

Bis(μ -pyridine-1-carbaldehyde azine- $\kappa^2N,N':\kappa N''$)disilver(I) bis(p -toluene-sulfonate)

Grant A. Broker and Edward R. T. Tiekink*

Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA

Correspondence e-mail: edward.tiekink@utsa.edu

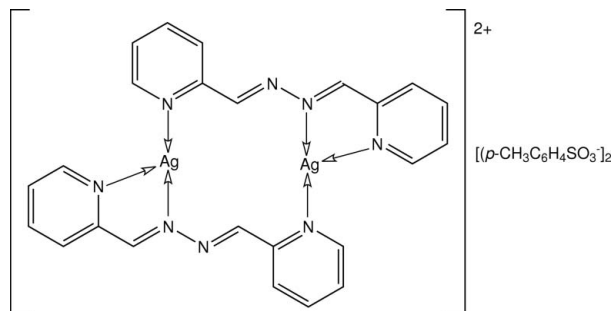
Received 16 August 2007; accepted 17 August 2007

 Key indicators: single-crystal X-ray study; $T = 98$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.020; wR factor = 0.052; data-to-parameter ratio = 14.9.

The title compound, $[Ag_2(C_{12}H_{10}N_4)_2](p-CH_3C_6H_4SO_3)_2$, features a centrosymmetric dication and T-shaped AgN_3 coordination geometry, as each ligand is tridentate, forming a bond to one Ag atom and chelating the other. The p -toluenesulfonate anion accepts a weak $Ag \cdots O$ contact [2.5023 (14) Å], as well as forming $C-H \cdots O$ interactions. The crystal structure comprises layers, stabilized by $C-H \cdots O$ contacts and connected by $C-H \cdots \pi$ interactions.

Related literature

For related dinuclear structures, see: Hamblin *et al.* (2002); Kennedy *et al.* (2005); Broker & Tiekink (2007). For a polymeric analogue, see: Guo *et al.* (2002).



Experimental

Crystal data

 $[Ag_2(C_{12}H_{10}N_4)_2](C_7H_7SO_3)_2$
 $M_r = 978.61$

 Triclinic, $P\bar{1}$
 $a = 7.9619$ (17) Å

 $b = 9.4382$ (11) Å

 $c = 13.468$ (3) Å

 $\alpha = 78.12$ (3)°

 $\beta = 76.75$ (3)°

 $\gamma = 70.13$ (3)°

 $V = 917.4$ (3) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 1.24$ mm⁻¹
 $T = 98$ (2) K

 $0.35 \times 0.10 \times 0.05$ mm

Data collection

Rigaku/MS

AFC12k/SATURN724

diffractometer

Absorption correction: multi-scan

(ABSCOR; Higashi, 1995)

 $T_{\min} = 0.715$, $T_{\max} = 1.000$

(expected range = 0.672–0.940)

10013 measured reflections

3776 independent reflections

 3713 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.052$
 $S = 1.07$

3776 reflections

254 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³
Table 1

Selected geometric parameters (Å, °).

Ag–N1 ⁱ	2.2596 (17)	Ag–N4	2.3900 (17)
Ag–N3	2.2948 (17)		
N1 ⁱ –Ag–N3	161.06 (6)	N3–Ag–N4	71.65 (6)
N1 ⁱ –Ag–N4	114.74 (6)		

 Symmetry code: (i) $-x, -y + 1, -z + 2$.

Table 2

Hydrogen-bond geometry (Å, °).

 C_g is the centroid of the N4/C8–C12 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C9–H9 \cdots O1 ⁱⁱ	0.95	2.36	3.025 (2)	126
C10–H10 \cdots O1 ⁱⁱ	0.95	2.56	3.109 (2)	117
C14–H14 \cdots O2	0.95	2.56	2.918 (2)	103
C7–H7 \cdots O3 ⁱⁱⁱ	0.95	2.53	3.116 (2)	120
C12–H12 \cdots O3 ⁱⁱⁱ	0.95	2.55	3.189 (2)	125
C15–H15 \cdots O3 ⁱⁱ	0.95	2.60	3.478 (2)	154
C17–H17 \cdots Cg ^{iv}	0.95	2.69	3.404 (2)	133

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

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2512).

