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A novel one-dimensional silver cylinder stabilized by mixed 2-mercaptobenzoic acid and ethylenediamine ligands

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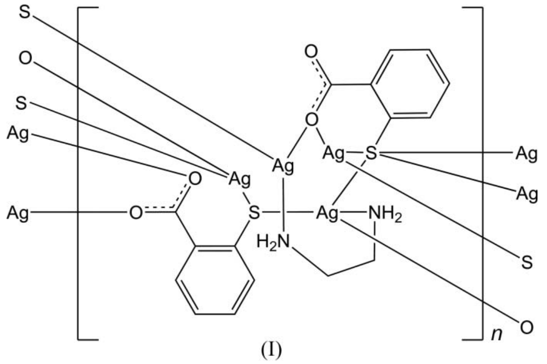
A novel infinite one-dimensional silver cylinder, namely poly[μ-ethylenediamine-μ_5-(2-sulfanidylbenzoato)-μ_4-(2-sulfanidylbenzoato)-tetrasilver(I)], $[Ag_4(C_7H_4O_2S)_2(C_2H_8N_2)]_n$, has been synthesized by one-pot reaction of equivalent molar silver nitrate and 2-mercaptobenzoic acid (H_2mba) in the presence of ethylenediamine (eda). One Ag atom is located in an AgS_2NO four-coordinated tetrahedral geometry, two other Ag atoms are in an AgS_2O three-coordinated T-shaped geometry and the fourth Ag atom is in an AgSNO coordination environment. The two mba ligands show two different binding modes. The μ_2-*N*:*N*′-eda ligand, acting as a bridge, combines with mba ligands to extend the Ag^I ions into a one-dimensional silver cylinder incorporating abundant Ag$\cdots$Ag interactions ranging from 2.9298 (11) to 3.2165 (13) Å. Interchain N—H$\cdots$O hydrogen bonds extend the one-dimensional cylinder into an undulating two-dimensional sheet, which is further packed into a three-dimensional supramolecular framework by van der Waals interactions; no π–π interactions were observed in the crystal structure.

Comment

In recent decades, the crystal engineering of Ag^I coordination architectures has become a thriving and prosperous field that has attracted increasing interest because of the intriguing structural topologies and functional properties such as conductance and luminescence (Munakata *et al.*, 1997; Jia & Wang, 2009; Wu *et al.*, 2010; Kang *et al.*, 2010; Anson *et al.*, 2008). Ag^I-based coordination compounds, classified as discrete silver clusters or infinite coordination polymers, have been much studied (Mak *et al.*, 2007; Xie *et al.*, 2011; Jin *et al.*, 2009; Zhang *et al.*, 2007). The selection of chelating or bridging organic linkers favoring a structure-specific assembly is important for the construction of coordination architectures with expected structures and properties (Sun *et al.*, 2006; Sun, Dai *et al.*, 2011; Dai *et al.*, 2008). However, the factors that govern the formation of such compounds are complicated and include not only the nature of the Ag^I ion and ligand structure but also anion-directed interactions as well as reaction conditions. In addition to covalent bonds, noncovalent interactions, such as π–π, hydrogen bond, cation$\cdots\pi$, anion$\cdots\pi$ and Ag$\cdots$Ag interactions, also play important roles in controlling molecular packing (Domasevitch *et al.*, 2007; Yin *et al.*, 2012; Chen *et al.*, 2010; Li, Wei *et al.*, 2010; Li *et al.*, 2011). Thus, in reality, it is hard to predict the structure of a Ag^I coordination compound with given ligand(s) until it has been characterized by X-ray single-crystal diffraction.

The bifunctional 2-mercaptobenzoic acid (H_2mba) ligand has 'soft' S-atom and 'hard' O-atom donors, which could bind more than one Ag^I center by S- and O-atom donors with diverse binding modes. Ethylenediamine (eda) can act as a bridging or chelating ligand to anchor on any unsaturated Ag^I centers. Although Ag^I–mba (Sun, Wang, Liu *et al.*, 2011) and Ag^I–eda (Ren *et al.*, 2001; Yilmaz *et al.*, 2006) coordination compounds have been widely investigated, the Ag^I–mba–eda system has not yet been documented. Based on the above consideration and our previous work (Sun, Luo *et al.*, 2011; Sun, Wang, Han *et al.*, 2011; Sun, Yang *et al.*, 2010), herein we describe a novel, infinite, one-dimensional silver cylinder, namely poly[μ-ethylenediamine-μ_5-(2-sulfanidylbenzoato)-μ_4-(2-sulfanidylbenzoato)-tetrasilver(I)], $[Ag_4(mba)_2(eda)]_n$, (I), which was obtained by a one-pot reaction of molar equivalent silver nitrate and 2-mercaptobenzoic acid (H_2mba) in the presence of ethylenediamine (eda).



