Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Serendipitous Anion-Templated Self-assembly of a Sandwich-like $Ag_{20}S_{10}$ Macrocycle-based High-nuclearity Luminescent Nanocluster

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1. Synthetic procedures

General comments: AgS^tBu was prepared by using Et_3N as organic solvent and reacted with equivalent amounts of $AgNO_3$ with HS^tBu according to the literature.[1] In addition, $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ ($\{P_2W_{15}\}$) was synthesized according to the literature.[2] Other reagents and solvents for synthesis were obtained from commercial sources and used without further purification.

$\{[Ag_{20}(S^tBu)_{10}(CF_3COO)_2]Cl\cdot(CF_3COO)_7\cdot 5CH_3OH\}$ (1):

AgS^tBu (0.0598 g, 0.3035 mmol) was dissolved in methanol (20 mL) under stir at 50 ℃. CF_3COOH (0.1 mL) and Et_3N (0.3 mL) were in turn added to the above solution with stir, and then $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ ($\{P_2W_{15}\}$) (0.0410 g, 0.0093 mmol) and NaCl (0.0009 g, 0.0154 mmol) were added to the mixture after several minutes. The gray-violet suspension was stirred at room temperature for 5d and then was filtered. The filtrate was evaporated slowly in air at room temperature. Complex **1** was deposited as colourless block crystals. Yield: ca. 21% (based on Ag). Elemental analysis (%) calcd for $C_{63}H_{110}Ag_{20}F_{27}O_{23}S_{10}Cl_1$: C, 17.75; H, 2.60; S, 7.52; Ag, 50.62. Found: C, 17.83; H, 2.51; S, 7.47; Ag, 50.58.

2. Crystallographic studies

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at 293(2) K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. The structure of complex **1** was solved by direct methods and refined on F^2 by full-matrix least squares methods using the SHELXTL package.[3]

Crystal data for **1**: $C_{63}H_{110}Ag_{20}F_{27}O_{23}S_{10}Cl_1$; *C2/c*; *a* = 16.612(3) Å, *b* = 26.014(4) Å, *c* = 26.372(4) Å; *β* = 91.580(2)°; *V* = 11392(3) Å^3; Z = 4; 19314 reflns measured, 5954 unique (R_{int} = 0.0859); final R_1 = 0.0760, wR_2 = 0.1900 for 2957 observed reflections [$I > 2\sigma(I)$]. CCDC–880351 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif for **1**.

Discrete solvent molecules, such as CF_3COO^- and CH_3OH molecules in complex **1** could not been confirmed by single-crystal X-ray diffraction analysis, so that SQUEEZE is successfully used to identify the type and number of molecules in these large and poorly defined solvent voids by these areas of electron density. Finaly, we deduce the molecular formula of complex **1** is $[Ag_{20}(S^tBu)_{10}(CF_3COO)_2]Cl\cdot(CF_3COO)_7\cdot5CH_3OH$.

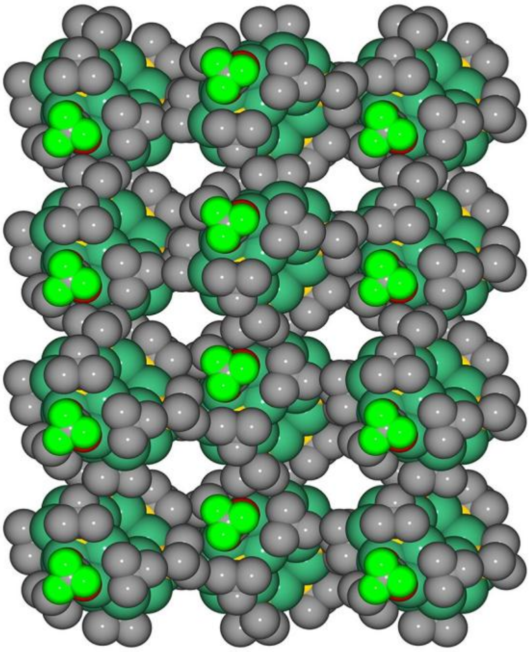

Fig. S1 Space-filling viewed of **1**. Hydrogen atoms and solvent molecules are omitted for clarity. Color code: Ag, sea green; C, gray-50%; S, gold; O, red; F, bright green.