References

- Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Brandenburg, K. (2006). *DIAMOND*. Release 3.1. Crystal Impact GbR, Bonn, Germany.
- Broker, G. A. & Tiekink, E. R. T. (2007). *Acta Cryst.* **E63**, m2368.
- Guo, D., He, C., Duan, C.-Y., Qian, C.-Q. & Meng, Q.-J. (2002). *New J. Chem.* **26**, 796–802.
- Hamblin, J., Jackson, A., Alcock, N. W. & Hannon, M. J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1635–1641.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kennedy, A. R., Brown, K. G., Graham, D., Kirkhouse, J. B., Kittner, M., Major, C., McHugh, C. J., Murdoch, P. & Smith, W. E. (2005). *New J. Chem.* **29**, 826–832.
- Rigaku/MS (2005). *CrystalClear*. Rigaku/MS Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E63, m2420 [doi:10.1107/S1600536807040809]

Bis(μ -pyridine-1-carbaldehyde azine- $\kappa^2N,N':\kappa N''$)disilver(I) bis(*p*-toluenesulfonate)

G. A. Broker and E. R. T. Tiekink

Comment

The title compound, $[\text{Ag}_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_2](p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ or $[\text{Ag}(2\text{-PA})]_2[(p\text{-tol})\text{SO}_3]_2$ (I), was investigated as a part of an on-going study of the structural chemistry of Ag salts of isomeric *n*-pyridinealdazine molecules, $n = 2, 3$ and 4 (Broker & Tiekink, 2007). The centrosymmetric dication adopts a ring structure as the two Ag atoms are bridged by two tridentate 2-PA molecules, each forming a single bond to one Ag atom and a chelating interaction to the other (Fig. 1 & Table 1). Within the chelate, the Ag–N_{azo} bond distance is significantly shorter than the Ag–N_{pyridine} bond; the coordination geometry around each Ag atom is T-shaped. The $[(p\text{-tol})\text{SO}_3]^-$ anion forms a close contact with Ag, *i.e.* Ag...O2 = 2.5023 (14) Å.

The dinuclear cation in (I) has three precedents in the literature, namely in the $[\text{CF}_3\text{SO}_3]^-$ (Hamblin *et al.*, 2002), $[\text{NO}_3]^-$ (Kennedy *et al.*, 2005) and $[\text{CH}_3\text{SO}_3]^-$ (Broker & Tiekink, 2007) salts for which similar ring structures have been reported. By contrast, in the $[\text{BF}_4]^-$ salt, characterized as an acetonitrile solvate, a polymeric structure is observed instead due to a rotation of one of the pyridine rings (Guo *et al.*, 2002); in this case, the 2-PA ligand is tetradentate forming two chelate rings.

The global crystal packing in (I) is based on the stacking of layers along the *c*-direction as illustrated in Fig. 2. Thus, the tosylate-O1 and O3 atoms connect dinuclear cations into layers in the *ab*-plane *via* C—H...O interactions (Table 2); the O2 atom accepts an intramolecular C—H...O contact exclusively. The primary interactions between layers appear to be of the type C—H... π , *i.e.* C17—H...Cg(N4, C8—C12) = 2.69 Å, with an angle at H17 of 133° for symmetry operation (1 - *x*, 1 - *y*, 1 - *z*).

Experimental

$[\text{Ag}(p\text{-tol})\text{SO}_3]$ (Aldrich, 0.05 g, 0.18 mmol) was dissolved in CH_3CN (20 ml) and layered on top of a CH_2Cl_2 solution (20 ml) containing (0.04 g, 0.18 mmol) of 2-pyridinealdazine (Aldrich). After three days, yellow prisms of (I) were observed at the interface between the two layers; m.p. 493–495 K.

