

Polymeric (μ_2 -nitrate- κ^2 O:O')(μ_2 -nitrate- κ^2 O:O)(μ_4 -pyridinium-4-thiolato- κ^4 S:S:S:S)disilver(I)

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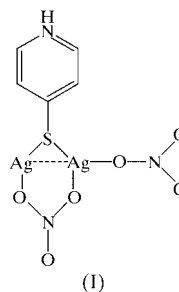
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The title compound, $[\text{Ag}_2(\text{NO}_3)_2(\text{C}_5\text{H}_5\text{NS})]_n$, was obtained from the reaction of silver nitrate with bis(4-pyridyl) disulfide (4-PDS) in a mixture of ethanol and water, which suggests that the disulfide bond of 4-PDS can be cleaved under mild conditions. The structure of the title compound is a two-dimensional infinite array in which the asymmetric unit contains two Ag atoms, a pyridinium-4-thiolate molecule and two nitrate groups. Each pyridinium-4-thiolate molecule acts as a μ_4 bridge, linking four Ag atoms, with Ag—S bond distances of 2.4870 (19), 2.5791 (19), 2.5992 (19) and 2.848 (2) Å. The Ag \cdots Ag distances lie in the range 2.889 (2)–3.049 (1) Å.

Comment

The design of inorganic–organic hybrid framework assemblies has become an active research area (Shimizu *et al.*, 1999; Shi *et al.*, 2000; Zhao *et al.*, 2001) because of the potential application of these assemblies as functional solid materials (Carlucci *et al.*, 1995; Wang *et al.*, 1995; Yaghi *et al.*, 1996; Matsumoto *et al.*, 1999; Triki *et al.*, 1999). Many studies have focused on inorganic–organic hybrid materials containing N-donor ligands, and the coordination chemistry of organosulfur compounds has also been studied intensively. We chose 4-PDS [bis(4-pyridyl) disulfide] as a ligand with both N and S donors. We found that, under mild conditions, the disulfide bond of 4-PDS could be cleaved, resulting in the title compound. A number of one-, two- and three-dimensional coordination polymers containing the pyridine-2-thiol ligand have been developed (Hong *et al.*, 1999; Lobana *et al.*, 1999; Su *et al.*, 1999, 2002; Kato *et al.*, 2002; Liaw *et al.*, 2002; Yih *et al.*, 2003). However, only a few crystal structures of discrete and one-dimensional complexes containing the pyridine-4-thiol ligand have been reported (Paw *et al.*, 1998; Brand & Shapley, 2000). We report here the synthesis and crystal structure of a two-dimensional

lamellar polymer, (I), containing pyridine-4-thiol as a bridging ligand. As far as we know, this is the first example of a two-dimensional polymer in which pyridine-4-thiol acts as a μ_4 -bridging ligand.



The structure of (I) is a two-dimensional infinite array in which the asymmetric unit contains two silver(I) ions, a pyridinium-4-thiolate molecule and two NO_3^- anions. The pyridinium-4-thiolate ligand exists in a tautomeric form, with the H^+ ion transferred from the S atom to the more basic N atom (Maresca *et al.*, 2000). The Ag atoms are bridged by both pyridinium-4-thiolate ligands and nitrate groups, and all the Ag atoms are coordinated by two S atoms from two different ligands and two O atoms from two different nitrate groups in a distorted tetrahedral coordination (Fig. 1). Each pyridinium-4-thiolate ligand acts as a μ_4 bridge, linking four Ag atoms, with Ag—S bond distances of 2.4870 (19), 2.5791 (19), 2.5992 (19) and 2.848 (2) Å, respectively (Table 1). Interestingly, the nitrate groups have two different bridging patterns, which is unusual (Hashimoto *et al.*, 2000). In one pattern, two O atoms of one group bond to two different Ag atoms, with Ag—O bond distances of 2.494 (6) and 2.412 (6) Å. In the other pattern, one O atom bonds to two different Ag^I atoms, with Ag—O bond distances of 2.538 (6) and 2.356 (5) Å. As expected, the mean Ag—O bond distance [2.450 (6) Å] is shorter than the mean Ag—S distance [2.628 (2) Å]. The Ag \cdots Ag separations range from 2.889 (2) to 3.049 (1) Å; all

