

catena-Poly[[[aqua(pyridine-4-carboxylato- κ N)silver(I)]- μ -hexamethylenetetraamine- κ^2 N:N'] dihydrate]

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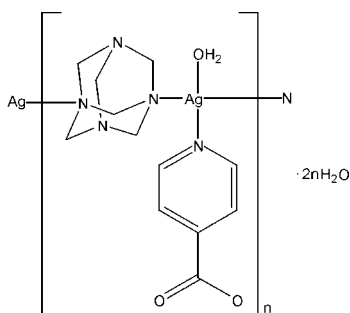
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}–\text{C}) = 0.003$ Å; R factor = 0.016; wR factor = 0.041; data-to-parameter ratio = 10.5.

In the title compound, $\{[\text{Ag}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_{12}\text{N}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$, the Ag^{I} atom shows a distorted triangular pyramidal geometry, formed by two N atoms from two hexamethylenetetraamine (hmt) ligands and one N atom from a pyridine-4-carboxylate (4-pdc) ligand and one water molecule. The hmt ligands bridge the Ag atoms, forming a chain along [001]. The carboxylate group of the 4-pdc ligand is uncoordinated. $\text{O}–\text{H} \cdots \text{O}$ hydrogen bonds between the water molecules and carboxylate groups stabilize the structure.

Related literature

For general background to the design and synthesis of coordination polymers, see: Eddaoudi *et al.* (2001).



Experimental

Crystal data

$[\text{Ag}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_{12}\text{N}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$
 $M_r = 424.22$
 Orthorhombic, $Pna2_1$
 $a = 11.8271$ (5) Å
 $b = 13.2122$ (5) Å
 $c = 10.2560$ (4) Å
 $V = 1602.62$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 1.29$ mm⁻¹
 $T = 293$ K

0.24 × 0.20 × 0.19 mm

Data collection

Bruker APEX CCD diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.747$, $T_{\text{max}} = 0.792$

7849 measured reflections
 2380 independent reflections
 2347 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.041$
 $S = 1.08$
 2380 reflections
 226 parameters
 10 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³
 Absolute structure: Flack (1983), 876 Friedel pairs
 Flack parameter: 0.01 (2)

Table 1

Selected bond lengths (Å).

Ag1–N1	2.287 (2)	Ag1–N5 ⁱ	2.306 (2)
Ag1–N2	2.256 (2)	Ag1–O1W	2.673 (2)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D–H \cdots A$	$D–H$	$H \cdots A$	$D \cdots A$	$D–H \cdots A$
O1W–H1A ⁱⁱ ···O2W ⁱⁱ	0.85 (3)	1.91 (3)	2.743 (3)	169 (3)
O1W–H1B ⁱⁱⁱ ···O1 ⁱⁱⁱ	0.85 (1)	1.91 (2)	2.714 (2)	157 (3)
O2W–H2A ⁱⁱⁱ ···O2	0.84 (1)	1.88 (1)	2.722 (3)	173 (3)
O2W–H2B ^{iv} ···O3W ^{iv}	0.84 (3)	1.99 (3)	2.787 (3)	161 (3)
O3W–H3A ^v ···O1W ^v	0.85 (1)	1.95 (1)	2.788 (3)	169 (3)
O3W–H3B ^v ···O1	0.85 (1)	1.89 (1)	2.728 (2)	169 (3)

Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (iii) $-x + 1, -y, z - \frac{1}{2}$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, z - \frac{1}{2}$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$.

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2384).

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supplementary materials

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catena-Poly[[[aqua(pyridine-4-carboxylato- κ N)silver(I)]- μ -hexamethylenetetraamine- κ^2 N:N'] dihydrate]

D. Sun, L. Han and H. Zang

Comment

The design and synthesis of coordination polymers have been a research field of rapid expansion not only because of their fascinating structures, but also owing to their interesting properties as new functional materials of tremendous potential applications in molecular recognition, ion-exchange, and catalysis for reactions (Eddaoudi *et al.*, 2001). In this work, the reaction of pyridine-4-carboxylic acid (4-Hpdc) and hexamethylenetetraamine (hmt) with Ag^I ion yielded a new coordination polymer.

As shown in Fig. 1, the asymmetric unit of the title compound contains one Ag^I atom, one 4-pdc ligand, one hmt ligand, one coordinated water molecule and two uncoordinated water molecules. The Ag^I atom shows a distorted triangle pyramidal geometry, completed by three N atoms from two hmt ligands and one 4-pdc ligand and one O atom from a water molecule. The hmt ligands bridge the Ag atoms, forming a one-dimensional chain. The carboxylate group of the 4-pdc ligand is uncoordinated. O—H \cdots O hydrogen bonds between the water molecules and carboxylate groups stabilize the structure.

