

**catena-Poly[[*(pyridin-4-ol- κ N)*-
silver(I)]- μ -pyridin-4-olato- κ^2 N:O]**

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The title complex, $[\text{Ag}(\text{C}_5\text{H}_4\text{NO})(\text{C}_5\text{H}_5\text{NO})]_n$, consists of a polymeric neutral chain involving both a neutral pyridin-4-ol ligand and a deprotonated pyridin-4-olate monoanion. The Ag^{I} atom shows a T-shaped coordination geometry, defined by one N atom of the pyridin-4-ol and one O and one N atom of two independent pyridin-4-olate bridges; the N—Ag—N moiety is approximately linear. The polymeric chains are connected *via* strong O—H \cdots O hydrogen bonds and offset π — π interactions into a three-dimensional network.

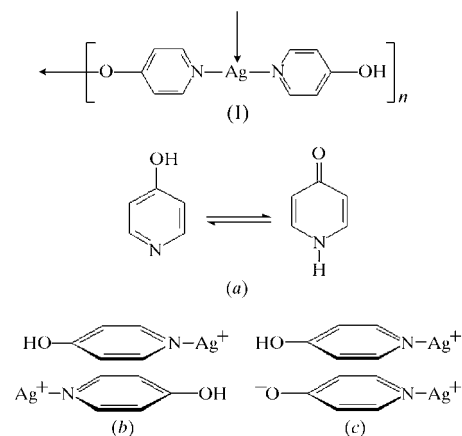
Comment

Hydroxypyridines (PyOH), including 2-, 3- and 4-PyOH, are widely used in pharmaceutical syntheses. Furthermore, they have attracted growing attention in the field of crystal engineering as good candidates for the construction of supramolecular systems. They are bifunctional ligands that are not only capable of binding to metal centres but can also form classical hydrogen bonds as both donors and acceptors (Breeze & Wang, 1993; Kawata *et al.*, 1997).

Another important feature of 2- or 4-PyOH is tautomerization to their pyridone isomers, *viz.* 2- or 4-pyridone. In the solid state, the pyridone is the observed tautomeric form for 2- or 4-PyOH (Yang & Craven, 1998; Wheeler & Ammon, 1974; Trikoupi *et al.*, 2002; Jones, 2001), whereas the 3-isomer is a true hydroxypyridine (Flakus *et al.*, 2003). For 4-PyOH, the equilibrium between the two tautomers is dominated by the presence of the keto form in polar solvents (Johnson, 1984; Gilchrist, 1985). Because the N atom is protonated, 4-PyOH would be expected to coordinate, if at all, through the O atom, which has only weak donor properties (Masse & Le Fur, 1998). It is therefore predictably difficult to obtain complexes with the 4-PyOH tautomer. As a contribution to this field, we have recently reported the structures of two mononuclear Co complexes and one dimeric Cu complex coordinated by the O atoms of 4-pyridone ligands, namely $[\text{CoCl}_2(4\text{-pyridone})_2]$, $[\text{Co}(\text{NO}_3)_2(4\text{-pyridone})_2(\text{H}_2\text{O})_2](\text{NO}_3)$ and $[\text{Cu}_2(\text{acetate})_4(4\text{-pyridone})_2]$, in which the Co atoms exhibit tetrahedral and octahedral geometries, while the Cu atom displays a square-

pyramidal coordination environment (Gao *et al.*, 2004; Lu, Gao, Huo, Zhang *et al.*, 2004; Lu, Gao, Huo, Zhao & Zhao, 2004).

In order to gain further insight into the metal-binding modes of the 4-PyOH ligand, we have now introduced the Ag^{I} ion into the coordination system of the 4-PyOH ligand. Our most unexpected discovery, reported here, is that the Ag^{I} atom favours coordination *via* the N atom and effectively reverses the usual tautomerization to the 4-pyridone tautomer, producing the title novel coordination polymer, $[\text{Ag}(\mu\text{-pyridine-4-olate-}\kappa^2\text{N,O})(4\text{-PyOH})]_n$, (I), based on both neutral and deprotonated forms of the 4-PyOH tautomer. To the best of our knowledge, (I) is the first example of a metal complex containing the 4-PyOH tautomer in either form.



The crystal structure of complex (I) consists of polymeric neutral $[\text{Ag}(\mu\text{-pyridine-4-olate-}\kappa^2\text{N,O})(4\text{-PyOH})]_n$ chains, in which the Ag^{I} atoms are bridged sequentially by *N,O*-bidentate pyridine-4-olate ligands (Figs. 1 and 2).