Refinement

All the H atoms were included in the riding-model approximation, with C—H = 0.95–0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Figures

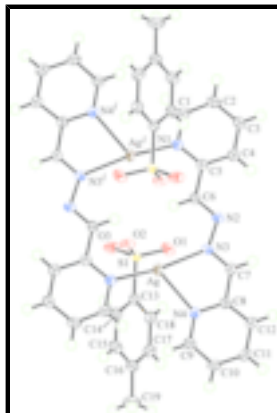


Fig. 1. Molecular structure of (I) showing atom-labelling scheme and displacement ellipsoids at the 70% probability level (arbitrary spheres for the H atoms). Primed atoms are generated by the symmetry operation $(-x, 1 - y, 2 - z)$.

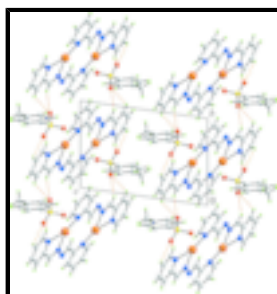


Fig. 2. View of the crystal packing in (I) down the a axis highlighting the layer arrangement. The C–H \cdots O interactions are shown as orange-dashed lines. Colour code: orange (silver), yellow (sulfur), red (oxygen), blue (nitrogen), grey (carbon) and green (hydrogen).

Bis(μ -pyridine-1-carbaldehyde azine- $\kappa^2N,N':\kappa N''$)disilver(I) bis(p -toluenesulfonate)

Crystal data

$[\text{Ag}_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_2](\text{C}_7\text{H}_7\text{SO}_3)_2$

$M_r = 978.61$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.9619(17)\ \text{\AA}$

$b = 9.4382(11)\ \text{\AA}$

$c = 13.468(3)\ \text{\AA}$

$\alpha = 78.12(3)^\circ$

$\beta = 76.75(3)^\circ$

$\gamma = 70.13(3)^\circ$

$V = 917.4(3)\ \text{\AA}^3$

$Z = 1$

$F_{000} = 492$

$D_x = 1.771\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71070\ \text{\AA}$

Cell parameters from 2621 reflections

$\theta = 2.6\text{--}30.2^\circ$

$\mu = 1.24\ \text{mm}^{-1}$

$T = 98(2)\ \text{K}$

Prism, yellow

$0.35 \times 0.10 \times 0.05\ \text{mm}$

Data collection

Rigaku/MSM AFC12 κ /SATURN724
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

3776 independent reflections

3713 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$T = 98(2)$ K	$\theta_{\max} = 26.5^\circ$
ω scans	$\theta_{\min} = 2.6^\circ$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -9 \rightarrow 9$
$T_{\min} = 0.715$, $T_{\max} = 1.000$	$k = -11 \rightarrow 11$
10013 measured reflections	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.020$	H-atom parameters constrained
$wR(F^2) = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 0.8243P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
3776 reflections	$(\Delta/\sigma)_{\max} = 0.005$
254 parameters	$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag	0.270539 (16)	0.533834 (14)	0.880628 (10)	0.01623 (5)
S1	0.11139 (5)	0.33155 (5)	0.76383 (3)	0.01453 (9)
O1	0.00032 (19)	0.46865 (17)	0.71172 (12)	0.0307 (3)
O2	0.12104 (17)	0.34521 (16)	0.86852 (10)	0.0209 (3)
O3	0.06566 (18)	0.19598 (16)	0.76129 (11)	0.0228 (3)
N1	-0.45024 (19)	0.65008 (17)	1.01938 (11)	0.0142 (3)
N2	-0.12641 (19)	0.81213 (17)	0.85496 (12)	0.0161 (3)
N3	0.06292 (19)	0.75793 (17)	0.82718 (11)	0.0143 (3)
N4	0.4262 (2)	0.67661 (17)	0.74678 (11)	0.0152 (3)
C1	-0.6304 (2)	0.6843 (2)	1.05199 (14)	0.0161 (3)
H1	-0.6753	0.6118	1.1009	0.019*
C2	-0.7532 (2)	0.8191 (2)	1.01822 (14)	0.0186 (4)