3. Physical Measurements

Luminescence was measured on an F-7000 FL Spectrophotometer. NMR data were recorded on a Bruker AV spectrometer (500 MHz). Elemental analyses (C, H, and S) were performed on an Elementar Vario EL III elemental analyzer. Ag was analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. The UV-vis-NIR absorption spectroscopy was measured with a U-3010 Spectrophotometer.

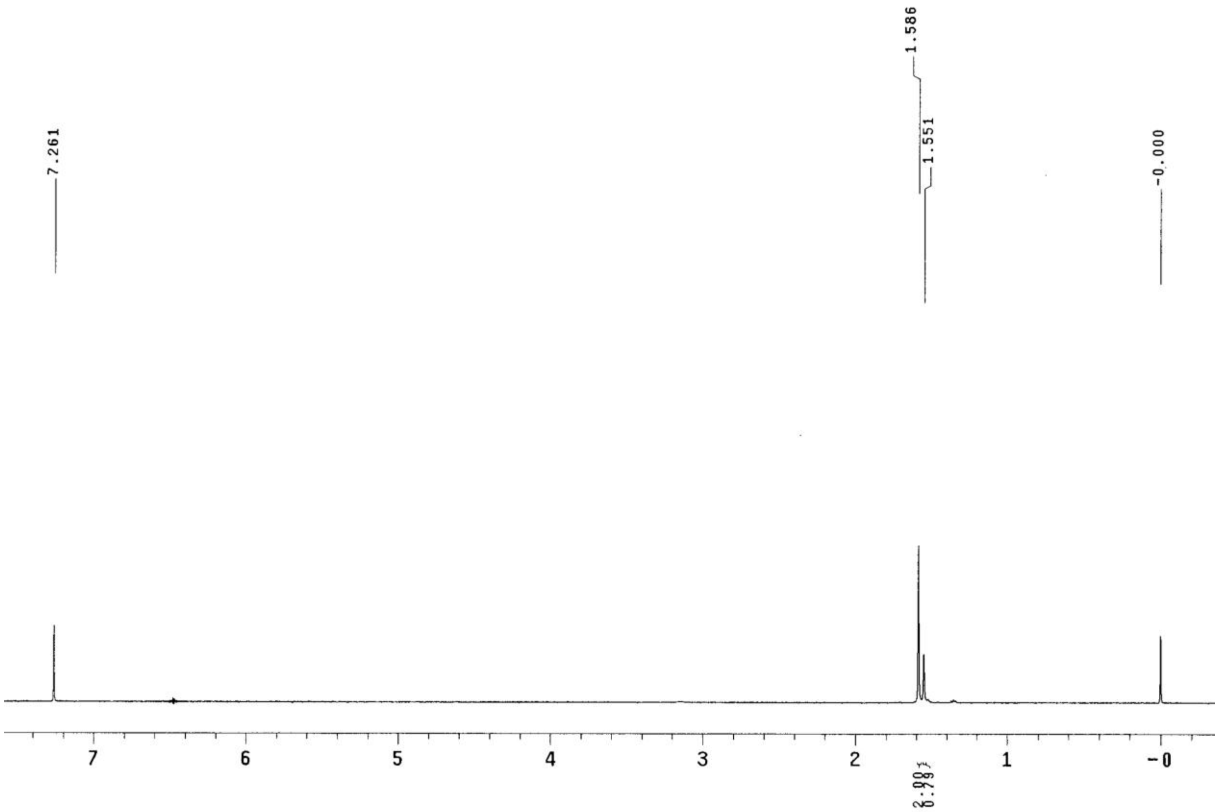

Fig. S2 The ^{1}H NMR spectrum of AgS^{t}Bu ligand (500MHz, $CDCl_3$, RT).

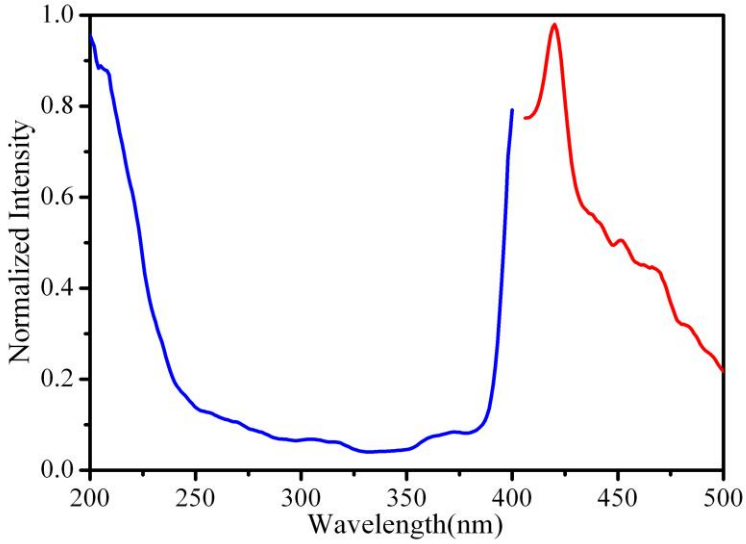

Fig. S3 Excitation (blue trace) and emission spectra (red trace) of AgS^{t}Bu ligand in CH_3OH solution.