Experimental

A mixture of 4-Hpdc (0.615 g, 0.5 mmol), Ag(NO₃)₂ (0.085 g, 0.5 mmol) and hmt (0.070 g, 0.5 mmol) in water was heated at 150°C in a Teflon-lined stainless steel autoclave for 5 d. The reaction system was then slowly cooled to room temperature. Crystals suitable for X-ray diffraction analysis were collected by filtration.

Refinement

C-bound H atoms were positioned geometrically and refined using a riding mode, with C—H = 0.93 and 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atoms were located in a difference Fourier map and refined with restraints of O—H = 0.85 (1) and H \cdots H = 1.38 (1) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Figures

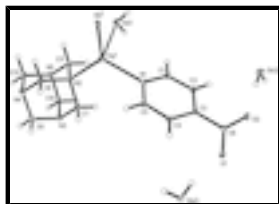


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, -y, z+1/2$].

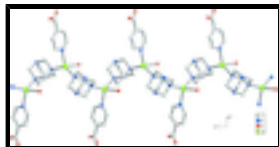


Fig. 2. View of the chain structure in the title compound.

catena-Poly[[[aqua(pyridine-4-carboxylato- κ N)silver(I)]- μ -hexamethylenetetraamine- κ^2 N:N'] dihydrate]

Crystal data

[Ag(C₆H₄NO₂)(C₆H₁₂N₄)(H₂O)]·2H₂O

$M_r = 424.22$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 11.8271$ (5) Å

$b = 13.2122$ (5) Å

$c = 10.2560$ (4) Å

$V = 1602.62$ (11) Å³

$Z = 4$

$F(000) = 864$

$D_x = 1.758$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2380 reflections

$\theta = 3.0$ – 26.1°

$\mu = 1.29$ mm⁻¹

$T = 293$ K

Block, colorless

$0.24 \times 0.20 \times 0.19$ mm

Data collection

Bruker APEX CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.747$, $T_{\max} = 0.792$

7849 measured reflections

2380 independent reflections

2347 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -13 \rightarrow 14$

$k = -15 \rightarrow 15$

$l = -10 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.016$

$wR(F^2) = 0.041$

$S = 1.08$

2380 reflections

226 parameters

10 restraints

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H atoms treated by a mixture of independent and
constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.3127P]$