supplementary materials

H2	-0.8793	0.8389	1.0440	0.022*
C3	-0.6897 (2)	0.9254 (2)	0.94594 (14)	0.0187 (4)
H3	-0.7708	1.0198	0.9218	0.022*
C4	-0.5054 (2)	0.8904 (2)	0.91000 (14)	0.0167 (3)
H4	-0.4581	0.9597	0.8593	0.020*
C5	-0.3897 (2)	0.75296 (19)	0.94858 (13)	0.0134 (3)
C6	-0.1924 (2)	0.7123 (2)	0.91352 (13)	0.0139 (3)
H6	-0.1156	0.6136	0.9341	0.017*
C7	0.1246 (2)	0.8529 (2)	0.75909 (14)	0.0153 (3)
H7	0.0433	0.9466	0.7340	0.018*
C8	0.3194 (2)	0.8182 (2)	0.71959 (13)	0.0139 (3)
C9	0.6040 (2)	0.6460 (2)	0.71350 (14)	0.0166 (3)
H9	0.6807	0.5462	0.7316	0.020*
C10	0.6828 (2)	0.7538 (2)	0.65329 (14)	0.0182 (4)
H10	0.8106	0.7283	0.6322	0.022*
C11	0.5717 (2)	0.8983 (2)	0.62486 (14)	0.0179 (4)
H11	0.6218	0.9737	0.5837	0.021*
C12	0.3859 (2)	0.9314 (2)	0.65742 (14)	0.0166 (3)
H12	0.3060	1.0291	0.6377	0.020*
C13	0.3356 (2)	0.30503 (19)	0.69408 (13)	0.0138 (3)
C14	0.4828 (2)	0.2515 (2)	0.74534 (14)	0.0154 (3)
H14	0.4638	0.2270	0.8182	0.018*
C15	0.6573 (2)	0.2336 (2)	0.69066 (15)	0.0183 (4)
H15	0.7570	0.1982	0.7264	0.022*
C16	0.6874 (2)	0.2671 (2)	0.58368 (15)	0.0179 (4)
C17	0.5387 (3)	0.3178 (2)	0.53321 (14)	0.0193 (4)
H17	0.5576	0.3392	0.4602	0.023*
C18	0.3635 (2)	0.3377 (2)	0.58741 (14)	0.0167 (3)
H18	0.2636	0.3733	0.5518	0.020*
C19	0.8762 (3)	0.2497 (3)	0.52383 (17)	0.0287 (5)
H19A	0.9352	0.1436	0.5120	0.043*
H19B	0.9463	0.2783	0.5631	0.043*
H19C	0.8698	0.3158	0.4575	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag	0.01410 (8)	0.01331 (8)	0.01916 (8)	-0.00401 (5)	-0.00385 (5)	0.00307 (5)
S1	0.00972 (19)	0.0146 (2)	0.0176 (2)	-0.00285 (16)	-0.00073 (15)	-0.00194 (16)
O1	0.0153 (7)	0.0281 (8)	0.0343 (8)	0.0036 (6)	-0.0024 (6)	0.0073 (6)
O2	0.0184 (6)	0.0280 (7)	0.0188 (7)	-0.0117 (6)	0.0031 (5)	-0.0083 (5)
O3	0.0160 (6)	0.0270 (7)	0.0301 (7)	-0.0125 (6)	0.0026 (5)	-0.0111 (6)
N1	0.0123 (7)	0.0148 (7)	0.0153 (7)	-0.0042 (6)	-0.0028 (5)	-0.0009 (6)
N2	0.0095 (7)	0.0172 (7)	0.0188 (8)	-0.0025 (6)	-0.0006 (6)	-0.0011 (6)
N3	0.0096 (7)	0.0149 (7)	0.0166 (7)	-0.0026 (6)	-0.0010 (5)	-0.0019 (6)
N4	0.0133 (7)	0.0148 (7)	0.0160 (7)	-0.0043 (6)	-0.0016 (6)	-0.0001 (6)
C1	0.0143 (8)	0.0201 (9)	0.0146 (8)	-0.0078 (7)	-0.0014 (6)	-0.0006 (7)
C2	0.0118 (8)	0.0246 (10)	0.0184 (9)	-0.0048 (7)	-0.0016 (7)	-0.0032 (7)