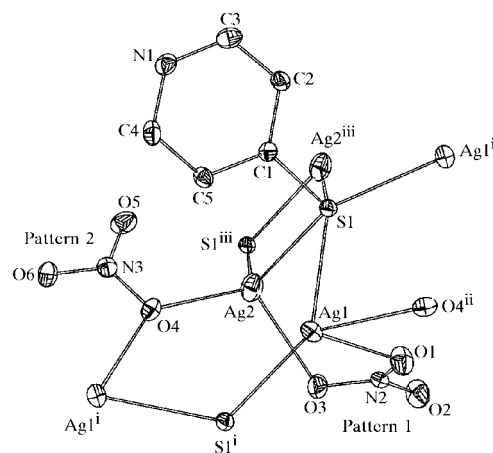


Figure 1

A section of the crystal structure of (I), shown with ellipsoids at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $-x, 2 - y, -z$.]

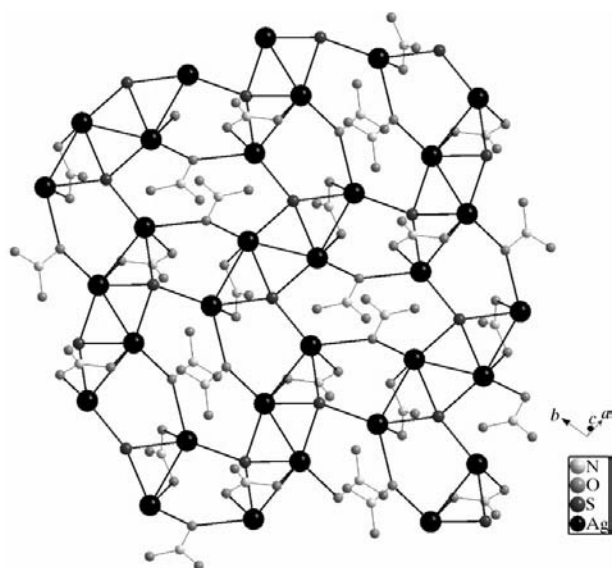


Figure 2
A view of a single lamella of the structure of (I). Pyridyl groups have been omitted for clarity.

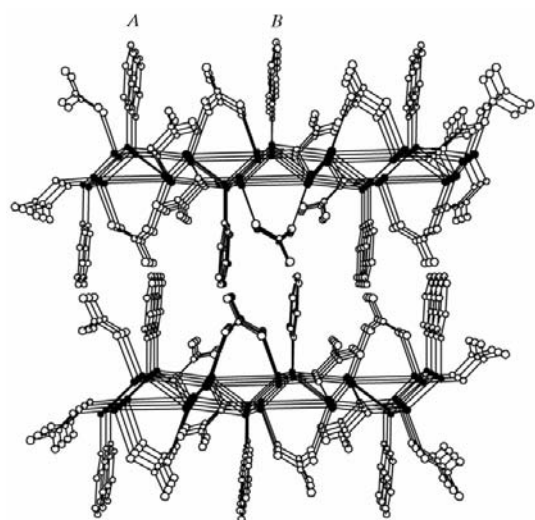


Figure 3
The structure of (I), showing the overall lamellar structure, with pyridyl groups protruding into the interlayer region. The view is along the *b* axis.

are best considered as non-bonding, although some of the values are very similar to those in metallic silver (2.88 Å; Raper, 1985; Blower & Dilworth, 1987). Together, the Ag—S and Ag—O bonds and the Ag...Ag interactions link the repeat units into a two-dimensional lamellar structure (Fig. 2). Fig. 3 shows that (I) is a good example of a layered inorganic-organic solid, where the inorganic layer contains sulfido/oxygen-bridged silver(I) centers and the organic layer contains the pyridyl groups. The interlayer distance is 9.86 Å. The pyridyl groups stack in an *ABAB*... pattern, the dihedral angle between the *A* and *B* planes of pyridyl rings being 10.91°.