(I)

Single-crystal X-ray diffraction reveals that the asymmetric unit of (I) contains four crystallographically independent Ag^I ions, two dianionic mba ligands and one neutral eda ligand. As shown in Fig. 1, Ag1 is located in a distorted AgS_2NO four-coordinated tetrahedral geometry with a distortion parameter τ_4 of 0.82. The τ_4 index is defined as the sum of the two largest angles around the four-coordinated metal center subtracted from 360°, all divided by 141° (Yang *et al.*, 2007). The values of τ_4 range from 1.00 for a perfect tetrahedral geometry to 0 for a perfect square-planar geometry. Ag2 and Ag3 are in the AgS_2O three-coordinated T-shaped geometry with the largest angles being 152.41 (11) and 162.44 (12)°, respectively. Ag4 is also in a three-coordinated geometry, but in an AgSNO coordination environment. The Ag—S [2.458 (3)–2.718 (3) Å],

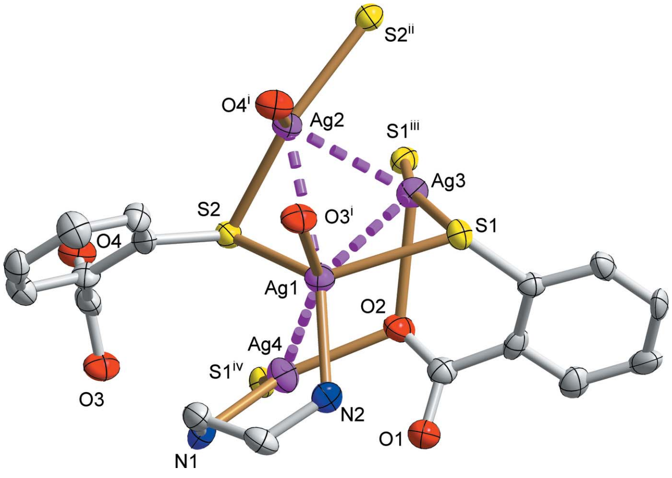


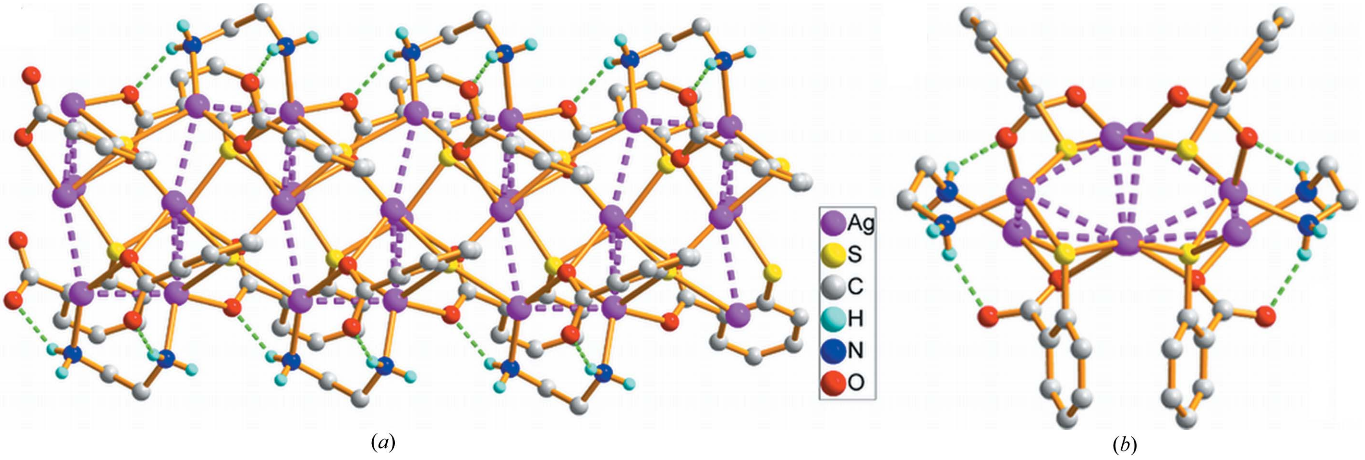
Figure 1
The structure of (I), showing the coordination environments around the Ag^I centers. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Dashed lines indicate Ag$\cdots$Ag interactions, as described in the *Comment*. [Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, z$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (iv) $x, y - 1, z$.]

Ag—N [2.253 (9) and 2.310 (8) Å] and Ag—O [2.308 (8)–2.532 (7) Å] bond lengths (Table 1) are comparable with reported values (Schottel *et al.*, 2006; Tsyba *et al.*, 2003). The two mba ligands show different binding modes. The μ_2-N^1:N^1 eda ligand acts as a bridge between Ag^I ions. Notably, the N1—C1—C2—N2 torsion angle of eda is 70.9 (13)° which fits well with a *gauche* conformation of eda according to stereochemical terminology (Moss, 1996). The Ag$\cdots$Ag interactions vary from 2.9298 (11) to 3.2165 (13) Å, with an average of 3.1123 (12) Å, which is 0.3 Å shorter than twice the van der Waals radius of Ag^I (3.44 Å; Bondi, 1964), indicating argentophilic interaction. This weak bonding interaction between two closed-shell d^{10} cations is possible *via* the participation of 5*s* and 5*p* orbitals which have similar energy to the 4*d* orbital. Similar argentophilic interactions were also found in the related cluster compounds {[$Ag_{62}S_{13}(SBu^t)_{32}$]($BF_4$)$_4$} (Li, Lei *et al.*, 2010) and {$(NH_4)_{17}[(\mu_6\text{-}S)Ag_{17}(mba)_{16}]\cdot 22H_2O$} (Sun, Liu *et al.*, 2011), as well as in the coordination polymer $[Ag_4(mba)_2(H_2O)_2]_n$ (Sun, Luo *et al.*, 2010).