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

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

$\Delta\rho_{\max} = 0.20$ e Å⁻³

$\Delta\rho_{\min} = -0.55$ e Å⁻³

Absolute structure: Flack (1983), 876 Friedel pairs

Flack parameter: 0.01 (2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag1	0.128363 (13)	0.013803 (11)	0.15278 (4)	0.02268 (7)
C1	0.3975 (2)	0.04853 (19)	0.1327 (3)	0.0235 (6)
H1	0.3756	0.0961	0.0708	0.028*
C2	0.51160 (18)	0.03798 (16)	0.1607 (3)	0.0213 (5)
H2	0.5645	0.0788	0.1190	0.026*
C3	0.5467 (2)	-0.03375 (17)	0.2511 (2)	0.0180 (5)
C4	0.4633 (2)	-0.09081 (18)	0.3108 (3)	0.0226 (5)
H4	0.4826	-0.1395	0.3724	0.027*
C5	0.3513 (2)	-0.0753 (2)	0.2786 (3)	0.0253 (6)
H5	0.2968	-0.1145	0.3200	0.030*
C6	0.6705 (2)	-0.04864 (19)	0.2834 (2)	0.0195 (5)
C7	0.1034 (2)	-0.1856 (2)	-0.0106 (3)	0.0232 (6)
H7A	0.1690	-0.1589	-0.0556	0.028*
H7B	0.1299	-0.2228	0.0651	0.028*
C8	-0.0697 (2)	-0.14419 (19)	0.0997 (2)	0.0214 (5)
H8A	-0.0454	-0.1812	0.1764	0.026*
H8B	-0.1189	-0.0898	0.1281	0.026*
C9	-0.0568 (2)	-0.29341 (18)	-0.0278 (3)	0.0298 (6)
H9A	-0.0977	-0.3395	-0.0842	0.036*
H9B	-0.0321	-0.3312	0.0482	0.036*
C10	0.0045 (2)	-0.19809 (17)	-0.2111 (2)	0.0216 (5)
H10A	-0.0355	-0.2433	-0.2696	0.026*
H10B	0.0696	-0.1715	-0.2573	0.026*
C11	-0.0086 (2)	-0.04628 (17)	-0.0847 (3)	0.0188 (5)
H11A	-0.0572	0.0093	-0.0586	0.023*
H11B	0.0560	-0.0179	-0.1301	0.023*
C12	-0.1700 (2)	-0.15591 (19)	-0.1010 (3)	0.0207 (5)
H12A	-0.2195	-0.1012	-0.0741	0.025*
H12B	-0.2126	-0.2005	-0.1579	0.025*
N1	0.31739 (18)	-0.00721 (15)	0.1914 (2)	0.0226 (6)
N2	0.03133 (16)	-0.10028 (15)	0.0333 (2)	0.0175 (4)
N3	0.04299 (17)	-0.25501 (15)	-0.0976 (2)	0.0238 (4)
N4	-0.13283 (16)	-0.21224 (17)	0.0138 (2)	0.0225 (5)
N5	-0.07120 (15)	-0.11312 (15)	-0.1745 (2)	0.0165 (4)
O1	0.69699 (14)	-0.13139 (13)	0.33372 (19)	0.0263 (4)
O2	0.73760 (15)	0.02175 (13)	0.2588 (2)	0.0294 (5)
O1W	0.11516 (14)	0.16451 (15)	-0.0205 (2)	0.0254 (4)
H1A	0.145 (2)	0.2117 (19)	0.024 (3)	0.038*
H1B	0.161 (2)	0.147 (2)	-0.080 (2)	0.038*
O2W	0.73929 (16)	0.19124 (15)	0.1080 (2)	0.0344 (5)
H2A	0.736 (2)	0.1415 (17)	0.159 (2)	0.052*
H2B	0.777 (3)	0.176 (2)	0.042 (2)	0.052*
O3W	0.60916 (15)	-0.31522 (14)	0.4000 (3)	0.0330 (5)
H3A	0.5402 (12)	-0.313 (2)	0.423 (3)	0.049*
H3B	0.629 (2)	-0.2569 (14)	0.373 (4)	0.049*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.01850 (10)	0.02679 (10)	0.02274 (11)	-0.00070 (6)	-0.00291 (10)	-0.00824 (17)
C1	0.0231 (11)	0.0237 (11)	0.0236 (19)	0.0030 (9)	-0.0032 (12)	0.0047 (12)
C2	0.0200 (10)	0.0214 (10)	0.0226 (12)	-0.0030 (8)	0.0014 (14)	0.0042 (15)
C3	0.0193 (12)	0.0163 (11)	0.0185 (13)	0.0030 (9)	-0.0024 (10)	-0.0034 (10)
C4	0.0203 (12)	0.0220 (12)	0.0256 (14)	0.0024 (9)	0.0013 (11)	0.0062 (11)
C5	0.0201 (12)	0.0263 (14)	0.0295 (15)	-0.0025 (10)	0.0028 (11)	0.0048 (12)
C6	0.0177 (12)	0.0225 (12)	0.0184 (13)	0.0003 (10)	0.0004 (10)	0.0004 (10)
C7	0.0202 (12)	0.0234 (14)	0.0262 (16)	0.0054 (10)	-0.0018 (12)	-0.0043 (12)
C8	0.0206 (12)	0.0248 (13)	0.0188 (12)	-0.0023 (10)	0.0012 (10)	0.0021 (10)
C9	0.0414 (16)	0.0176 (13)	0.0305 (15)	-0.0053 (11)	-0.0100 (13)	0.0024 (11)
C10	0.0216 (12)	0.0223 (12)	0.0208 (13)	0.0025 (9)	-0.0006 (11)	-0.0039 (10)
C11	0.0179 (12)	0.0157 (10)	0.0228 (13)	-0.0002 (9)	0.0000 (10)	0.0016 (10)
C12	0.0154 (12)	0.0257 (13)	0.0208 (13)	-0.0046 (10)	-0.0008 (11)	0.0032 (11)
N1	0.0158 (10)	0.0237 (10)	0.0284 (16)	0.0010 (8)	-0.0010 (9)	-0.0004 (8)
N2	0.0132 (9)	0.0191 (10)	0.0202 (11)	0.0020 (8)	-0.0010 (8)	-0.0002 (8)
N3	0.0290 (11)	0.0179 (10)	0.0244 (11)	0.0055 (9)	-0.0075 (10)	-0.0041 (9)
N4	0.0232 (11)	0.0252 (12)	0.0190 (12)	-0.0077 (8)	-0.0014 (9)	0.0053 (9)
N5	0.0150 (10)	0.0167 (10)	0.0178 (11)	-0.0032 (8)	0.0000 (8)	0.0014 (8)
O1	0.0186 (8)	0.0235 (9)	0.0366 (11)	-0.0002 (7)	-0.0035 (8)	0.0104 (8)
O2	0.0190 (9)	0.0265 (10)	0.0427 (13)	-0.0057 (7)	-0.0055 (9)	0.0098 (8)
O1W	0.0196 (9)	0.0265 (11)	0.0300 (12)	-0.0025 (7)	0.0035 (8)	-0.0021 (9)
O2W	0.0317 (10)	0.0319 (10)	0.0396 (12)	0.0047 (8)	0.0038 (9)	0.0147 (8)
O3W	0.0219 (9)	0.0206 (10)	0.0564 (15)	-0.0012 (7)	-0.0013 (10)	0.0072 (10)