C3	0.0146 (8)	0.0173 (9)	0.0204 (9)	-0.0008 (7)	-0.0040 (7)	-0.0008 (7)
C4	0.0158 (8)	0.0164 (9)	0.0163 (8)	-0.0047 (7)	-0.0024 (7)	0.0007 (7)
C5	0.0128 (8)	0.0151 (8)	0.0127 (8)	-0.0042 (6)	-0.0024 (6)	-0.0026 (6)
C6	0.0131 (8)	0.0137 (8)	0.0135 (8)	-0.0025 (6)	-0.0033 (6)	-0.0007 (6)
C7	0.0132 (8)	0.0127 (8)	0.0181 (8)	-0.0027 (6)	-0.0022 (6)	-0.0007 (7)
C8	0.0127 (8)	0.0136 (8)	0.0152 (8)	-0.0041 (6)	-0.0024 (6)	-0.0016 (6)
C9	0.0125 (8)	0.0181 (9)	0.0166 (8)	-0.0029 (7)	-0.0019 (6)	-0.0002 (7)
C10	0.0128 (8)	0.0248 (10)	0.0162 (8)	-0.0070 (7)	-0.0005 (7)	-0.0012 (7)
C11	0.0182 (9)	0.0190 (9)	0.0173 (9)	-0.0101 (7)	0.0005 (7)	-0.0009 (7)
C12	0.0171 (8)	0.0147 (8)	0.0160 (8)	-0.0046 (7)	-0.0010 (7)	-0.0002 (7)
C13	0.0118 (8)	0.0115 (8)	0.0179 (8)	-0.0043 (6)	-0.0013 (6)	-0.0016 (6)
C14	0.0155 (8)	0.0143 (8)	0.0157 (8)	-0.0036 (7)	-0.0022 (7)	-0.0031 (6)
C15	0.0133 (8)	0.0180 (9)	0.0247 (9)	-0.0036 (7)	-0.0047 (7)	-0.0059 (7)
C16	0.0146 (8)	0.0142 (8)	0.0244 (9)	-0.0056 (7)	0.0021 (7)	-0.0057 (7)
C17	0.0221 (9)	0.0190 (9)	0.0161 (9)	-0.0084 (7)	0.0006 (7)	-0.0016 (7)
C18	0.0169 (8)	0.0151 (8)	0.0181 (9)	-0.0052 (7)	-0.0042 (7)	-0.0006 (7)
C19	0.0155 (9)	0.0343 (12)	0.0331 (11)	-0.0091 (8)	0.0065 (8)	-0.0070 (9)

Geometric parameters (Å, °)

Ag—N1 ⁱ	2.2596 (17)	C6—H6	0.9500
Ag—N3	2.2948 (17)	C7—C8	1.464 (2)
Ag—N4	2.3900 (17)	C7—H7	0.9500
Ag—O2	2.5023 (14)	C8—C12	1.391 (2)
S1—O1	1.4428 (15)	C9—C10	1.396 (3)
S1—O3	1.4530 (14)	C9—H9	0.9500
S1—O2	1.4636 (14)	C10—C11	1.382 (3)
S1—C13	1.7768 (18)	C10—H10	0.9500
N1—C1	1.345 (2)	C11—C12	1.387 (3)
N1—C5	1.346 (2)	C11—H11	0.9500
N1—Ag ⁱ	2.2596 (17)	C12—H12	0.9500
N2—C6	1.275 (2)	C13—C18	1.388 (3)
N2—N3	1.404 (2)	C13—C14	1.389 (2)
N3—C7	1.280 (2)	C14—C15	1.387 (3)
N4—C9	1.332 (2)	C14—H14	0.9500
N4—C8	1.346 (2)	C15—C16	1.392 (3)
C1—C2	1.379 (3)	C15—H15	0.9500
C1—H1	0.9500	C16—C17	1.394 (3)
C2—C3	1.388 (3)	C16—C19	1.506 (3)
C2—H2	0.9500	C17—C18	1.387 (3)
C3—C4	1.381 (3)	C17—H17	0.9500
C3—H3	0.9500	C18—H18	0.9500
C4—C5	1.389 (3)	C19—H19A	0.9800
C4—H4	0.9500	C19—H19B	0.9800
C5—C6	1.470 (2)	C19—H19C	0.9800
N1 ⁱ —Ag—N3	161.06 (6)	N3—C7—H7	119.8
N1 ⁱ —Ag—N4	114.74 (6)	C8—C7—H7	119.8
N3—Ag—N4	71.65 (6)	N4—C8—C12	123.14 (16)

