

catena-Poly[[[1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene]silver(I)] nitrate]**Yu-Jun Shi, Yi-Zhi Li, Wen-Jun Tong, Xue-Tai Chen and Xiao-Zeng You***

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The bipyridyl-base ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L) has been used in the synthesis of a new organometallic polymer. The reaction between AgNO_3 and L afforded a one-dimensional chain structure of the cation of the title compound, $\{[\text{Ag}(\text{C}_{12}\text{N}_4\text{H}_{10})]\text{NO}_3\}_n$. The Ag^{I} ion lies on a twofold axis and is in a linear environment with respect to the two terminal N atoms of pyridyl rings. Weak interactions between H and nitrate O atoms, and between the Ag and nitrate O atoms, generate a three-dimensional framework.

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Key indicators

Single-crystal X-ray study

 $T = 293 \text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$

Disorder in solvent or counterion

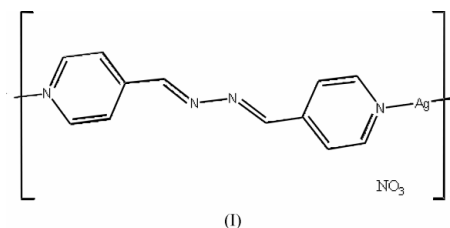
 R factor = 0.045 wR factor = 0.145

Data-to-parameter ratio = 11.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

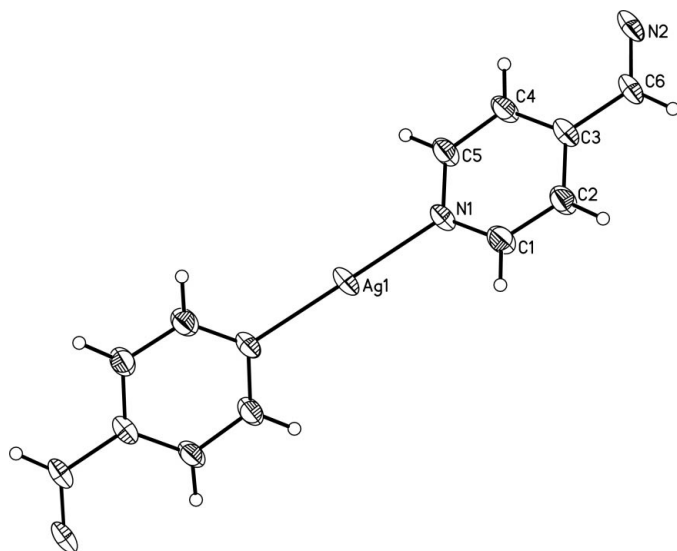
Comment

The synthesis and construction of new polymeric frameworks through the rational combination of organic ligands and metal ions are areas of intense current interest. In this context, rigid organic ligands containing pyridine rings separated by various spacers have proven popular in recent years and have resulted in a rich variety of structural motifs (Dong *et al.*, 2000). In particular, the formation of porous framework structures makes these materials potential candidates for use in applications ranging from catalysis and molecular recognition to selective sorption materials, while other structure types can potentially be useful in the areas of non-linear optics, ion exchange and magnetism (Ciurtin *et al.*, 2001).



The reaction of silver(I) nitrate with the long rigid bipyridyl-base ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L) leads to the formation of the title organometallic polymer, (I), where the coordination around the silver ion is approximately linear. The $\text{Ag}-\text{N}$ bond length is $2.180(5) \text{ \AA}$, and the $\text{N1}-\text{Ag}-\text{N1}^{\text{ii}}$ bond angle is $174.3(2)^\circ$ [Table 1; symmetry code: (ii) $1-x, y, -z+1/2$]. The asymmetric unit contains one-half of $\text{AgL}\cdot\text{NO}_3$. Each ligand L is linked to two silver(I) ions to form an infinite chain (Figs. 1 and 2). The dihedral angle between the two pyridyl rings in the ligand is $55.7(2)^\circ$. The $\text{C6}-\text{N2}-\text{N2}^{\text{i}}-\text{C6}^{\text{i}}$ torsion angle is $-140.10(1)^\circ$ [symmetry code: (i) $-x, y, -z-1/2$].

There is a $\text{C}-\text{H}\cdots\text{O}$ interaction between an H atom of ligand L and an O atom of NO_3^- . This type of non-classical hydrogen-bonding interaction is observed in other polymers (Dong *et al.*, 2000). The $\text{C}\cdots\text{O}$ distances range from $3.018(11)$ to $3.390(12) \text{ \AA}$. The non-classical hydrogen-bonding interac-


Figure 1

View of the basic repeating unit of the complex cation in (I), with displacement ellipsoids at the 50% probability level. The bipyrindyl-base ligands are shown for only half of the molecular structure.

tions extend the one-dimensional chains to a three-dimensional framework with channels. The channels, viewed along the *c* axis, are cylindrical (Fig. 2), and the sections are ellipses with a long axis of 5.498 (2) Å and a short axis of 1.247 (2) Å. In a direction perpendicular to N—Ag—N, there are channels with a width of 3.552 (1) Å and a height of 4.258 (2) Å.