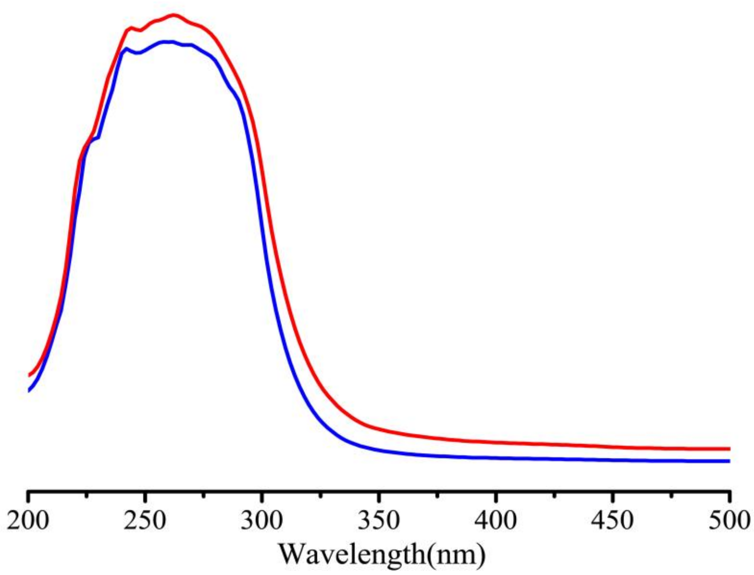

Fig. S4 Electronic absorption spectrum (blue trace) of **1** in CH_3OH solution and electronic absorption spectrum (red trace) of **1** in CH_3OH solution after being stored for about six months.

