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Polymeric (3-amino-2-chloropyridine)nitratosilver(I)

Ming-Liang Tong,[a]* Xiao-Ming Chen[a] and Seik Weng Ng[b]

[a]School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia
Correspondence e-mail: cestml@zsu.edu.cn

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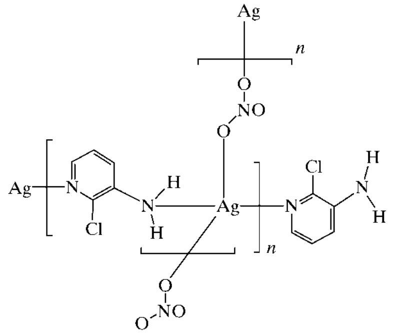
In the title compound {alternative name: poly[silver(I)-μ-(3-amino-2-chloropyridine)-μ-nitrato]}, $[Ag(NO_3)(C_5H_5Cl-N_2)]_n$ the Ag^I atom is in an irregular AgN_2O_3 geometry, surrounded by one pyridyl N atom [Ag—N 2.283 (5) Å], one amine N atom [Ag—N 2.364 (6) Å] and three O atoms from different nitrate ions [Ag—O 2.510 (6)–2.707 (6) Å]. The Ag ions are bridged by the 3-amino-2-chloropyridine ligands into helical chains. Adjacent uniform chiral chains are further interlinked through the NO_3 bridges into an interesting two-dimensional coordination network in the solid.

Comment

The field of metal-organic coordination polymers has recently attracted great interest, because such supramolecular architectures have potential as smart optoelectronic, magnetic or microporous materials (Abrahams *et al.*, 1994; Biradha *et al.*, 1999; Braga *et al.*, 1998; Fujita *et al.*, 1994; Gardner *et al.*, 1995; Kahn, 2000; Russell *et al.*, 1997). The structures of coordination polymers are highly influenced by factors such as the coordination nature of the metal ion, the structural characteristics of the polydentate organic ligand, the metal–ligand ratio and possible counter-ion influence. A subtle alteration in any of these factors can lead to new extended-network structures. Thus, a great variety of supramolecular architectures have been ingeniously constructed. These not only have aesthetic appeal, but occasionally exhibit interesting functions. We are interested in the preparation of one-, two- and three-dimensional coordination polymers with potential applications in optoelectronics and adsorption (Tong *et al.*, 1999; Zheng, Tong, Fu *et al.*, 2001; Zheng, Tong, Tan *et al.*, 2001). We report here the preparation and crystal structure of a two-dimensional coordination polymer, [Ag(μ-2-Clnpy)(μ-NO_3)], (I) (2-Clnpy is 3-amino-2-chloropyridine).



(I)

The crystal structure of (I) comprises a two-dimensional coordination network. As shown in Fig. 1, each Ag^I atom is coordinated in an irregular geometry, formed by one pyridyl N atom and one amine N atom from two different 2-Clnpy ligands, and three O atoms from different nitrate ions (Table 1). The Ag—N(pyridyl) distances in (I) are slightly longer than those in bis(3-amino-2-chloropyridine)silver(I) perchlorate [2.179 (4)–2.199 (4) Å; Li *et al.*, 2002] and that in bis(4-aminopyridine)silver(I) nitrate [2.122 (3) Å; Kristiansson, 2000]. The Ag^I atoms are bridged by 2-Clnpy ligands, forming polymeric helical motifs along the *c*-axis direction. Adjacent uniform infinite helical motifs are further interlinked through the NO_3 bridges into two-dimensional

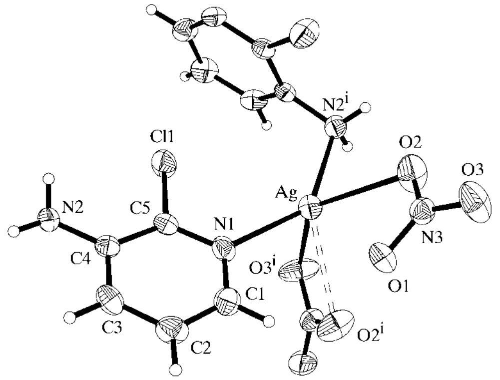


Figure 1
A view of the coordination environment in (I). Displacement ellipsoids are drawn at the 35% probability level and dashed lines indicate weak interactions [symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, -z$].