All the 4-PyOH ligands in (I) are coordinated to the Ag^{I} atoms in the 4-PyOH tautomer form, or its deprotonated counterpart, as evidenced by the C—O [1.300 (3) and 1.318 (3) Å] and C—N [1.340 (3)–1.349 (3) Å] bond lengths. A similar bond-length pattern is observed in free 3-PyOH [two independent molecules; C—O = 1.3462 and 1.3466 (12) Å, and C—N = 1.3361 (14)–1.3403 (13) Å; Flakus *et al.*, 2003]. In the

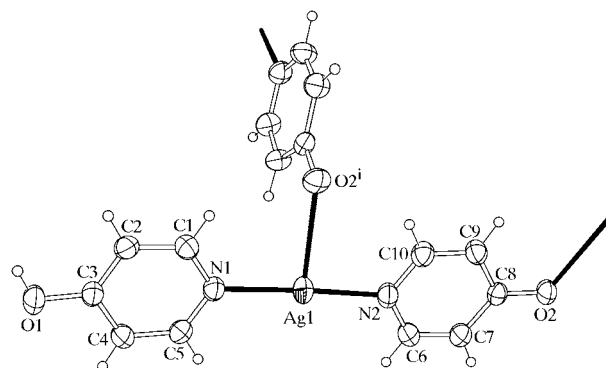


Figure 1
The coordination environment of the Ag^{I} atom in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

structure of free 4-pyridone (Jones, 2001), the C—O bond lengths [1.258 (2)–1.278 (2) Å] are significantly shorter than in (I), while the C—N bond distances [1.341 (3)–1.355 (3) Å] are slightly longer.

The C6—C7 and C9—C10 bond lengths [1.368 (4) and 1.362 (3) Å] are similar to the values observed in the terminal 4-PyOH ligand [1.375 (3) and 1.366 (4) Å]. The O2—C8 bond length [1.300 (3) Å] is shorter than the O1—C3 bond length [1.318 (3) Å], again indicating that the deprotonated 4-PyOH ligand assumes the pyridine-4-olate form. However, there is still a slight ‘pyridone-like’ pattern to the C—C bond lengths, albeit much less marked than in 4-pyridone, with averages of 1.362 and 1.426 Å.

Fig. 1 shows the coordination environment of the Ag^I centre of (I). The main interatomic bond distances and angles are listed in Table 1. Each Ag^I atom shows a T-shaped coordination geometry, involving two N atoms, one each from a neutral terminal 4-PyOH ligand and a deprotonated pyridine-4-olate bridging ligand [N2—Ag1—N1 = 174.12 (8)°], and one deprotonated hydroxyl O atom of a pyridine-4-olate ligand in a neighbouring asymmetric unit. The N1—Ag1—O2 and N2—Ag1—O2 bond angles are 91.5 (2) and 92.9 (2)°, respectively. The Ag—N bond length is as expected [mean 2.130 (2) Å; Cai *et al.*, 2001], while the Ag—O bond [2.743 (2) Å] is longer than common Ag—O distances reported for Ag^I complexes with a T-shaped geometry, which range from 2.235 (4) Å in [Ag₂(PPh₃)₄(SO₄)]·2H₂O (Bowmaker *et al.*, 2001) to 2.613 (4) Å in [Ag(ODOQ)]_n(ClO₄)_n [ODOQ = *O,O'*-bis(8-quinoly)-1,8-dioxaoctane] (Cai *et al.*, 2001), but shorter than the value observed in the complex [Ag₂CA] (CA = cyanuric acid; 2.76 Å; Rao *et al.*, 2000).

As a consequence of the pyridine-4-olate bridges, adjacent Ag^I atoms are linked into a one-dimensional zigzag chain structure, which has terminal branches (the neutral hydroxypyridines). The intrachain Ag···Ag separation across the pyridine-4-olate ligand is 7.672 (3) Å. The polymeric chains are parallel to the *b* axis of the unit cell and show a corrugated arrangement, with an Ag···Ag···Ag angle of 85.40 (4)° between three successive Ag^I ions along the chain (Fig. 2).

The aromatic rings of the terminal and bridging ligands (those involving atoms N1 and O2, respectively) are almost coplanar, with an interplanar angle of 1.26 (3)°, while the mean planes of adjacent pyridine-4-olate bridges are almost

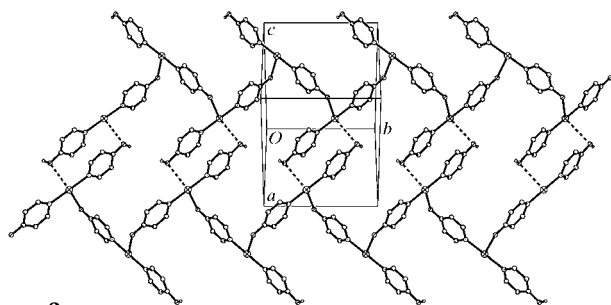


Figure 2

A perspective view of the chain and layer structure of (I). The weak Ag···O [3.265 (3) Å] contacts are denoted by dashed lines and the H atoms of the aromatic rings have been omitted.

perpendicular to each other [84.95 (6)°]. There are offset face-to-face interactions [(*b*) in the scheme], with a ‘head-to-tail’ arrangement between the terminal 4-PyOH ligands and a centre-to-centre separation of 3.474 (3) Å (symmetry code: 2 - *x*, 1 - *y*, 1 - *z*). Such strong facial interactions may be considered as a cause of the weak Ag···O_{OH} interactions between adjacent chains [3.265 (3) Å]. These weak Ag···O_{OH} and the strong π-π interactions constitute small rectangular grids [Ag···Ag = 7.407 (3) Å] between adjacent chains and form a layer structure parallel to the *bc* plane (Fig. 2). Each layer includes the one-dimensional hydrogen-bonded chains *via* strong ionic O—H···O⁻ interactions between the O atoms of the terminal 4-PyOH ligand and the anionic pyridine-4-olate bridge [O···O = 2.476 (3) Å]. The shortest Ag···Ag distance is 3.835 (3) Å, between adjacent hydrogen-bonded chains.

