Supporting Information

Anion-templated silver thiolated clusters effected by carboxylate ligands

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Contents

X-ray crystallography

Single crystal X-ray data of **1-3** were collected on a Bruker D8 Quest diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Data processing, absorption correction, integration and reduction were performed by multi-scan method and implemented in software Bruker APEX3 v2017.3-0. Space groups were determined using XPREP implemented in APEX3. The structures were further solved with the direct method and refined by full-matrix least-squares techniques against Fo^2 using the SHELXL program[1] through the OLEX2 interface.[2] It was found that the solvent molecules in the crystal lattice were disordered, which were removed using solvent

mask command with OLEX2 program.[2] Appropriate restraints and constraints were applied to the geometric shape and atomic displacement parameters of the atoms in the cluster. The ADDSYM subroutine of PLATON[3] was used to check all structures to ensure that no additional symmetry could be applied to the model.

Crystallographic data parameters of **1-3** are given in Tables S1-S3.

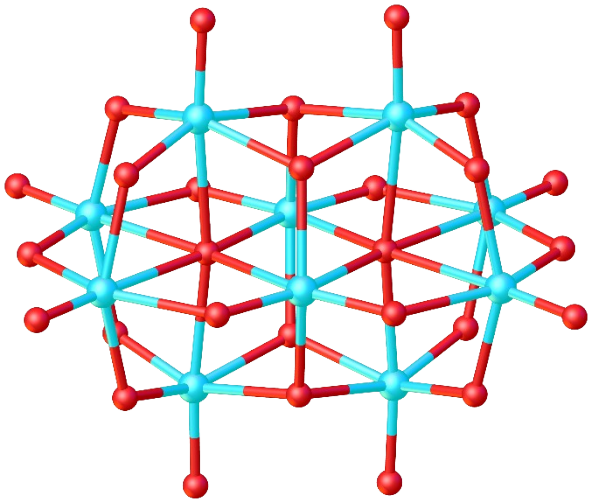

Fig. S1 The structure of $V_{10}O_{28}^{6-}$ anion template.

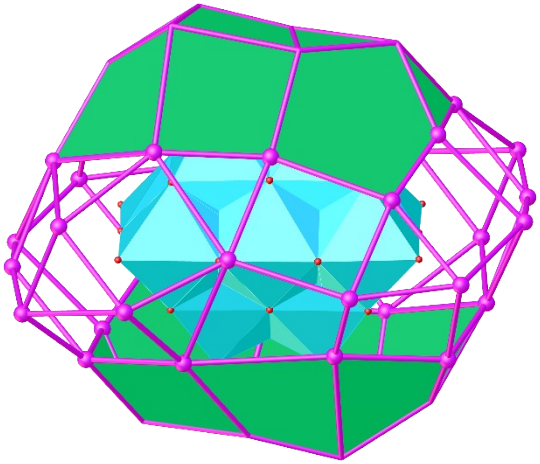

Fig. S2 The formation of **2** by covering two boat-shaped Ag_{16} on the tire-shaped Ag_{34} and wrapping $V_{10}O_{28}^{6-}$ inside.

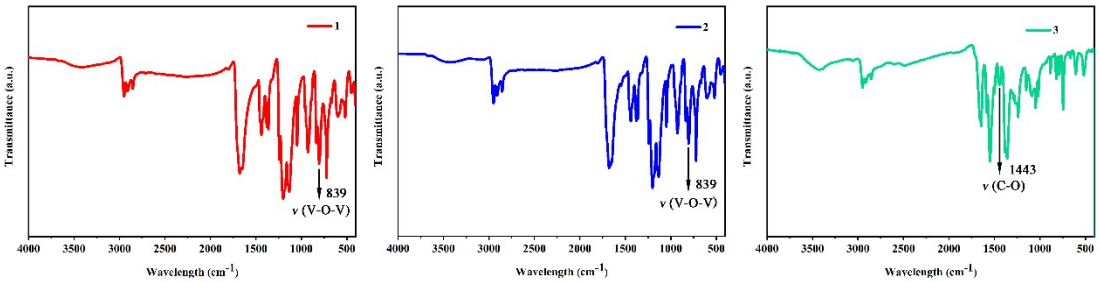

Fig. S3 The FT-IR spectra of **1**-**3**.

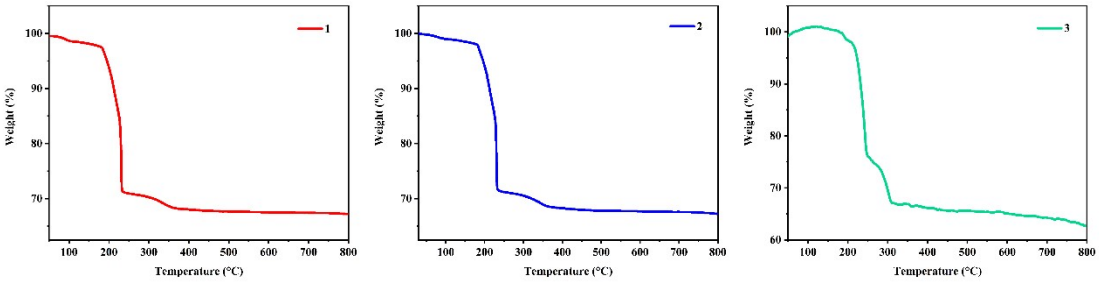

Fig. S4 The TG analysis of **1** and **2** (carried out in nitrogen atmospheres).