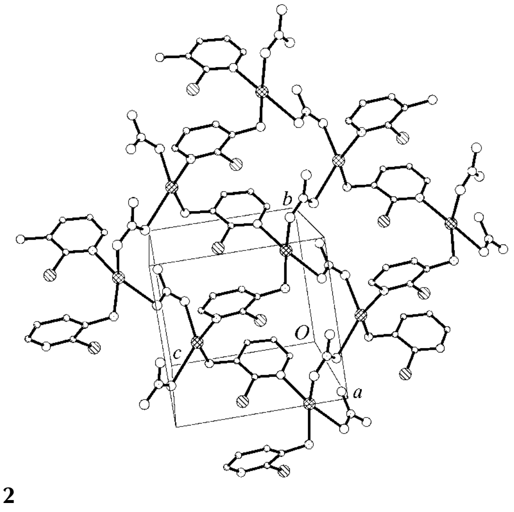


Figure 2
A view of the two-dimensional coordination layer of (I). Cl atoms are shown hatched and Ag atoms are cross-hatched.

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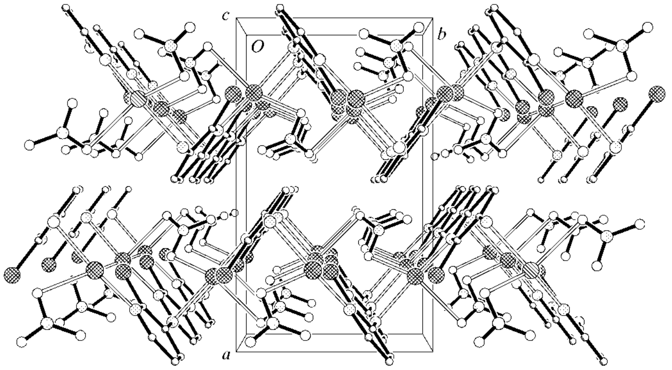

Figure 3
The three-dimensional supramolecular architecture of (I), viewed along the *c* axis.

layers (Fig. 2). Within each layer, there are hydrogen-bonding interactions between adjacent NO_3^- ions and amine groups (Table 2).

It should be also noted that π–π-stacking interactions play a role in consolidating the solid-state structure of (I). Adjacent coordination layers are stacked *via* interlayer pyridyl groups with a face-to-face separation of 3.38–3.58 Å, resulting in a three-dimensional supramolecular architecture (Fig. 3).

Experimental

To a solution of $AgNO_3$ (1.0 mmol) in $MeCN/H_2O$ [10 ml; 1:1 (*v*/*v*)], a solution of 2-Clnpy (1.0 mmol) in MeOH (5 ml) was added slowly with stirring over 15 min at 333 K. The mixture was left to crystallize at room temperature and colourless polyhedral crystals of (I) were deposited within 2 d (75% yield).

Crystal data

$[Ag(NO_3)(C_5H_5ClN_2)]$
$M_r = 298.44$
Orthorhombic, $P2_12_12$
$a = 13.343$ (5) Å
$b = 7.832$ (2) Å
$c = 8.270$ (2) Å
$V = 864.2$ (4) Å^3
$Z = 4$
$D_x = 2.294$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7$–15°
$\mu = 2.62$ mm^{-1}
$T = 298$ (2) K
Polyhedral, colourless
0.34 × 0.30 × 0.20 mm

Data collection

Siemens *R*3*m* four-circle diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.427$, $T_{\max} = 0.593$
1268 measured reflections
1248 independent reflections
1080 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 17$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 10$
2 standard reflections every 150 reflections intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Ag—N1	2.283 (5)	Ag—O3^{ii}	2.594 (6)
Ag—N2^{i}	2.364 (6)	O2—Ag^{iii}	2.707 (6)
Ag—O2	2.510 (6)		
N1—Ag—N2^{i}	140.44 (18)	N1—Ag—O3^{ii}	96.2 (2)
N1—Ag—O2	122.09 (18)	N2^{i}—Ag—O3^{ii}	88.0 (2)
N2^{i}—Ag—O2	82.25 (19)	O2—Ag—O3^{ii}	129.2 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N1···O1^{i}	0.86 (5)	2.35 (5)	3.160 (8)	159 (5)
N2—H2N2···O3^{ii}	0.85 (5)	2.20 (4)	3.020 (8)	160 (6)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.083$
$S = 1.07$
1248 reflections
124 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.76$ e Å^{-3}
Absolute structure: Flack (1983), 74 Friedel pairs
Flack parameter = 0.20 (8)

The amino H atoms were located and refined subject to the constraints N—H = 0.85 (1) Å, H···H = 1.39 (1) Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(N)$. The carbon-bound H atoms were generated geometrically, with C—H = 0.93 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1379). Services for accessing these data are described at the back of the journal.

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