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Poly[μ_2-(*N*-hydroxypyridine-2-carboxamidine)-μ_2-nitrato-silver(I)]

Ai-Li Cui, Peng Han, Hui-Juan Yang, Ru-Ji Wang and Hui-Zhong Kou*

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Correspondence e-mail: kouhz@mail.tsinghua.edu.cn

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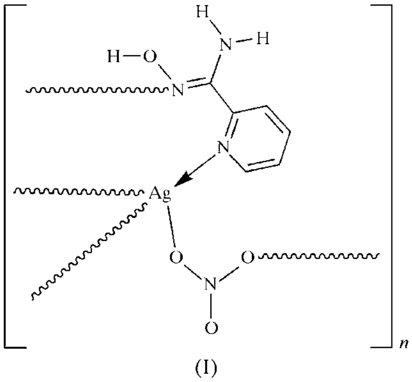
In the title complex, $[Ag(NO_3)(C_6H_7N_3O)]_n$ or $[Ag(NO_3)(pyaoxH_2)]$ ($pyaoxH_2$ is *N*-hydroxypyridine-2-carboxamidine), the Ag^+ ion is bridged by the $pyaoxH_2$ ligands and nitrate anions, giving rise to a two-dimensional molecular structure. Each $pyaoxH_2$ ligand coordinates to two Ag^+ ions using its pyridyl and carboxamidine N atoms, and the OH and the NH_2 groups are uncoordinated. Each nitrate anion uses two O atoms to coordinate to two Ag^+ ions. The Ag$\cdots$Ag separation *via* the $pyaoxH_2$ bridge is 2.869 (1) Å, markedly shorter than that of 6.452 (1) Å *via* the nitrate bridge. The two-dimensional structure is fishscale-like, and can be described as $pyaoxH_2$-bridged Ag_2 nodes that are further linked by nitrate anions. Hydrogen bonding between the amidine groups and the nitrate O atoms connects adjacent layers into a three-dimensional network.

Comment

N-Hydroxypyridine-2-carboxamidine ($pyaoxH_2$) is structurally similar to pyridine-2-carbaldehyde oxime (paoH), which has been widely studied as a bridging ligand to construct polynuclear species. Such compounds have been found to show interesting magnetic properties and have therefore attracted much interest in recent years (Chaudhuri, 2003; Milios *et al.*, 2006). However, $pyaoxH_2$ has received much less attention, and only a few mononuclear complexes have been structurally characterized, more than ten years ago (Näsäkkälä *et al.*, 1989; Pearse, Raithby, Hay & Lewis, 1989; Pearse, Raithby & Lewis, 1989; Werner *et al.*, 1996; Orama & Saarinen, 1996). The coordination chemistry of $pyaoxH_2$ awaits further elucidation. It is worth mentioning that special interest has been devoted to the oxime–Ag^I compounds with hydrogen-bonded supramolecular architectures (Aakeröy *et al.*, 1998). In the present paper, we report the novel two-dimensional complex $[Ag(NO_3)(pyaoxH_2)]$, (I), which exhibits a three-dimensional hydrogen-bonded architecture.



(I)

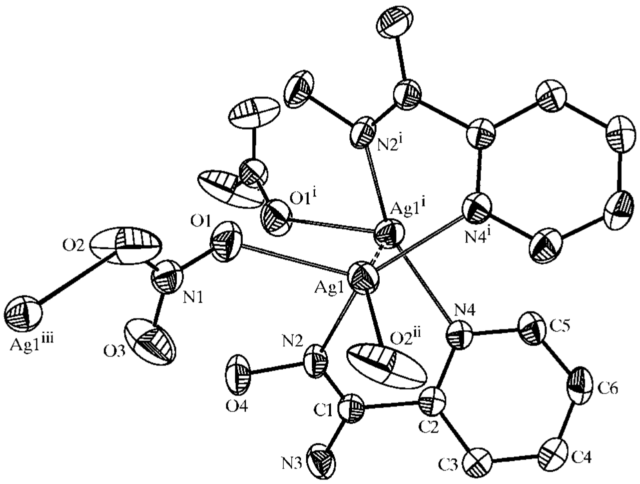


Figure 1
A view of complex (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

Fig. 1 shows the environment of Ag1, coordinated by two N atoms from two $pyaoxH_2$ ligands and two O atoms from two nitrate anions. The Ag—N/O bond distances are in the range 2.274 (1)–2.531 (5) Å (Table 1), with the Ag—N bonds longer than the Ag—O bonds. The coordination configuration is distorted tetrahedral. The deviation of atom Ag1 from the coordination plane defined by atoms N2, O1 and N4^i [symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$] is 0.284 (1) Å, showing significant distortion toward trigonal–bipyrimidal geometry, possibly as a result of the weak Ag$\cdots$Ag contact [2.869 (1) Å]. The $pyaoxH_2$ ligand coordinates two Ag ions *via* the pyridyl and carboxamidine N atoms; therefore, the pyridine and the carboxamidine groups are not coplanar in order to avoid steric hindrance. Interestingly, the hydroxy O atoms are not involved in coordination. The N—O bond distance is 1.414 (2) Å, similar to that in mononuclear Zn^{II} or Cu^{II} complexes (Näsäkkälä *et al.*, 1989; Pearse, Raithby, Hay & Lewis, 1989; Pearse, Raithby & Lewis, 1989; Werner *et al.*, 1996; Orama & Saarinen, 1996). The dimeric Ag^I units bridged by one $pyaoxH_2$ ligand are related by a twofold axis and are further linked by nitrate anions, giving rise to a two-dimensional layer structure (Fig. 2). Two O atoms of each nitrate anion are involved in coordination. The layer is fishscale-like, and each scale consists of six Ag atoms. Within each layer, atom H4*A*

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attached to hydroxy atom O4 interacts with the nonbridging atom O3 of the nitrate anion (Table 2).