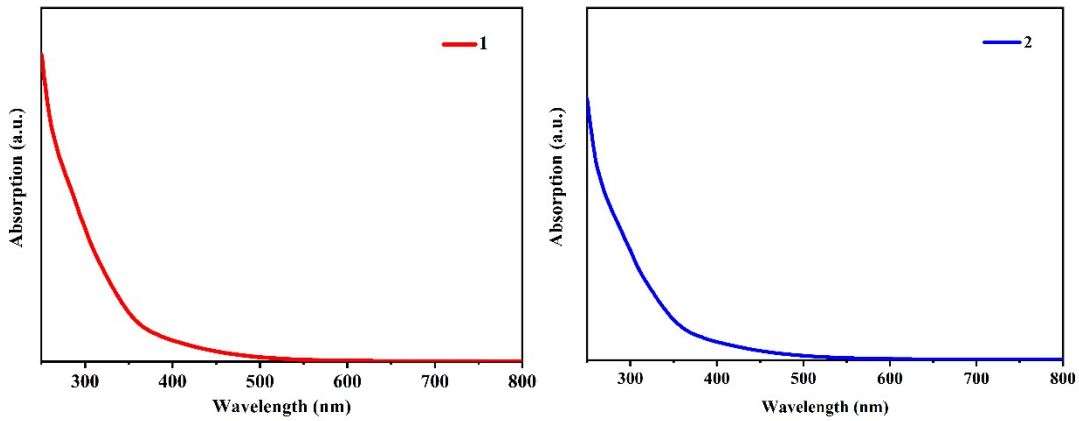

Fig. S5 The UV-vis spectra of **1** and **2** (dissolved in CH_2Cl_2).

Table S1. Crystal data and structure refinement for **1**

Codes	**1**
Formula	$C_{114}H_{210}Ag_{46}F_{36}N_2O_{54}S_{28}V_{10}$
F_w	9525.93
Temperature/K	305.3
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.1391(7)
b/Å	39.1409(16)

c/Å	18.9060(9)
α/°	90
β/°	114.1710(10)
γ/°	90
Volume/Å^3	12246.1(9)
Z	2
ρ_{calc}g/cm^3	2.583
μ/mm^{-1}	4.262
F(000)	9008.0
λ/Å	MoKα (λ = 0.71073)
Independent reflections	R_{int} = 0.0695, R_{sigma} = 0.0810
GOF on F^2	1.022
R_1[a][I > 2σ(I)]	R_1 = 0.0896, wR_2 = 0.2222
wR_2[b](all data)	R_1 = 0.1568, wR_2 = 0.2577

Table S2. Crystal data and structure refinement for **2**

Codes	**2**
Formula	$C_{132}H_{248}Ag_{46}F_{24}N_4O_{52}S_{30}V_{10}$
F_w	9612.55
Temperature/K	298.2
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	20.0954(6)
b/Å	28.1776(9)
c/Å	22.1646(8)
α/°	90
β/°	93.5630(10)
γ/°	90
Volume/Å^3	12526.2(7)
Z	2
ρ_{calc}g/cm^3	2.549
μ/mm^{-1}	4.177
F(000)	9148.0
λ/Å	MoKα (λ = 0.71073)
Independent reflections	R_{int} = 0.0583, R_{sigma} = 0.0605
GOF on F^2	1.025
R_1[a][I > 2σ(I)]	R_1 = 0.0578, wR_2 = 0.1318
wR_2[b](all data)	R_1 = 0.1011, wR_2 = 0.1521

Table S3. Crystal data and structure refinement for **3**

Codes	**3**

Formula	$C_{35}H_{46}Ag_{10}O_{12}S_{5.5}$
F_w	1913.75
Temperature/K	296.3
Crystal system	monoclinic
Space group	C2/c
a/Å	30.032(2)
b/Å	26.7363(18)
c/Å	15.9173(12)
α/°	90
β/°	97.531(2)
γ/°	90
Volume/Å^3	12670.4(16)
Z	8
ρ_{calc}g/cm^3	2.006
μ/mm^{-1}	3.242
F(000)	7280.0
λ/Å	MoKα (λ = 0.71073)
Independent reflections	R_{int} = 0.0489, R_{sigma} = 0.0647
GOF on F^2	1.046
R_1[a][I > 2σ(I)]	R_1 = 0.0799, wR_2 = 0.1953
wR_2[b](all data)	R_1 = 0.1454, wR_2 = 0.2505

a $R_1 = \sum \| |F_0| - |F_c| \| / \sum |F_0|$. b $wR_2 = \left\{ \sum \left[w\left(F_0^2 - F_c^2\right)^2 \right] / \sum \left[w\left(F_0^2\right) \right]^2 \right\}^{1/2}$

Table S4. Selected bond length in **1**.