Table S1 Selected bond lengths (Å) and bond angles (º) for compound **1**

O(1)-Ag(1)	2.25(2)	O(1)-Ag(1)-Ag(2)	102.3(5)
O(2)-Ag(7)	2.273(19)	S(1)-Ag(1)-Ag(2)	93.04(14)
Ag(1)-S(1)	2.524(6)	S(5)#1-Ag(1)-Ag(2)	50.31(14)
Ag(1)-S(5)#1	2.538(6)	Ag(7)-Ag(1)-Ag(2)	63.02(6)
Ag(1)-Ag(7)	3.024(3)	O(1)-Ag(1)-Ag(4)#1	132.0(5)
Ag(1)-Ag(2)	3.132(3)	S(1)-Ag(1)-Ag(4)#1	110.32(16)
Ag(1)-Ag(4)#1	3.143(3)	S(5)#1-Ag(1)-Ag(4)#1	51.71(15)
Ag(1)-Ag(8)	3.209(3)	Ag(7)-Ag(1)-Ag(4)#1	147.77(9)
Ag(2)-S(2)	2.463(7)	Ag(2)-Ag(1)-Ag(4)#1	94.22(7)
Ag(2)-S(5)#1	2.469(6)	O(1)-Ag(1)-Ag(8)	159.2(5)
Ag(2)-Ag(7)	3.219(3)	S(1)-Ag(1)-Ag(8)	48.26(15)
Ag(2)-Ag(5)#1	3.248(3)	S(5)#1-Ag(1)-Ag(8)	91.46(15)
Ag(2)-Ag(3)	3.344(3)	Ag(7)-Ag(1)-Ag(8)	93.06(8)
Ag(3)-S(2)	2.473(6)	Ag(2)-Ag(1)-Ag(8)	89.65(7)
Ag(3)-S(4)	2.503(7)	Ag(4)#1-Ag(1)-Ag(8)	62.59(7)
Ag(3)-Ag(9)	3.135(5)	S(2)-Ag(2)-S(5)#1	157.8(2)
Ag(3)-Ag(10)	3.182(4)	S(2)-Ag(2)-Ag(1)	107.01(16)
Ag(4)-S(5)	2.537(7)	S(5)#1-Ag(2)-Ag(1)	52.28(14)
Ag(4)-S(4)	2.541(8)	S(2)-Ag(2)-Ag(7)	50.27(15)
Ag(4)-Ag(9)	3.052(3)	S(5)#1-Ag(2)-Ag(7)	108.93(15)
Ag(4)-Ag(1)#1	3.143(3)	Ag(1)-Ag(2)-Ag(7)	56.85(6)
Ag(4)-Ag(8)#1	3.300(4)	S(2)-Ag(2)-Ag(5)#1	152.04(16)
Ag(5)-S(5)	2.442(6)	S(5)#1-Ag(2)-Ag(5)#1	48.24(14)
Ag(5)-S(3)	2.465(7)	Ag(1)-Ag(2)-Ag(5)#1	91.36(8)
Ag(5)-Ag(9)	3.122(5)	Ag(7)-Ag(2)-Ag(5)#1	140.60(10)
Ag(5)-Ag(2)#1	3.248(3)	S(2)-Ag(2)-Ag(3)	47.48(14)
Ag(5)-Ag(6)	3.340(3)	S(5)#1-Ag(2)-Ag(3)	152.65(17)
Ag(6)-S(3)	2.419(7)	Ag(1)-Ag(2)-Ag(3)	137.98(9)
Ag(6)-S(1)	2.440(6)	Ag(7)-Ag(2)-Ag(3)	88.97(8)
Ag(6)-Ag(10)	3.214(4)	Ag(5)#1-Ag(2)-Ag(3)	104.98(8)
Ag(6)-Ag(8)	3.277(3)	S(2)-Ag(3)-S(4)	155.1(3)
Ag(6)-Ag(7)	3.285(4)	S(2)-Ag(3)-Ag(9)	107.2(2)
Ag(7)-S(2)	2.508(6)	S(4)-Ag(3)-Ag(9)	50.2(2)
Ag(7)-S(1)	2.520(7)	S(2)-Ag(3)-Ag(10)	49.88(18)
Ag(7)-Ag(10)	3.149(3)	S(4)-Ag(3)-Ag(10)	106.9(2)
Ag(8)-S(4)#1	2.425(8)	Ag(9)-Ag(3)-Ag(10)	57.35(8)
Ag(8)-S(1)	2.425(6)	S(2)-Ag(3)-Ag(2)	47.23(15)
Ag(8)-Ag(4)#1	3.300(4)	S(4)-Ag(3)-Ag(2)	154.81(18)
Ag(9)-S(4)	2.458(9)	Ag(9)-Ag(3)-Ag(2)	135.32(10)
Ag(9)-S(3)	2.484(8)	Ag(10)-Ag(3)-Ag(2)	87.50(7)
Ag(9)-Ag(10)	3.032(3)	S(5)-Ag(4)-S(4)	121.6(2)
Ag(10)-S(2)	2.470(8)	S(5)-Ag(4)-Ag(9)	102.17(16)
Ag(10)-S(3)	2.520(9)	S(4)-Ag(4)-Ag(9)	51.16(19)
S(4)-Ag(8)#1	2.425(8)	S(5)-Ag(4)-Ag(1)#1	51.76(14)
S(5)-Ag(2)#1	2.469(6)	S(4)-Ag(4)-Ag(1)#1	106.54(19)
S(5)-Ag(1)#1	2.538(6)	Ag(9)-Ag(4)-Ag(1)#1	134.66(9)
C(21)-O(1)-Ag(1)	128.3(16)	S(5)-Ag(4)-Ag(8)#1	89.41(14)
C(21)-O(2)-Ag(7)	121.0(13)	S(4)-Ag(4)-Ag(8)#1	46.87(18)
O(1)-Ag(1)-S(1)	113.3(5)	Ag(9)-Ag(4)-Ag(8)#1	87.79(10)
O(1)-Ag(1)-S(5)#1	109.3(5)	Ag(1)#1-Ag(4)-Ag(8)#1	59.68(7)
S(1)-Ag(1)-S(5)#1	128.72(19)	S(5)-Ag(5)-S(3)	151.1(3)
O(1)-Ag(1)-Ag(7)	77.8(5)	S(5)-Ag(5)-Ag(9)	102.49(18)
S(1)-Ag(1)-Ag(7)	53.11(15)	S(3)-Ag(5)-Ag(9)	51.2(2)
S(5)#1-Ag(1)-Ag(7)	113.11(15)	S(5)-Ag(5)-Ag(2)#1	48.96(15)