The crystal structure of (I) features a one-dimensional Ag^I cylinder (Fig. 2) running along the *b* axis which is reinforced by intrachain N1—H1*C*$\cdots$O3 and N2—H2*C*$\cdots$O1 hydrogen bonds (Table 2), with an average distance of 2.981 (12) Å, a C—H$\cdots\pi$ interaction [C1—H1*A*$\cdots$*Cg*1 = 138°, H1*A*$\cdots$*Cg*1 = 2.96 Å and C1$\cdots$*Cg*1 = 3.738 (11) Å; *Cg*1 is the centroid of the C21–C26 ring], a nonclassical C22—H22*A*$\cdots$O4 hydrogen bond of 3.449 (13) Å and argentophilic interactions. Moreover, interchain N1—H1*D*$\cdots$O1^v and N2—H2*D*$\cdots$O1^{vi} hydrogen bonds extend the one-dimensional cylinders into an undulating two-dimensional sheet (Fig. 3), which is further packed into a three-dimensional supramolecular framework by van der Waals interactions; π–π interactions are not observed in the crystal structure. To the best of our knowledge, most of the reported Ag^I–mba compounds are discrete clusters, such as mononuclear [Ag(Hmba)(triphenylphosphane)$_3$] (Nomiya *et al.*, 1998), tetranuclear [Ag_4(Hmba)$_4$(triphenylphosphane)$_4$] (Noguchi *et al.*, 2005) and octanuclear $K_{12}[Ag_8(mba)_{10}]$ (Nomiya *et al.*, 2000). Infinite coordination polymers are still rare, which may be due to the strong coordinative ability of the S-atom donor to the Ag^I ion, and, as a result, the metastable polynuclear Ag^I aggregates are protected by them.