Experimental

A mixture of AgNO₃ (0.39 g, 2.3 mmol), 4-PDS (0.18 g, 0.82 mmol), ethanol (20 ml) and water (20 ml) was stirred at 323 K for 1 h. The

solution was then filtered and the filtrate was kept in a container covered with filter paper. After 90 d, colorless block-shaped crystals were isolated (yield 0.069 g, 13%) from the remaining solution (about 5 ml). Analysis calculated for C₅H₅Ag₂N₃O₆S: C 13.32, H 1.12, N 9.32, S 7.11%; found: C 13.36, H 1.18, N 9.26, S 7.13%. IR (KBr, cm⁻¹): 1763 (*w*), 1745 (*w*), 1614 (*s*), 1583 (*s*), 1531 (*w*), 1470 (*s*), 1381 (*s*), 1281 (*m*), 1223 (*m*), 1198 (*m*), 1103 (*s*), 1030 (*m*), 1012 (*m*), 999 (*m*), 922 (*w*), 823 (*w*), 800 (*s*), 715 (*s*), 640 (*w*), 492 (*s*), 422 (*s*). The emission spectrum of (I) in the solid state showed a broad band at 538 nm when irradiated at 238 nm; this spectrum is almost the same as that of the free pyridine-4-thiol ligand.

Crystal data

[Ag₂(NO₃)₂(C₅H₅NS)]
M_r = 450.92
 Monoclinic, *P*2₁/*n*
a = 11.1738 (9) Å
b = 8.2212 (7) Å
c = 12.1466 (10) Å
 β = 116.224 (2)°
V = 1000.96 (14) Å³
Z = 4

D_x = 2.992 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 1859 reflections
 θ = 2.1–25.0°
 μ = 4.14 mm⁻¹
T = 293 (2) K
 Block, colorless
 0.30 × 0.16 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.376, *T_{max}* = 0.618
 3067 measured reflections

1735 independent reflections
 1446 reflections with *I* > 2σ(*I*)
R_{int} = 0.029
 θ_{max} = 25.0°
h = -12 → 13
k = -9 → 9
l = -14 → 6

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.108
S = 1.05
 1735 reflections
 155 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0467*P*)² + 9.1855*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.29 e Å⁻³
 Δρ_{min} = -1.46 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0052 (5)

Table 1

Selected geometric parameters (Å, °).

Ag1—S1 ⁱ	2.4870 (19)	Ag2—O4	2.356 (5)
Ag1—O1	2.494 (6)	Ag2—O3	2.412 (6)
Ag1—O4 ⁱⁱ	2.538 (6)	Ag2—S1 ⁱⁱⁱ	2.5992 (19)
Ag1—S1	2.5791 (19)	Ag2—S1	2.848 (2)
Ag1—Ag2	3.0492 (10)	Ag2—Ag2 ⁱⁱⁱ	2.8889 (16)
S1 ⁱ —Ag1—O1	119.89 (16)	O4—Ag2—O3	111.1 (2)
S1 ⁱ —Ag1—O4 ⁱⁱ	123.17 (13)	O4—Ag2—S1 ⁱⁱⁱ	120.16 (14)
O1—Ag1—O4 ⁱⁱ	77.18 (18)	O3—Ag2—S1 ⁱⁱⁱ	102.59 (17)
S1 ⁱ —Ag1—S1	145.35 (5)	O4—Ag2—S1	102.58 (13)
O1—Ag1—S1	85.40 (17)	O3—Ag2—S1	103.16 (15)
O4 ⁱⁱ —Ag1—S1	83.13 (13)	S1 ⁱⁱⁱ —Ag2—S1	116.14 (5)

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

H atoms were placed in idealized positions and treated as riding on their parent atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *XPREP* (Siemens, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1154). Services for accessing these data are described at the back of the journal.

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