S(3)-Ag(5)-Ag(2)#1	156.24(17)
Ag(9)-Ag(5)-Ag(2)#1	132.98(10)
S(5)-Ag(5)-Ag(6)	158.71(16)
S(3)-Ag(5)-Ag(6)	46.26(16)
Ag(9)-Ag(5)-Ag(6)	86.45(9)
Ag(2)#1-Ag(5)-Ag(6)	111.19(9)
S(3)-Ag(6)-S(1)	155.8(3)
S(3)-Ag(6)-Ag(10)	50.8(2)
S(1)-Ag(6)-Ag(10)	107.37(19)
S(3)-Ag(6)-Ag(8)	154.51(18)
S(1)-Ag(6)-Ag(8)	47.48(15)
Ag(10)-Ag(6)-Ag(8)	136.70(11)
S(3)-Ag(6)-Ag(7)	108.4(2)
S(1)-Ag(6)-Ag(7)	49.57(16)
Ag(10)-Ag(6)-Ag(7)	57.95(8)
Ag(8)-Ag(6)-Ag(7)	87.19(8)
S(3)-Ag(6)-Ag(5)	47.43(17)
S(1)-Ag(6)-Ag(5)	154.69(18)
Ag(10)-Ag(6)-Ag(5)	87.90(9)
Ag(8)-Ag(6)-Ag(5)	107.74(10)
Ag(7)-Ag(6)-Ag(5)	138.67(11)
O(2)-Ag(7)-S(2)	112.1(5)
O(2)-Ag(7)-S(1)	113.9(5)
S(2)-Ag(7)-S(1)	125.5(2)
O(2)-Ag(7)-Ag(1)	81.1(5)
S(2)-Ag(7)-Ag(1)	109.07(17)
S(1)-Ag(7)-Ag(1)	53.22(15)
O(2)-Ag(7)-Ag(10)	135.1(5)
S(2)-Ag(7)-Ag(10)	50.22(17)
S(1)-Ag(7)-Ag(10)	107.22(16)
Ag(1)-Ag(7)-Ag(10)	140.64(9)
O(2)-Ag(7)-Ag(2)	105.6(4)
S(2)-Ag(7)-Ag(2)	49.05(15)
S(1)-Ag(7)-Ag(2)	91.07(15)
Ag(1)-Ag(7)-Ag(2)	60.13(6)
Ag(10)-Ag(7)-Ag(2)	90.31(7)
O(2)-Ag(7)-Ag(6)	158.2(5)
S(2)-Ag(7)-Ag(6)	89.69(16)
S(1)-Ag(7)-Ag(6)	47.47(14)
Ag(1)-Ag(7)-Ag(6)	91.39(8)
Ag(10)-Ag(7)-Ag(6)	59.89(8)
Ag(2)-Ag(7)-Ag(6)	87.86(7)
S(4)#1-Ag(8)-S(1)	156.7(3)
S(4)#1-Ag(8)-Ag(1)	107.6(2)
S(1)-Ag(8)-Ag(1)	50.93(16)
S(4)#1-Ag(8)-Ag(6)	152.92(18)
S(1)-Ag(8)-Ag(6)	47.85(15)
Ag(1)-Ag(8)-Ag(6)	88.33(8)
S(4)#1-Ag(8)-Ag(4)#1	49.9(2)
S(1)-Ag(8)-Ag(4)#1	108.14(18)
Ag(1)-Ag(8)-Ag(4)#1	57.73(7)
Ag(6)-Ag(8)-Ag(4)#1	139.46(10)
S(4)-Ag(9)-S(3)	135.6(2)
S(4)-Ag(9)-Ag(10)	112.9(2)
S(3)-Ag(9)-Ag(10)	53.26(19)
S(4)-Ag(9)-Ag(4)	53.63(19)
S(3)-Ag(9)-Ag(4)	117.6(2)
Ag(10)-Ag(9)-Ag(4)	153.95(11)
S(4)-Ag(9)-Ag(5)	97.58(18)
S(3)-Ag(9)-Ag(5)	50.62(19)
Ag(10)-Ag(9)-Ag(5)	95.34(10)
Ag(4)-Ag(9)-Ag(5)	67.76(9)
S(4)-Ag(9)-Ag(3)	51.45(18)
S(3)-Ag(9)-Ag(3)	95.52(16)
Ag(10)-Ag(9)-Ag(3)	62.11(9)
Ag(4)-Ag(9)-Ag(3)	98.21(10)
Ag(5)-Ag(9)-Ag(3)	94.21(9)
S(2)-Ag(10)-S(3)	128.9(2)
S(2)-Ag(10)-Ag(9)	110.48(17)
S(3)-Ag(10)-Ag(9)	52.17(18)
S(2)-Ag(10)-Ag(7)	51.30(14)
S(3)-Ag(10)-Ag(7)	109.81(19)
Ag(9)-Ag(10)-Ag(7)	142.79(10)
S(2)-Ag(10)-Ag(3)	49.97(15)
S(3)-Ag(10)-Ag(3)	93.64(15)
Ag(9)-Ag(10)-Ag(3)	60.55(9)
Ag(7)-Ag(10)-Ag(3)	93.18(8)
S(2)-Ag(10)-Ag(6)	92.03(16)
S(3)-Ag(10)-Ag(6)	48.03(17)
Ag(9)-Ag(10)-Ag(6)	90.27(10)
Ag(7)-Ag(10)-Ag(6)	62.16(8)
Ag(3)-Ag(10)-Ag(6)	90.41(8)
C(1)-S(1)-Ag(8)	115.2(6)
C(1)-S(1)-Ag(6)	114.8(6)
Ag(8)-S(1)-Ag(6)	84.7(2)
C(1)-S(1)-Ag(7)	111.7(6)
Ag(8)-S(1)-Ag(7)	132.4(2)
Ag(6)-S(1)-Ag(7)	83.0(2)
C(1)-S(1)-Ag(1)	113.6(6)
Ag(8)-S(1)-Ag(1)	80.8(2)
Ag(6)-S(1)-Ag(1)	131.1(2)
Ag(7)-S(1)-Ag(1)	73.67(18)
C(5)-S(2)-Ag(2)	113.4(6)
C(5)-S(2)-Ag(10)	113.8(6)
Ag(2)-S(2)-Ag(10)	132.5(3)
C(5)-S(2)-Ag(3)	114.6(6)
Ag(2)-S(2)-Ag(3)	85.3(2)
Ag(10)-S(2)-Ag(3)	80.1(2)
C(5)-S(2)-Ag(7)	110.3(6)
Ag(2)-S(2)-Ag(7)	80.68(18)
Ag(10)-S(2)-Ag(7)	78.5(2)
Ag(3)-S(2)-Ag(7)	134.8(3)
C(9)-S(3)-Ag(6)	111.6(5)
C(9)-S(3)-Ag(5)	112.7(5)
Ag(6)-S(3)-Ag(5)	86.3(2)
C(9)-S(3)-Ag(9)	119.1(5)
Ag(6)-S(3)-Ag(9)	129.2(3)
Ag(5)-S(3)-Ag(9)	78.2(2)
C(9)-S(3)-Ag(10)	115.3(5)
Ag(6)-S(3)-Ag(10)	81.2(2)
Ag(5)-S(3)-Ag(10)	131.7(3)
Ag(9)-S(3)-Ag(10)	74.6(3)