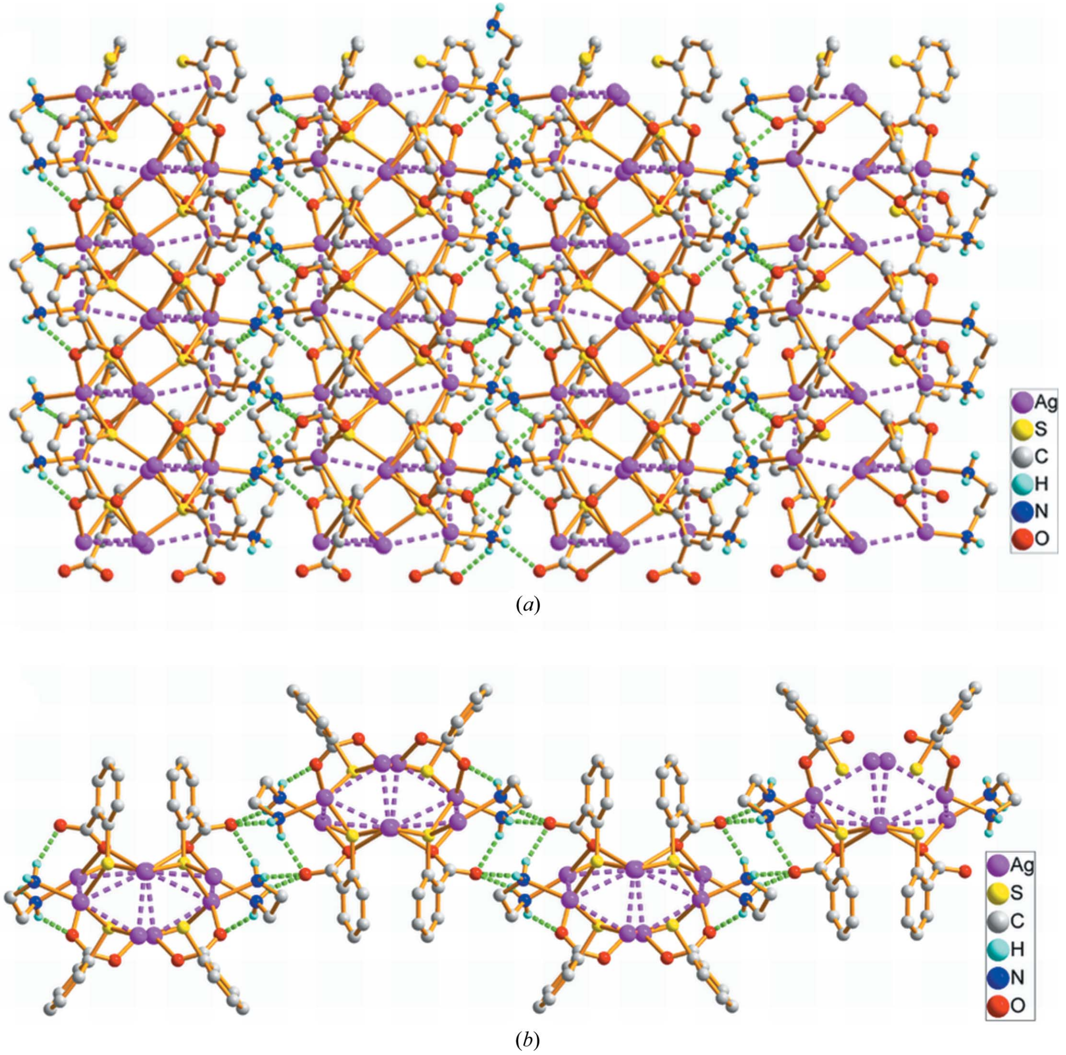
Experimental

All reagents and solvents were used as obtained commercially without further purification. A mixture of $AgNO_3$ (85 mg, 0.5 mmol), H_2mba (78 mg, 0.5 mmol) and eda (1 ml) was added to a CH_3OH–H_2O mixture (12 ml, 1:2 *v*/*v*) under ultrasonic conditions which helped to dissolve the white precipitate. An aqueous NH_3 solution (25%) was then dropped into the mixture to give a clear solution. The resultant solution was allowed to evaporate slowly in darkness at room temperature over a period of two weeks to give colorless block-shaped crystals of (I). The crystals were washed with deionized water and dried in air (yield *ca* 52%, based on Ag). Elemental analysis calculated for $C_{64}H_{64}Ag_4N_8O_{16}S_8$: C 40.69, H 3.41, N 5.93%; found: C 40.18, H. 3.09, N 5.29%.



(*a*) (*b*)

Figure 2
A ball-and-stick perspective view of the one-dimensional cylinder in (I) viewed (*a*) along *c* and (*b*) along *b*. The argentophilic interactions and hydrogen bonds are highlighted by dashed lines (purple and green, respectively, in the electronic version of the paper).



(*a*)

(*b*)

Figure 3
A perspective view of the two-dimensional undulating sheet viewed (*a*) along *c* and (*b*) along *b*. The argentophilic interactions and hydrogen bonds are highlighted by dashed lines (purple and green, respectively, in the electronic version of the paper).

Crystal data

$[Ag_4(C_7H_4O_2S)_2(C_2H_8N_2)]$
M_r = 795.91
Orthorhombic, *Pbca*
a = 22.1562 (2) Å
b = 6.9556 (7) Å
c = 25.0366 (5) Å

V = 3858.4 (4) Å^3
Z = 8
Mo *Kα* radiation
μ = 4.24 mm^{-1}
T = 298 K
0.15 × 0.08 × 0.05 mm

Data collection

Oxford Diffraction Gemini S Ultra CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.569, T_{max} = 0.816

22503 measured reflections
3392 independent reflections
2660 reflections with $I > 2\sigma(I)$
R_{int} = 0.075

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.113
S = 1.20
3392 reflections

254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.74 e Å^{-3}
$\Delta\rho_{min}$ = −1.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—N2	2.310 (8)	Ag2—S2^{ii}	2.506 (3)
Ag1—O3^{i}	2.356 (7)	Ag2—Ag3	2.9298 (11)
Ag1—S2	2.616 (3)	Ag3—S1^{iii}	2.458 (3)
Ag1—S1	2.696 (3)	Ag3—S1	2.499 (3)
Ag1—Ag2	3.0300 (12)	Ag3—O2	2.532 (7)
Ag1—Ag3	3.2102 (12)	Ag3—Ag4^{ii}	3.1980 (13)
Ag1—Ag4	3.2165 (13)	Ag4—N1	2.253 (9)
Ag2—O4^{i}	2.365 (8)	Ag4—O2	2.308 (8)
Ag2—S2	2.474 (3)	Ag4—S1^{iv}	2.718 (3)
N2—Ag1—O3^{i}	101.0 (3)	S2—Ag2—S2^{ii}	152.41 (11)
N2—Ag1—S2	122.5 (2)	S1^{iii}—Ag3—S1	162.44 (12)
O3^{i}—Ag1—S2	111.3 (2)	S1^{iii}—Ag3—O2	95.62 (19)
N2—Ag1—S1	103.3 (2)	S1—Ag3—O2	81.54 (19)
O3^{i}—Ag1—S1	91.1 (2)	N1—Ag4—O2	142.4 (3)
S2—Ag1—S1	121.58 (9)	N1—Ag4—S1^{iv}	116.9 (3)
O4^{i}—Ag2—S2	116.7 (2)	O2—Ag4—S1^{iv}	98.9 (2)
O4^{i}—Ag2—S2^{ii}	90.6 (2)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22*A*···O4$^{\rm i}$	0.93	2.54	3.449 (13)	165
N1—H1*C*···O3	0.90	2.17	2.942 (12)	143
N1—H1*D*···O1$^{\rm v}$	0.90	2.16	3.007 (12)	156
N2—H2*C*···O1	0.90	2.17	3.019 (12)	157
N2—H2*D*···O1$^{\rm vi}$	0.90	2.42	3.233 (12)	151

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

All H atoms were generated geometrically and were allowed to ride on their parent atoms in the riding-model approximation, with C—H = 0.93 (aromatic) or 0.97 Å (CH_2) and N—H = 0.90 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: QS3015). Services for accessing these data are described at the back of the journal.

