Refinement

Aromatic H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95 Å and $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$.

**Figure 1**

An ellipsoid plot of the title compound (viewed down the c axis). Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $y, -x, -z + 1$; (ii) $-x, -y, z$; (iii) $-y, x, -z + 1$.

**Figure 2**

Three kinds of coordination patterns of the title compound. (a) Two-fold bidentate, (b) bidentate, and (c) tripodal. M represents a transition metal ion.

Tetrakis(pyridin-2-yl)methane

Crystal data

$C_{21}H_{16}N_4$
 $M_r = 324.38$
 Tetragonal, $P4_2/c$

$a = 10.60 (1) \text{ \AA}$
 $c = 7.03 (1) \text{ \AA}$
 $V = 790 (2) \text{ \AA}^3$

$Z = 2$
 $F(000) = 340$
 $D_x = 1.364 \text{ Mg m}^{-3}$
 Melting point: 259 K
 Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$
 Cell parameters from 6223 reflections

$\theta = 3.5\text{--}27.5^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 200 \text{ K}$
 Prism, colourless
 $0.5 \times 0.5 \times 0.4 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID imaging plate diffractometer
 Detector resolution: 10.00 pixels mm^{-1}
 ω scans
 7257 measured reflections
 904 independent reflections

858 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.5^\circ$
 $h = -10 \rightarrow 13$
 $k = -12 \rightarrow 13$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.090$
 $S = 1.07$
 904 reflections
 57 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
 $w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.1368P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0000	0.0000	0.5000	0.0209 (6)
C2	-0.02294 (14)	0.11449 (14)	0.3685 (2)	0.0224 (4)
C3	-0.11972 (16)	0.10889 (16)	0.2328 (3)	0.0290 (4)
H1	-0.1706	0.0355	0.2218	0.035*
C4	-0.14016 (17)	0.21120 (17)	0.1155 (3)	0.0340 (4)
H2	-0.2061	0.2101	0.0241	0.041*
C5	-0.06207 (18)	0.31595 (17)	0.1342 (3)	0.0337 (4)
H3	-0.0741	0.3884	0.0567	0.040*
C6	0.03280 (17)	0.31239 (17)	0.2670 (3)	0.0345 (5)
H4	0.0873	0.3833	0.2765	0.041*
N1	0.05294 (13)	0.21395 (13)	0.3845 (2)	0.0283 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0205 (9)	0.0205 (9)	0.0216 (14)	0.000	0.000	0.000

C2	0.0216 (7)	0.0233 (7)	0.0222 (7)	0.0020 (5)	0.0033 (6)	0.0006 (7)
C3	0.0279 (8)	0.0315 (8)	0.0275 (8)	-0.0007 (6)	-0.0028 (7)	0.0007 (7)
C4	0.0310 (9)	0.0430 (10)	0.0280 (8)	0.0076 (7)	-0.0026 (8)	0.0038 (8)
C5	0.0393 (9)	0.0316 (9)	0.0302 (9)	0.0077 (7)	0.0046 (8)	0.0093 (8)
C6	0.0382 (10)	0.0268 (9)	0.0386 (10)	-0.0028 (7)	0.0025 (8)	0.0075 (7)
N1	0.0294 (7)	0.0257 (7)	0.0299 (7)	-0.0022 (5)	-0.0014 (6)	0.0039 (6)

Geometric parameters (Å, °)

C1—C2 ⁱ	1.545 (2)	C3—H1	0.9500
C1—C2 ⁱⁱ	1.545 (2)	C4—C5	1.391 (3)
C1—C2 ⁱⁱⁱ	1.545 (2)	C4—H2	0.9500
C1—C2	1.545 (2)	C5—C6	1.373 (3)
C2—N1	1.330 (3)	C5—H3	0.9500
C2—C3	1.402 (3)	C6—N1	1.348 (3)
C3—C4	1.380 (3)	C6—H4	0.9500
C2 ⁱ —C1—C2 ⁱⁱ	111.01 (8)	C2—C3—H1	120.4
C2 ⁱ —C1—C2 ⁱⁱⁱ	106.43 (16)	C3—C4—C5	118.52 (16)
C2 ⁱⁱ —C1—C2 ⁱⁱⁱ	111.01 (8)	C3—C4—H2	120.7
C2 ⁱ —C1—C2	111.01 (8)	C5—C4—H2	120.7
C2 ⁱⁱ —C1—C2	106.43 (16)	C6—C5—C4	118.55 (15)
C2 ⁱⁱⁱ —C1—C2	111.01 (8)	C6—C5—H3	120.7
N1—C2—C3	122.22 (15)	C4—C5—H3	120.7
N1—C2—C1	118.44 (13)	N1—C6—C5	123.68 (17)
C3—C2—C1	119.30 (14)	N1—C6—H4	118.2
C4—C3—C2	119.26 (17)	C5—C6—H4	118.2
C4—C3—H1	120.4	C2—N1—C6	117.72 (15)
C2 ⁱ —C1—C2—N1	-0.78 (13)	C1—C2—C3—C4	179.97 (14)
C2 ⁱⁱ —C1—C2—N1	-121.70 (15)	C2—C3—C4—C5	1.1 (3)
C2 ⁱⁱⁱ —C1—C2—N1	117.39 (18)	C3—C4—C5—C6	0.7 (3)
C2 ⁱ —C1—C2—C3	177.21 (14)	C4—C5—C6—N1	-1.8 (3)
C2 ⁱⁱ —C1—C2—C3	56.30 (12)	C3—C2—N1—C6	1.2 (2)
C2 ⁱⁱⁱ —C1—C2—C3	-64.62 (12)	C1—C2—N1—C6	179.09 (13)
N1—C2—C3—C4	-2.1 (2)	C5—C6—N1—C2	0.8 (3)

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