C(13)-S(4)-Ag(8)#1	109.1(6)	C(17)-S(5)-Ag(5)	111.4(6)
C(13)-S(4)-Ag(9)	121.9(6)	C(17)-S(5)-Ag(2)#1	115.1(6)
Ag(8)#1-S(4)-Ag(9)	129.0(3)	Ag(5)-S(5)-Ag(2)#1	82.80(19)
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Ag(8)#1-S(4)-Ag(3)	86.8(2)	Ag(5)-S(5)-Ag(4)	87.5(2)
Ag(9)-S(4)-Ag(3)	78.4(2)	Ag(2)#1-S(5)-Ag(4)	133.4(2)
C(13)-S(4)-Ag(4)	113.1(6)	C(17)-S(5)-Ag(1)#1	115.8(6)
Ag(8)#1-S(4)-Ag(4)	83.2(2)	Ag(5)-S(5)-Ag(1)#1	132.9(2)
Ag(9)-S(4)-Ag(4)	75.2(3)	Ag(2)#1-S(5)-Ag(1)#1	77.41(17)
Ag(3)-S(4)-Ag(4)	136.0(3)	Ag(4)-S(5)-Ag(1)#1	76.53(18)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+1/2,-z+1

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3 (*a*) G. M. Sheldrick, *SHELX-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97*, *Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997.