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supplementary materials

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A novel one-dimensional silver cylinder stabilized by mixed 2-mercaptobenzoic acid and ethylenediamine ligands

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Crystal data

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$M_r = 795.91$
Orthorhombic, *Pbca*
$a = 22.1562$ (2) Å
$b = 6.9556$ (7) Å
$c = 25.0366$ (5) Å
$V = 3858.4$ (4) Å^3
$Z = 8$
$F(000) = 3024$

$D_x = 2.740$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 15021 reflections
$\theta = 6.1$–54.9°
$\mu = 4.24$ mm^{-1}
$T = 298$ K
Block, colorless
0.15 × 0.08 × 0.05 mm

Data collection

Oxford Diffraction Gemini S Ultra CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
$T_{min} = 0.569$, $T_{max} = 0.816$

22503 measured reflections
3392 independent reflections
2660 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.2°$
$h = -25 \rightarrow 26$
$k = -8 \rightarrow 8$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.113$
$S = 1.20$
3392 reflections
254 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 78.8999P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.74$ e Å^{-3}
$\Delta\rho_{min} = -1.47$ e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00033 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Ag1	0.61643 (4)	0.57842 (13)	0.65672 (3)	0.0333 (2)
Ag2	0.73427 (4)	0.59199 (12)	0.59542 (3)	0.0309 (2)
Ag3	0.74726 (4)	0.55368 (13)	0.71139 (3)	0.0341 (3)
Ag4	0.61174 (4)	0.14528 (14)	0.70152 (4)	0.0389 (3)
S1	0.67214 (12)	0.8166 (4)	0.72588 (11)	0.0292 (6)
S2	0.67417 (12)	0.2968 (4)	0.60997 (11)	0.0282 (6)
C1	0.4973 (5)	0.2825 (17)	0.6291 (4)	0.034 (3)
H1A	0.5276	0.3405	0.6062	0.041*
H1B	0.4647	0.2383	0.6064	0.041*
C2	0.4734 (5)	0.4330 (17)	0.6657 (5)	0.036 (3)
H2A	0.4492	0.5228	0.6452	0.044*
H2B	0.4473	0.3729	0.6919	0.044*
C11	0.6730 (5)	0.7783 (16)	0.7973 (4)	0.026 (2)
C12	0.6525 (5)	0.6025 (16)	0.8191 (4)	0.029 (2)
C13	0.6540 (5)	0.5820 (17)	0.8754 (4)	0.034 (3)
H13A	0.6402	0.4685	0.8908	0.041*
C14	0.6753 (5)	0.726 (2)	0.9077 (5)	0.045 (3)
H14A	0.6773	0.7085	0.9445	0.053*
C15	0.6939 (5)	0.8983 (18)	0.8852 (5)	0.038 (3)
H15A	0.7070	0.9977	0.9072	0.046*
C16	0.6931 (5)	0.9240 (17)	0.8303 (4)	0.033 (3)
H16A	0.7061	1.0396	0.8157	0.039*
C17	0.6293 (5)	0.4385 (16)	0.7879 (4)	0.030 (2)
C21	0.6315 (5)	0.2696 (17)	0.5497 (4)	0.029 (3)
C22	0.6116 (5)	0.4255 (15)	0.5207 (4)	0.030 (2)
H22A	0.6244	0.5481	0.5303	0.036*
C23	0.5732 (6)	0.4036 (18)	0.4779 (5)	0.042 (3)
H23A	0.5607	0.5110	0.4588	0.050*
C24	0.5533 (5)	0.2230 (18)	0.4633 (4)	0.036 (3)
H24A	0.5270	0.2093	0.4346	0.044*
C25	0.5725 (5)	0.0613 (17)	0.4915 (4)	0.032 (3)
H25A	0.5593	−0.0612	0.4823	0.039*
C26	0.6125 (5)	0.0890 (15)	0.5343 (4)	0.028 (2)
C27	0.6339 (5)	−0.0938 (17)	0.5635 (5)	0.036 (3)
N1	0.5246 (4)	0.1131 (14)	0.6561 (3)	0.032 (2)
H1C	0.5305	0.0223	0.6310	0.038*
H1D	0.4969	0.0664	0.6790	0.038*