Alternate fishscale layers have the opposite sense. The Ag^{I} ions are nearly coplanar within a layer, with the pyaoxH$_2$ ligands situated at two sides of the Ag layer. Two amide H atoms (H3*A* and H3*B*) of each pyaoxH$_2$ ligand are, respectively, connected to atoms O3^{iv} and O1^{v} [symmetry codes: (iv) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1$; (v) $x, -y+1, z+\frac{1}{2}$] of two nitrate anions in the adjacent layer. A weak interlayer C—H···O contact further links the neighbouring layers, giving rise to a three-dimensional supramolecular network.

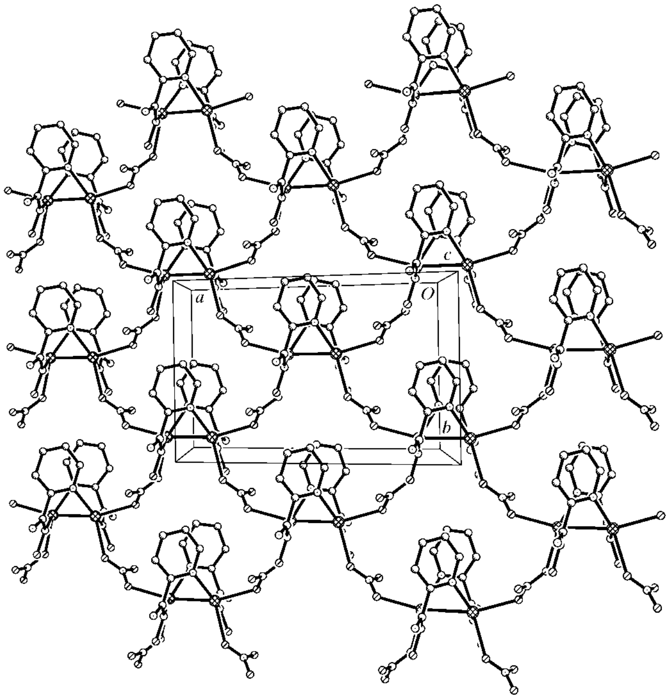

Figure 2
The layer structure in (I).

Experimental

The pyaoxH$_2$ ligand was prepared according to a literature method (Bernasek, 1957). Compound (I) was prepared in the dark by slow evaporation of an acetonitrile solution (10 ml) containing AgNO$_3$ (17.0 mg, 0.1 mmol) and pyaoxH$_2$ (13.7 mg, 0.1 mmol). After 3 d, colourless crystals were obtained (yield 60%).

Crystal data

[Ag(NO$_3$)(C$_6$H$_7$N$_3$O)]	$V = 1928.9$ (3) Å^3
$M_r = 307.03$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 15.0911$ (14) Å	$\mu = 2.09$ mm^{-1}
$b = 8.8890$ (8) Å	$T = 293$ (2) K
$c = 16.0727$ (15) Å	0.25 × 0.20 × 0.12 mm
$\beta = 116.536$ (2)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	6244 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	2110 independent reflections
$T_{min} = 0.623$, $T_{max} = 0.788$	1777 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	10 restraints
$wR(F^2) = 0.065$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 1.08$ e Å^{-3}
2110 reflections	$\Delta\rho_{min} = -0.47$ e Å^{-3}
155 parameters	

Table 1
Selected geometric parameters (Å, °).

Ag1—N4^{i}	2.2741 (17)	O2—Ag1^{iii}	2.450 (3)
Ag1—N2	2.280 (2)	O3—N1	1.233 (3)
Ag1—O2^{ii}	2.450 (3)	O2′—N1	1.246 (5)
Ag1—O1	2.4726 (18)	O3′—N1	1.211 (5)
Ag1—O2′^{ii}	2.531 (5)	O4—N2	1.414 (2)
Ag1—Ag1^{i}	2.8695 (5)	N2—C1	1.289 (3)
O1—N1	1.223 (2)	N3—C1	1.325 (3)
O2—N1	1.223 (4)		
N4^{i}—Ag1—N2	135.92 (7)	O2^{ii}—Ag1—O1	87.87 (9)
N4^{i}—Ag1—O2^{ii}	99.20 (8)	O2^{ii}—Ag1—Ag1^{i}	158.63 (9)
N2—Ag1—O2^{ii}	101.94 (9)	N1—O1—Ag1	135.09 (14)
N4^{i}—Ag1—O1	129.56 (7)	N1—O2—Ag1^{iii}	126.18 (18)
N2—Ag1—O1	89.61 (7)	O4—N2—Ag1	121.30 (14)

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

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O3	0.82	1.91	2.726 (4)	178
O4—H4*A*···O3′	0.82	2.26	3.061 (10)	166
N3—H3*A*···O3^{iv}	0.86	2.35	3.161 (3)	157
N3—H3*B*···O1^{v}	0.86	2.27	3.085 (3)	158
C3—H3···O2^{v}	0.93	2.57	3.274 (4)	133
C3—H3···O2′^{v}	0.93	2.51	3.284 (5)	141

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

H atoms were positioned geometrically and allowed for as riding atoms [C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(O)$]. Atoms O2 and O3 of the nitrate anion are disordered; the occupancies of the two sets of atom sites were initially refined and then fixed at the refined values 0.62 and 0.38. Restraints were applied to keep the NO$_3$ atoms in each orientation coplanar.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3152). Services for accessing these data are described at the back of the journal.

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