supplementary materials

N1 ⁱ —Ag—O2	88.50 (5)	N4—C8—C7	117.51 (15)
N3—Ag—O2	100.89 (5)	C12—C8—C7	119.34 (16)
N4—Ag—O2	129.62 (5)	N4—C9—C10	123.02 (17)
O1—S1—O3	113.74 (9)	N4—C9—H9	118.5
O1—S1—O2	113.34 (10)	C10—C9—H9	118.5
O3—S1—O2	111.55 (9)	C11—C10—C9	118.79 (16)
O1—S1—C13	105.70 (9)	C11—C10—H10	120.6
O3—S1—C13	106.41 (8)	C9—C10—H10	120.6
O2—S1—C13	105.28 (8)	C10—C11—C12	118.95 (17)
S1—O2—Ag	115.18 (8)	C10—C11—H11	120.5
C1—N1—C5	117.32 (15)	C12—C11—H11	120.5
C1—N1—Ag ⁱ	117.09 (12)	C11—C12—C8	118.39 (17)
C5—N1—Ag ⁱ	122.77 (11)	C11—C12—H12	120.8
C6—N2—N3	112.67 (15)	C8—C12—H12	120.8
C7—N3—N2	111.79 (15)	C18—C13—C14	119.87 (16)
C7—N3—Ag	116.87 (12)	C18—C13—S1	119.54 (14)
N2—N3—Ag	131.33 (11)	C14—C13—S1	120.59 (14)
C9—N4—C8	117.66 (15)	C15—C14—C13	120.36 (17)
C9—N4—Ag	128.25 (12)	C15—C14—H14	119.8
C8—N4—Ag	112.49 (11)	C13—C14—H14	119.8
N1—C1—C2	123.45 (17)	C14—C15—C16	120.44 (17)
N1—C1—H1	118.3	C14—C15—H15	119.8
C2—C1—H1	118.3	C16—C15—H15	119.8
C1—C2—C3	118.92 (17)	C15—C16—C17	118.51 (17)
C1—C2—H2	120.5	C15—C16—C19	120.79 (18)
C3—C2—H2	120.5	C17—C16—C19	120.70 (18)
C4—C3—C2	118.26 (17)	C18—C17—C16	121.39 (17)
C4—C3—H3	120.9	C18—C17—H17	119.3
C2—C3—H3	120.9	C16—C17—H17	119.3
C3—C4—C5	119.54 (17)	C17—C18—C13	119.41 (17)
C3—C4—H4	120.2	C17—C18—H18	120.3
C5—C4—H4	120.2	C13—C18—H18	120.3
N1—C5—C4	122.48 (16)	C16—C19—H19A	109.5
N1—C5—C6	116.29 (15)	C16—C19—H19B	109.5
C4—C5—C6	121.23 (16)	H19A—C19—H19B	109.5
N2—C6—C5	118.72 (16)	C16—C19—H19C	109.5
N2—C6—H6	120.6	H19A—C19—H19C	109.5
C5—C6—H6	120.6	H19B—C19—H19C	109.5
N3—C7—C8	120.49 (16)		
O1—S1—O2—Ag	-64.41 (10)	C4—C5—C6—N2	7.4 (3)
O3—S1—O2—Ag	165.65 (7)	N2—N3—C7—C8	179.92 (15)
C13—S1—O2—Ag	50.64 (10)	Ag—N3—C7—C8	-0.9 (2)
N1 ⁱ —Ag—O2—S1	-128.37 (9)	C9—N4—C8—C12	1.2 (3)
N3—Ag—O2—S1	68.20 (9)	Ag—N4—C8—C12	168.05 (14)
N4—Ag—O2—S1	-6.91 (11)	C9—N4—C8—C7	-178.06 (16)
C6—N2—N3—C7	172.35 (16)	Ag—N4—C8—C7	-11.25 (19)
C6—N2—N3—Ag	-6.7 (2)	N3—C7—C8—N4	8.7 (3)
N1 ⁱ —Ag—N3—C7	109.39 (19)	N3—C7—C8—C12	-170.59 (17)