N2	0.5216 (4)	0.5400 (14)	0.6937 (4)	0.033 (2)
H2C	0.5268	0.4829	0.7256	0.040*
H2D	0.5072	0.6586	0.7002	0.040*
O1	0.5762 (3)	0.3827 (12)	0.7951 (3)	0.0371 (19)
O2	0.6647 (3)	0.3566 (11)	0.7549 (3)	0.0345 (18)
O3	0.5989 (4)	−0.1657 (11)	0.5971 (3)	0.0358 (19)
O4	0.6855 (3)	−0.1518 (11)	0.5508 (3)	0.0353 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0353 (5)	0.0319 (5)	0.0325 (5)	−0.0016 (4)	0.0007 (4)	0.0010 (4)
Ag2	0.0320 (5)	0.0289 (5)	0.0319 (4)	−0.0033 (4)	0.0004 (3)	0.0015 (4)
Ag3	0.0329 (5)	0.0376 (5)	0.0318 (4)	0.0046 (4)	0.0007 (4)	0.0019 (4)
Ag4	0.0391 (5)	0.0357 (5)	0.0421 (5)	0.0009 (4)	−0.0073 (4)	0.0002 (4)
S1	0.0302 (15)	0.0291 (15)	0.0284 (14)	−0.0004 (12)	−0.0042 (11)	−0.0009 (12)
S2	0.0279 (14)	0.0286 (15)	0.0281 (13)	−0.0026 (12)	−0.0025 (11)	0.0020 (12)
C1	0.031 (6)	0.042 (7)	0.029 (6)	−0.006 (6)	0.001 (5)	0.000 (5)
C2	0.031 (6)	0.032 (6)	0.046 (7)	−0.009 (5)	0.002 (5)	−0.001 (6)
C11	0.024 (5)	0.026 (6)	0.029 (6)	0.002 (5)	0.005 (4)	−0.003 (5)
C12	0.029 (6)	0.031 (6)	0.028 (6)	0.008 (5)	0.004 (5)	−0.007 (5)
C13	0.031 (6)	0.036 (7)	0.034 (6)	0.007 (5)	0.005 (5)	−0.008 (5)
C14	0.030 (7)	0.076 (10)	0.027 (6)	−0.012 (7)	0.007 (5)	0.006 (6)
C15	0.040 (7)	0.040 (7)	0.033 (6)	−0.008 (6)	0.007 (5)	−0.029 (6)
C16	0.028 (6)	0.031 (6)	0.040 (6)	−0.005 (5)	0.010 (5)	−0.015 (5)
C17	0.034 (6)	0.023 (6)	0.033 (6)	0.000 (5)	0.003 (5)	0.003 (5)
C21	0.023 (5)	0.046 (7)	0.019 (5)	−0.010 (5)	−0.001 (4)	−0.002 (5)
C22	0.045 (7)	0.016 (5)	0.028 (6)	−0.004 (5)	−0.002 (5)	0.003 (4)
C23	0.046 (8)	0.031 (7)	0.048 (7)	0.003 (6)	−0.010 (6)	0.003 (6)
C24	0.036 (6)	0.045 (7)	0.028 (6)	0.001 (6)	−0.015 (5)	−0.004 (5)
C25	0.029 (6)	0.030 (6)	0.038 (6)	−0.006 (5)	−0.013 (5)	0.000 (5)
C26	0.035 (6)	0.023 (6)	0.027 (5)	−0.003 (5)	0.008 (5)	0.007 (5)
C27	0.037 (7)	0.035 (7)	0.035 (6)	−0.015 (6)	−0.006 (5)	−0.002 (5)
N1	0.033 (5)	0.043 (6)	0.019 (4)	0.006 (5)	0.004 (4)	0.000 (4)
N2	0.027 (5)	0.032 (6)	0.040 (5)	0.008 (4)	0.009 (4)	−0.002 (4)
O1	0.033 (5)	0.039 (5)	0.039 (4)	−0.004 (4)	0.003 (4)	−0.001 (4)
O2	0.034 (4)	0.030 (4)	0.040 (4)	−0.006 (4)	0.008 (4)	0.001 (4)
O3	0.042 (5)	0.021 (4)	0.044 (5)	0.000 (4)	0.004 (4)	0.008 (4)
O4	0.025 (4)	0.035 (5)	0.046 (5)	0.007 (4)	0.001 (4)	0.006 (4)

Geometric parameters (Å, º)

Ag1—N2	2.310 (8)	C11—C16	1.381 (15)
Ag1—O3^{i}	2.356 (7)	C11—C12	1.415 (15)
Ag1—S2	2.616 (3)	C12—C13	1.418 (15)
Ag1—S1	2.696 (3)	C12—C17	1.476 (15)
Ag1—Ag2	3.0300 (12)	C13—C14	1.372 (17)
Ag1—Ag3	3.2102 (12)	C13—H13A	0.9300
Ag1—Ag4	3.2165 (13)	C14—C15	1.386 (18)
Ag2—O4^{i}	2.365 (8)	C14—H14A	0.9300