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

Ag1—N1	2.287 (2)	C8—H8B	0.9700
Ag1—N2	2.256 (2)	C9—N4	1.463 (3)
Ag1—N5 ⁱ	2.306 (2)	C9—N3	1.470 (4)
Ag1—O1W	2.673 (2)	C9—H9A	0.9700
C1—N1	1.342 (3)	C9—H9B	0.9700
C1—C2	1.387 (3)	C10—N3	1.459 (3)
C1—H1	0.9300	C10—N5	1.484 (3)
C2—C3	1.390 (4)	C10—H10A	0.9700
C2—H2	0.9300	C10—H10B	0.9700
C3—C4	1.384 (3)	C11—N5	1.476 (3)
C3—C6	1.513 (3)	C11—N2	1.482 (3)
C4—C5	1.380 (3)	C11—H11A	0.9700
C4—H4	0.9300	C11—H11B	0.9700
C5—N1	1.330 (3)	C12—N4	1.461 (3)
C5—H5	0.9300	C12—N5	1.501 (3)
C6—O2	1.249 (3)	C12—H12A	0.9700
C6—O1	1.249 (3)	C12—H12B	0.9700
C7—N3	1.465 (3)	O1W—H1A	0.85 (3)

C7—N2	1.483 (3)	O1W—H1B	0.85 (1)
C7—H7A	0.9700	O2W—H2A	0.84 (1)
C7—H7B	0.9700	O2W—H2B	0.84 (3)
C8—N4	1.464 (3)	O3W—H3A	0.85 (1)
C8—N2	1.492 (3)	O3W—H3B	0.85 (1)
C8—H8A	0.9700		
N2—Ag1—N1	120.67 (7)	N3—C10—N5	112.10 (19)
N2—Ag1—N5 ⁱ	130.41 (7)	N3—C10—H10A	109.2
N1—Ag1—N5 ⁱ	102.86 (7)	N5—C10—H10A	109.2
N2—Ag1—O1W	96.13 (7)	N3—C10—H10B	109.2
N1—Ag1—O1W	105.23 (6)	N5—C10—H10B	109.2
N5 ⁱ —Ag1—O1W	94.00 (7)	H10A—C10—H10B	107.9
N1—C1—C2	122.6 (3)	N5—C11—N2	112.42 (18)
N1—C1—H1	118.7	N5—C11—H11A	109.1
C2—C1—H1	118.7	N2—C11—H11A	109.1
C1—C2—C3	119.8 (2)	N5—C11—H11B	109.1
C1—C2—H2	120.1	N2—C11—H11B	109.1
C3—C2—H2	120.1	H11A—C11—H11B	107.9
C4—C3—C2	116.9 (2)	N4—C12—N5	111.27 (19)
C4—C3—C6	121.5 (2)	N4—C12—H12A	109.4
C2—C3—C6	121.6 (2)	N5—C12—H12A	109.4
C5—C4—C3	119.8 (2)	N4—C12—H12B	109.4
C5—C4—H4	120.1	N5—C12—H12B	109.4
C3—C4—H4	120.1	H12A—C12—H12B	108.0
N1—C5—C4	123.4 (2)	C5—N1—C1	117.3 (2)
N1—C5—H5	118.3	C5—N1—Ag1	119.57 (17)
C4—C5—H5	118.3	C1—N1—Ag1	123.05 (17)
O2—C6—O1	125.1 (2)	C11—N2—C7	107.5 (2)
O2—C6—C3	118.3 (2)	C11—N2—C8	107.76 (18)
O1—C6—C3	116.6 (2)	C7—N2—C8	107.63 (19)
N3—C7—N2	112.35 (19)	C11—N2—Ag1	106.48 (14)
N3—C7—H7A	109.1	C7—N2—Ag1	112.35 (14)
N2—C7—H7A	109.1	C8—N2—Ag1	114.77 (15)
N3—C7—H7B	109.1	C10—N3—C7	108.4 (2)
N2—C7—H7B	109.1	C10—N3—C9	108.41 (19)
H7A—C7—H7B	107.9	C7—N3—C9	108.1 (2)
N4—C8—N2	111.90 (19)	C12—N4—C9	108.8 (2)
N4—C8—H8A	109.2	C12—N4—C8	109.0 (2)
N2—C8—H8A	109.2	C9—N4—C8	108.17 (19)
N4—C8—H8B	109.2	C11—N5—C10	107.94 (17)
N2—C8—H8B	109.2	C11—N5—C12	107.64 (19)
H8A—C8—H8B	107.9	C10—N5—C12	108.15 (19)
N4—C9—N3	112.48 (19)	C11—N5—Ag1 ⁱⁱ	106.63 (14)
N4—C9—H9A	109.1	C10—N5—Ag1 ⁱⁱ	114.39 (15)
N3—C9—H9A	109.1	C12—N5—Ag1 ⁱⁱ	111.83 (14)
N4—C9—H9B	109.1	H1A—O1W—H1B	108.9 (15)
N3—C9—H9B	109.1	H2A—O2W—H2B	110.2 (16)