N4—Ag—N3—C7	-3.67 (13)	C8—N4—C9—C10	0.6 (3)
O2—Ag—N3—C7	-132.02 (13)	Ag—N4—C9—C10	-163.79 (14)
N1 ⁱ —Ag—N3—N2	-71.6 (2)	N4—C9—C10—C11	-1.4 (3)
N4—Ag—N3—N2	175.35 (16)	C9—C10—C11—C12	0.3 (3)
O2—Ag—N3—N2	47.01 (15)	C10—C11—C12—C8	1.5 (3)
N1 ⁱ —Ag—N4—C9	12.19 (17)	N4—C8—C12—C11	-2.3 (3)
N3—Ag—N4—C9	172.99 (16)	C7—C8—C12—C11	176.99 (16)
O2—Ag—N4—C9	-97.93 (16)	O1—S1—C13—C18	-38.59 (17)
N1 ⁱ —Ag—N4—C8	-152.90 (11)	O3—S1—C13—C18	82.66 (16)
N3—Ag—N4—C8	7.90 (11)	O2—S1—C13—C18	-158.82 (14)
O2—Ag—N4—C8	96.97 (13)	O1—S1—C13—C14	141.67 (15)
C5—N1—C1—C2	-1.3 (3)	O3—S1—C13—C14	-97.07 (16)
Ag ⁱ —N1—C1—C2	160.20 (14)	O2—S1—C13—C14	21.44 (17)
N1—C1—C2—C3	0.7 (3)	C18—C13—C14—C15	1.4 (3)
C1—C2—C3—C4	0.8 (3)	S1—C13—C14—C15	-178.83 (14)
C2—C3—C4—C5	-1.6 (3)	C13—C14—C15—C16	-0.9 (3)
C1—N1—C5—C4	0.5 (3)	C14—C15—C16—C17	-0.4 (3)
Ag ⁱ —N1—C5—C4	-159.94 (13)	C14—C15—C16—C19	179.30 (18)
C1—N1—C5—C6	-179.49 (15)	C15—C16—C17—C18	1.2 (3)
Ag ⁱ —N1—C5—C6	20.1 (2)	C19—C16—C17—C18	-178.54 (18)
C3—C4—C5—N1	1.0 (3)	C16—C17—C18—C13	-0.6 (3)
C3—C4—C5—C6	-179.05 (17)	C14—C13—C18—C17	-0.7 (3)
N3—N2—C6—C5	-179.77 (14)	S1—C13—C18—C17	179.58 (14)
N1—C5—C6—N2	-172.63 (16)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C9—H9 \cdots O1 ⁱⁱ	0.95	2.36	3.025 (2)	126
C10—H10 \cdots O1 ⁱⁱ	0.95	2.56	3.109 (2)	117
C14—H14 \cdots O2	0.95	2.56	2.918 (2)	103
C7—H7 \cdots O3 ⁱⁱⁱ	0.95	2.53	3.116 (2)	120
C12—H12 \cdots O3 ⁱⁱⁱ	0.95	2.55	3.189 (2)	125
C15—H15 \cdots O3 ⁱⁱ	0.95	2.60	3.478 (2)	154

Symmetry codes: (ii) $x+1, y, z$; (iii) $x, y+1, z$.