Ag2—S2	2.474 (3)	C15—C16	1.387 (16)
Ag2—S2^{ii}	2.506 (3)	C15—H15A	0.9300
Ag2—Ag3	2.9298 (11)	C16—H16A	0.9300
Ag3—S1^{iii}	2.458 (3)	C17—O1	1.253 (13)
Ag3—S1	2.499 (3)	C17—O2	1.273 (13)
Ag3—O2	2.532 (7)	C21—C22	1.376 (15)
Ag3—Ag4^{ii}	3.1980 (13)	C21—C26	1.380 (15)
Ag4—N1	2.253 (9)	C22—C23	1.376 (16)
Ag4—O2	2.308 (8)	C22—H22A	0.9300
Ag4—S1^{iv}	2.718 (3)	C23—C24	1.381 (16)
Ag4—S2	2.877 (3)	C23—H23A	0.9300
Ag4—Ag3^{iii}	3.1980 (13)	C24—C25	1.396 (16)
S1—C11	1.808 (11)	C24—H24A	0.9300
S1—Ag3^{ii}	2.458 (3)	C25—C26	1.404 (15)
S1—Ag4^{i}	2.718 (3)	C25—H25A	0.9300
S2—C21	1.791 (10)	C26—C27	1.541 (16)
S2—Ag2^{iii}	2.506 (3)	C27—O3	1.248 (13)
C1—C2	1.487 (16)	C27—O4	1.254 (14)
C1—N1	1.486 (14)	N1—H1C	0.9000
C1—H1A	0.9700	N1—H1D	0.9000
C1—H1B	0.9700	N2—H2C	0.9000
C2—N2	1.479 (14)	N2—H2D	0.9000
C2—H2A	0.9700	O3—Ag1^{iv}	2.356 (7)
C2—H2B	0.9700	O4—Ag2^{iv}	2.365 (8)

N2—Ag1—O3^{i}	101.0 (3)	Ag2^{iii}—S2—Ag1	152.47 (12)
N2—Ag1—S2	122.5 (2)	C21—S2—Ag4	112.3 (4)
O3^{i}—Ag1—S2	111.3 (2)	Ag2—S2—Ag4	132.85 (11)
N2—Ag1—S1	103.3 (2)	Ag2^{iii}—S2—Ag4	107.26 (10)
O3^{i}—Ag1—S1	91.1 (2)	Ag1—S2—Ag4	71.51 (7)
S2—Ag1—S1	121.58 (9)	C2—C1—N1	115.1 (9)
N2—Ag1—Ag2	171.8 (2)	C2—C1—H1A	108.5
O3^{i}—Ag1—Ag2	78.32 (19)	N1—C1—H1A	108.5
S2—Ag1—Ag2	51.34 (6)	C2—C1—H1B	108.5
S1—Ag1—Ag2	84.93 (7)	N1—C1—H1B	108.5
N2—Ag1—Ag3	130.1 (2)	H1A—C1—H1B	107.5
O3^{i}—Ag1—Ag3	117.4 (2)	N2—C2—C1	112.8 (9)
S2—Ag1—Ag3	73.08 (6)	N2—C2—H2A	109.0
S1—Ag1—Ag3	49.13 (6)	C1—C2—H2A	109.0
Ag2—Ag1—Ag3	55.91 (3)	N2—C2—H2B	109.0
N2—Ag1—Ag4	73.9 (2)	C1—C2—H2B	109.0
O3^{i}—Ag1—Ag4	157.4 (2)	H2A—C2—H2B	107.8
S2—Ag1—Ag4	58.03 (6)	C16—C11—C12	120.4 (10)
S1—Ag1—Ag4	111.50 (7)	C16—C11—S1	119.1 (9)
Ag2—Ag1—Ag4	103.51 (3)	C12—C11—S1	120.4 (8)
Ag3—Ag1—Ag4	80.23 (3)	C11—C12—C13	117.6 (10)
O4^{i}—Ag2—S2	116.7 (2)	C11—C12—C17	125.1 (9)
O4^{i}—Ag2—S2^{ii}	90.6 (2)	C13—C12—C17	117.3 (10)
S2—Ag2—S2^{ii}	152.41 (11)	C14—C13—C12	121.4 (12)