supplementary materials

H9A—C9—H9B

107.8

H3A—O3W—H3B

108.7 (15)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1A \cdots O2W ⁱⁱⁱ	0.85 (3)	1.91 (3)	2.743 (3)	169 (3)
O1W—H1B \cdots O1 ^{iv}	0.85 (1)	1.91 (2)	2.714 (2)	157 (3)
O2W—H2A \cdots O2	0.84 (1)	1.88 (1)	2.722 (3)	173 (3)
O2W—H2B \cdots O3W ^v	0.84 (3)	1.99 (3)	2.787 (3)	161 (3)
O3W—H3A \cdots O1W ^{vi}	0.85 (1)	1.95 (1)	2.788 (3)	169 (3)
O3W—H3B \cdots O1	0.85 (1)	1.89 (1)	2.728 (2)	169 (3)

Symmetry codes: (iii) $x-1/2, -y+1/2, z$; (iv) $-x+1, -y, z-1/2$; (v) $-x+3/2, y+1/2, z-1/2$; (vi) $-x+1/2, y-1/2, z+1/2$.

Fig. 1

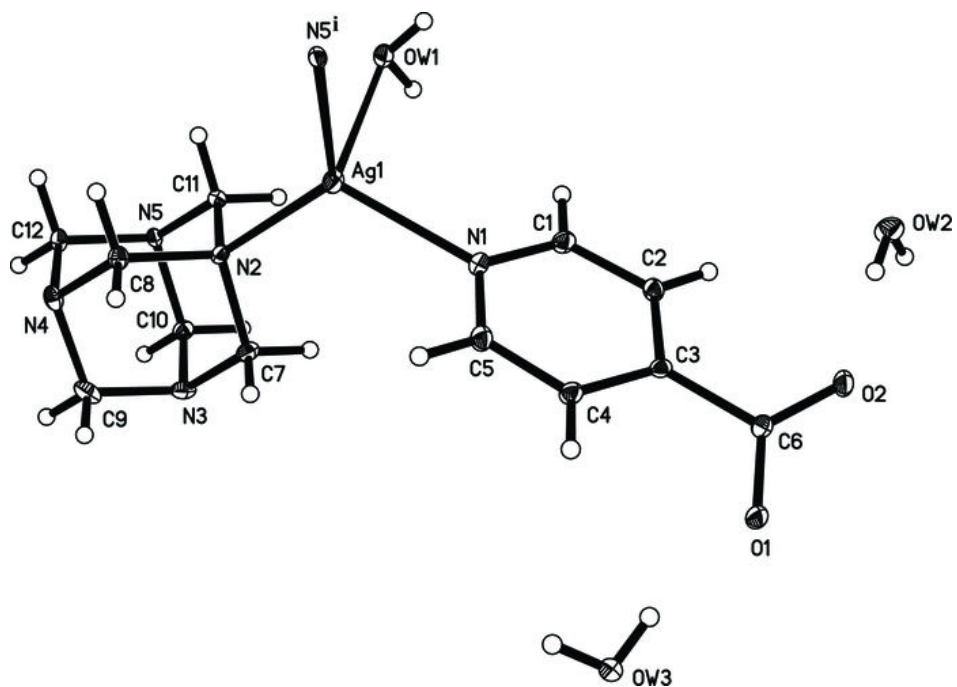


Fig. 2