The layers are further linked into a three-dimensional supramolecular framework (Fig. 3) *via* another offset π-π interaction [(*c*) in the scheme] in a ‘head-to-head’ fashion, between the terminal 4-PyOH ligand and the monoanionic pyridine-4-olate bridge, with a centre-to-centre separation of 3.678 (3) Å (symmetry code: 1 - *x*, 1 - *y*, 1 - *z*), which is significantly longer than the value observed in the head-to-tail arrangement. This is explained by the fact that the head-to-tail arrangement may be energetically more favourable than the head-to-head orientation, due to the more effective charge separation, thus reducing Coulombic repulsion between the cationic centres. The facial interactions between the aromatic groups of the 4-PyOH ligands seem to play a critical role in the self-assembly process.

Experimental

The title complex, (I), was synthesized by the addition of AgNO₃ (2 mmol) to an ethanol solution of 4-hydroxypyridine (6 mmol). The mixed solution was protected from light and allowed to evaporate

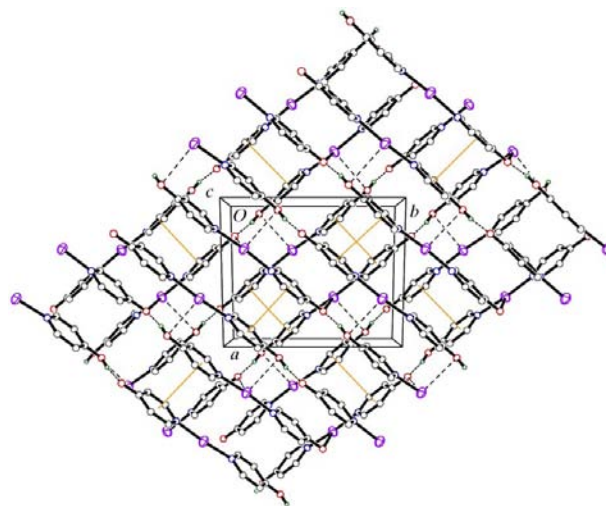


Figure 3

A diagram of the three-dimensional supramolecular framework of (I), showing the two types of π-π pairs (solid lines for head-to-head mode; the head-to-tail mode is not shown) and hydrogen-bonding interactions (short dashed lines). The weak Ag···O [3.265 (3) Å] contacts are denoted by long dashed lines.

slowly at room temperature. Colourless prismatic crystals of (I) were isolated after about 15 d. Analysis calculated for $C_{10}H_9AgN_2O_2$: C 40.43, H 3.05, N 9.43%; found: C 40.20, H 3.11, N 9.47%.

Crystal data

$[Ag(C_5H_4NO)(C_5H_5NO)]$
 $M_r = 297.06$
 Monoclinic, $P2_1/c$
 $a = 9.1673(18) \text{ \AA}$
 $b = 10.401(2) \text{ \AA}$
 $c = 11.026(2) \text{ \AA}$
 $\beta = 111.81(3)^\circ$
 $V = 976.1(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.022 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 8987 reflections
 $\theta = 3.1\text{--}27.5^\circ$
 $\mu = 2.04 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism, colourless
 $0.37 \times 0.24 \times 0.15 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.519, T_{\max} = 0.749$
 9387 measured reflections
 2234 independent reflections
 1929 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 13$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.056$
 $S = 1.06$
 2234 reflections
 139 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.2855P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Ag1—N2	2.129 (2)	C6—C7	1.368 (4)
Ag1—N1	2.131 (2)	C7—C8	1.406 (3)
Ag1—O2 ⁱ	2.743 (2)	C8—C9	1.405 (3)
O1—C3	1.318 (3)	C9—C10	1.362 (3)
O2—C8	1.300 (3)	N1—C5	1.341 (3)
C1—C2	1.375 (3)	N1—C1	1.349 (3)
C2—C3	1.396 (3)	N2—C10	1.340 (3)
C3—C4	1.393 (3)	N2—C6	1.349 (3)
C4—C5	1.366 (4)		
N1—Ag1—O2 ⁱ	91.5 (2)	N2—Ag1—N1	174.12 (8)
N2—Ag1—O2 ⁱ	92.9 (2)		

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

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H11 \cdots O2 ⁱ	0.84 (3)	1.64 (3)	2.476 (3)	171 (4)

Symmetry code: (i) $1 + x, y - 1, z$.

The H atoms of the hydroxy groups were located in a difference map and refined with O—H distance restraints of $0.85(1) \text{ \AA}$, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. H atoms bound to C atoms were placed in calculated positions, with C—H = 0.93 \AA , and refined using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MS, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1667). Services for accessing these data are described at the back of the journal.

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