O4^{i}—Ag2—Ag3	125.55 (19)	C14—C13—H13A	119.3
S2—Ag2—Ag3	80.30 (7)	C12—C13—H13A	119.3
S2^{ii}—Ag2—Ag3	80.10 (7)	C13—C14—C15	119.6 (11)
O4^{i}—Ag2—Ag1	82.46 (18)	C13—C14—H14A	120.2
S2—Ag2—Ag1	55.65 (7)	C15—C14—H14A	120.2
S2^{ii}—Ag2—Ag1	129.92 (7)	C16—C15—C14	120.7 (11)
Ag3—Ag2—Ag1	65.16 (3)	C16—C15—H15A	119.7
S1^{iii}—Ag3—S1	162.44 (12)	C14—C15—H15A	119.7
S1^{iii}—Ag3—O2	95.62 (19)	C11—C16—C15	120.2 (11)
S1—Ag3—O2	81.54 (19)	C11—C16—H16A	119.9
S1^{iii}—Ag3—Ag2	106.18 (7)	C15—C16—H16A	119.9
S1—Ag3—Ag2	90.68 (7)	O1—C17—O2	122.3 (10)
O2—Ag3—Ag2	113.88 (18)	O1—C17—C12	119.3 (10)
S1^{iii}—Ag3—Ag4^{ii}	55.61 (7)	O2—C17—C12	118.4 (10)
S1—Ag3—Ag4^{ii}	121.06 (7)	C22—C21—C26	118.2 (9)
O2—Ag3—Ag4^{ii}	147.85 (18)	C22—C21—S2	122.0 (9)
Ag2—Ag3—Ag4^{ii}	90.07 (3)	C26—C21—S2	119.5 (9)
S1^{iii}—Ag3—Ag1	139.03 (8)	C21—C22—C23	121.4 (10)
S1—Ag3—Ag1	54.65 (7)	C21—C22—H22A	119.3
O2—Ag3—Ag1	63.92 (18)	C23—C22—H22A	119.3
Ag2—Ag3—Ag1	58.93 (3)	C22—C23—C24	120.3 (11)
Ag4^{ii}—Ag3—Ag1	146.98 (4)	C22—C23—H23A	119.8
N1—Ag4—O2	142.4 (3)	C24—C23—H23A	119.8
N1—Ag4—S1^{iv}	116.9 (3)	C23—C24—C25	120.0 (10)
O2—Ag4—S1^{iv}	98.9 (2)	C23—C24—H24A	120.0
N1—Ag4—S2	92.6 (2)	C25—C24—H24A	120.0
O2—Ag4—S2	89.06 (19)	C24—C25—C26	117.9 (10)
S1^{iv}—Ag4—S2	104.49 (9)	C24—C25—H25A	121.0
N1—Ag4—Ag3^{iii}	148.9 (2)	C26—C25—H25A	121.0
O2—Ag4—Ag3^{iii}	65.49 (19)	C21—C26—C25	122.1 (10)
S1^{iv}—Ag4—Ag3^{iii}	48.25 (6)	C21—C26—C27	121.7 (9)
S2—Ag4—Ag3^{iii}	70.42 (6)	C25—C26—C27	116.2 (10)
N1—Ag4—Ag1	86.8 (2)	O3—C27—O4	127.4 (12)
O2—Ag4—Ag1	65.74 (19)	O3—C27—C26	117.4 (11)
S1^{iv}—Ag4—Ag1	148.22 (7)	O4—C27—C26	115.2 (10)
S2—Ag4—Ag1	50.47 (6)	C1—N1—Ag4	119.9 (7)
Ag3^{iii}—Ag4—Ag1	100.49 (3)	C1—N1—H1C	107.3
C11—S1—Ag3^{ii}	103.7 (4)	Ag4—N1—H1C	107.3
C11—S1—Ag3	91.7 (3)	C1—N1—H1D	107.3
Ag3^{ii}—S1—Ag3	89.18 (9)	Ag4—N1—H1D	107.3
C11—S1—Ag1	123.3 (4)	H1C—N1—H1D	106.9
Ag3^{ii}—S1—Ag1	130.56 (11)	C2—N2—Ag1	121.7 (7)
Ag3—S1—Ag1	76.22 (8)	C2—N2—H2C	106.9
C11—S1—Ag4^{i}	110.5 (4)	Ag1—N2—H2C	106.9
Ag3^{ii}—S1—Ag4^{i}	76.14 (8)	C2—N2—H2D	106.9
Ag3—S1—Ag4^{i}	155.60 (12)	Ag1—N2—H2D	106.9
Ag1—S1—Ag4^{i}	98.47 (9)	H2C—N2—H2D	106.7
C21—S2—Ag2	104.3 (4)	C17—O2—Ag4	110.3 (7)
C21—S2—Ag2^{iii}	104.1 (4)	C17—O2—Ag3	118.8 (7)

Ag2—S2—Ag2^{iii}	90.84 (9)	Ag4—O2—Ag3	117.6 (3)
C21—S2—Ag1	101.4 (4)	C27—O3—Ag1^{iv}	128.9 (8)
Ag2—S2—Ag1	73.01 (8)	C27—O4—Ag2^{iv}	122.7 (7)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+3/2, y+1/2, z$; (iii) $-x+3/2, y-1/2, z$; (iv) $x, y-1, z$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22*A*···O4^{i}	0.93	2.54	3.449 (13)	165
N1—H1*C*···O3	0.90	2.17	2.942 (12)	143
N1—H1*D*···O1^{v}	0.90	2.16	3.007 (12)	156
N2—H2*C*···O1	0.90	2.17	3.019 (12)	157
N2—H2*D*···O1^{vi}	0.90	2.42	3.233 (12)	151

Symmetry codes: (i) $x, y+1, z$; (v) $-x+1, y-1/2, -z+3/2$; (vi) $-x+1, y+1/2, -z+3/2$.