Fig. 1

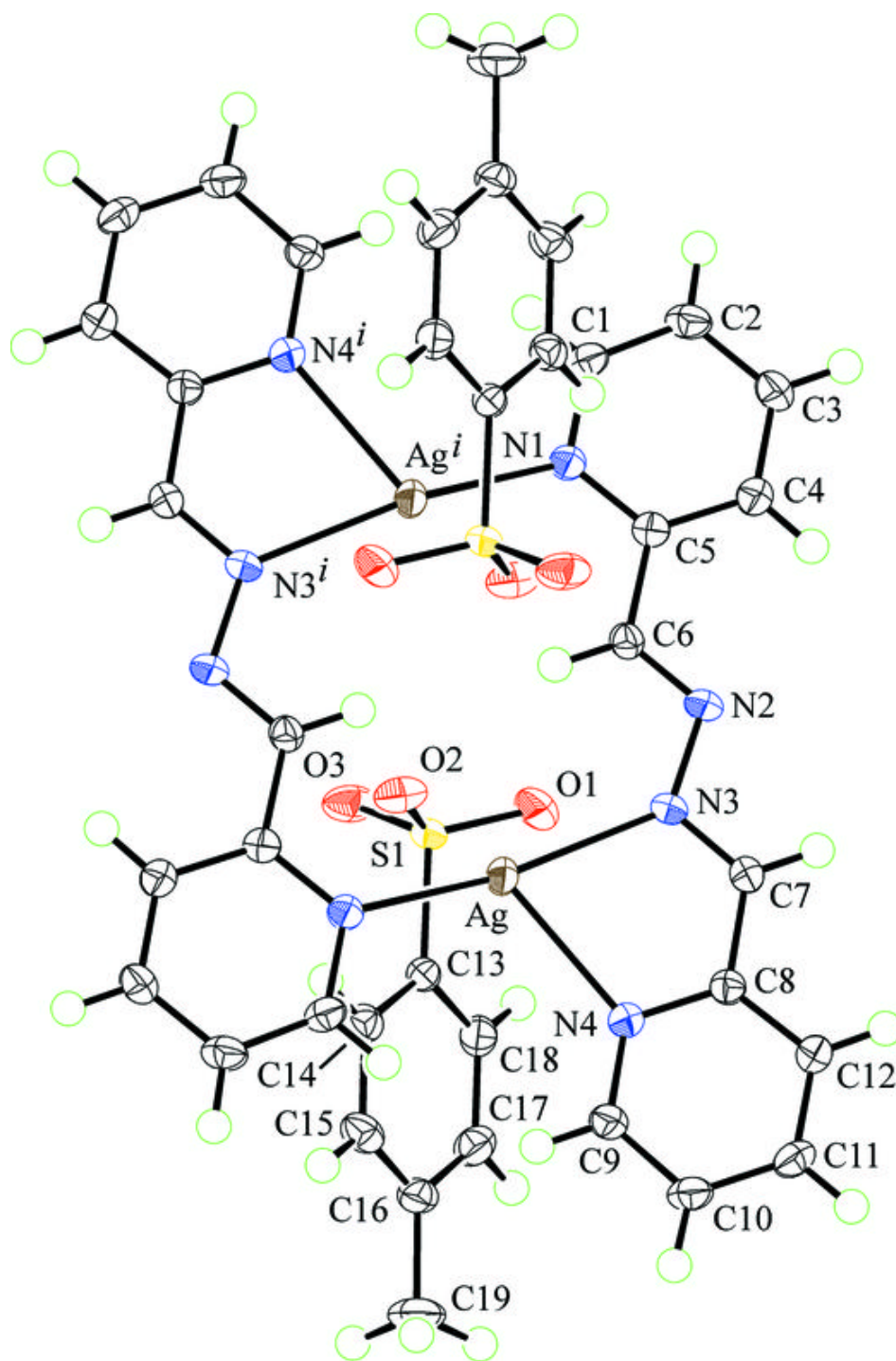


Fig. 2