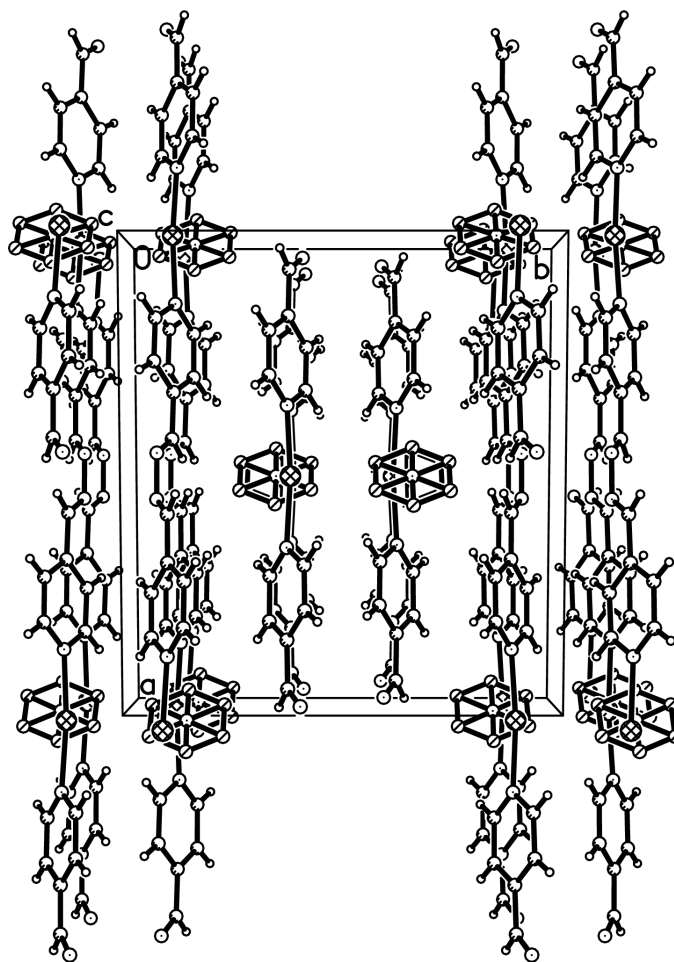
Experimental

The ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L) was prepared as follows: 10 mmol of hydrazine was added dropwise to a solution of pyridine-4-carboxaldehyde (20 mmol) dissolved in ethanol (10 ml). Two drops of formic acid were added and the mixture was stirred at room temperature for 24 h. The yellow solid that formed was filtered off and washed several times with ethanol/ether (1:1). Single crystals of the title complex were grown in the dark at room temperature, using a layered-solution approach. The bottom solution layer, contained within a long straight tube, consisted of 0.5 mmol L dissolved in CH₂Cl₂. A mixed-solvent layer of CH₂Cl₂/CH₃CN was carefully placed on top of the L(ligand) solution using a syringe. Finally, AgNO₃ (a stoichiometric quantity relative to L), dissolved in CH₃CN, was added to the top of the buffer. As the layers slowly diffused together, well-formed crystals, suitable for X-ray single-crystal analysis, appeared.

Crystal data

[Ag(C₁₂H₁₀N₄)]NO₃
M_r = 380.12
 Monoclinic, *C*2/*c*
a = 15.053 (1) Å
b = 13.703 (1) Å
c = 6.772 (1) Å
 β = 97.93 (1)°
V = 1383.5 (2) Å³
Z = 4

D_x = 1.825 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 4.7–10.0°
 μ = 1.47 mm⁻¹
T = 293 (2) K
 Block, yellow
 0.3 × 0.2 × 0.2 mm


Figure 2

The crystal packing of (I), viewed down the *c* axis. The NO₃⁻ ion is disordered in the crystal.

Data collection

Bruker *P4* diffractometer
 2 θ / ω scans
 Absorption correction: empirical
 via ψ scans (Sheldrick, 1990)
T_{min} = 0.709, *T_{max}* = 0.745
 1490 measured reflections
 1214 independent reflections
 1064 reflections with *I* > 2 σ (*I*)

R_{int} = 0.020
 θ_{\max} = 25.0°
h = -1 → 17
k = -1 → 16
l = -8 → 8
 3 standard reflections
 every 97 reflections
 intensity decay: 8.1%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.045
wR(*F*²) = 0.145
S = 1.07
 1214 reflections
 104 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.99P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.56 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.31 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ag1—N1	2.180 (5)	N2—N2 ⁱ	1.403 (11)
N2—C6	1.250 (9)		
N1—Ag1—N1 ⁱⁱ	174.3 (2)	C5—N1—Ag1	118.8 (4)
C1—N1—Ag1	124.4 (4)	C6—N2—N2 ⁱ	114.1 (7)

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

The NO_3^- ion is disordered. Each O atom has two possible positions, equally occupied. The positions of all H atoms were fixed geometrically and distances to H atoms were set by the refinement program.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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