Ag5-Ag6	3.003(2)	Ag3-Ag27	3.020(3)
Ag5-Ag16	3.162(3)	Ag8-Ag14	3.110(2)
Ag5-Ag10[1]	3.151(3)	Ag8-S5	2.526(6)
Ag5-Ag11[1]	3.158(3)	Ag8-O13	2.572(9)
Ag5-S12[1]	2.493(4)	Ag8-Ag9	3.068(5)
Ag5-S3	2.462(5)	Ag8-S7	2.413(8)
Ag5-O3	2.423(8)	Ag8-O20	2.460(3)
Ag6-Ag16	3.277(2)	Ag8-O9A	2.440(5)
Ag6-S12[1]	2.544(5)	V4-V5	3.045(3)
Ag6-S4	2.511(5)	V4-O5	2.277(8)
Ag6-O12	2.474(8)	V4-O6[1]	2.050(9)
Ag6-O27[1]	2.479(14)	V4-O7	1.865(10)
Ag19-Ag20	3.000(2)	V4-O2	1.932(10)
Ag19-Ag18	3.214(9)	V4-O11	1.843(9)
Ag19-S11	2.526(5)	V4-O4	1.596(9)
Ag19-S1	2.397(5)	V4-V1	3.108(3)

Ag19-O2	2.504(8)	V5-O5	2.272(8)
Ag16-Ag15	3.322(4)	V5-O12	2.049(9)
Ag16-S4	2.483(5)	V5-O11	1.842(9)
Ag16-S3	2.549(6)	V5-O10	1.871(10)
Ag16-S9	2.663(5)	V5-O13	1.902(10)
Ag16-O10	2.528(9)	V5-O14	1.613(9)
Ag1-Ag8[1]	3.125(3)	V5-V1	3.088(3)
Ag1-S1	2.421(5)	Ag2-S1	2.420(6)
Ag1-S51	2.476(6)	Ag2-S2	2.456(7)
Ag7-Ag15	3.279(3)	Ag2-O9[1]	2.581(9)
Ag7-Ag14	3.075(19)	Ag2-O66A[1]	2.130(6)
Ag7-S4	2.513(5)	Ag15-Ag14	2.987(9)
Ag7-S5	2.523(6)	Ag15-S4	2.533(5)
Ag7-O18	2.300(8)	Ag15-S8	2.525(6)
Ag7-O2A	2.420(7)	Ag15-O17	2.380(3)
Ag7-Ag26	2.924(14)	Ag15-Ag26	2.996(14)
Ag21-Ag22	2.913(4)	Ag4-S3	2.480(9)
Ag21-S11	2.447(5)	Ag4-O16	2.380(3)
Ag21-S13	2.455(6)	Ag14-S5	2.444(13)
Ag21-Ag4A	3.200(2)	Ag14-O14	2.570(2)
Ag21-O25	2.270(3)	Ag14-Ag13	2.790(3)
Ag21-Ag25	3.160(4)	Ag14-S8	2.291(17)
Ag20-S12	2.446(5)	Ag22-S13	2.605(7)
Ag20-S11	2.438(5)	Ag22-S14	2.422(7)
Ag20-O26	2.462(16)	Ag22-Ag12	2.900(6)
Ag20-Ag4A	3.078(19)	Ag22-O24	2.340(3)
Ag10-S3[1]	2.796(6)	Ag22-O22	2.440(6)
Ag10-S2[1]	2.472(6)	S12-Ag4A	2.301(9)
Ag10-S6	2.431(6)	S11-Ag25	2.572(17)
Ag10-Ag6A	3.044(9)	S3-Ag27	2.400(3)
Ag10-Ag27[1]	3.340(4)	S13-Ag12	2.333(6)
Ag23-Ag17	2.943(8)	S13-Ag8A	2.700(10)
Ag23-S9	2.505(7)	S13-Ag4A	2.219(12)
Ag23-S14	2.448(6)	S5-Ag26	2.490(2)
Ag23-Ag13	3.249(12)	S9-Ag	2.530(2)
Ag23-S8	2.936(7)	S14-Ag8A	2.691(11)
Ag23-Ag24	2.698(8)	S14-Ag24	2.684(13)
Ag18-Ag17	2.900(3)	S14-Ag25	2.380(2)
Ag18-S11	2.728(19)	S10-Ag	2.460(4)
Ag18-S14	2.528(10)	S10-Ag25	2.920(5)
Ag18-S10	2.470(16)	S2-Ag27	2.620(3)
Ag17-Ag3	2.962(5)	O5-V1	2.238(8)
Ag17-Ag4	2.969(17)	O3-V1	2.035(8)

Ag17-S9	2.366(6)	O8-V1[1]	1.991(8)
Ag17-S10	2.395(7)	O7-Ag7A	2.507(11)
V2-V4[1]	3.069(3)	O2-V1	1.790(8)
V2-V5	3.064(3)	O10-V1	1.822(9)
V2-O5[1]	2.148(8)	O1-V1	1.626(10)
V2-O5	2.137(8)	S6-Ag9	2.407(8)
V2-O3	1.915(9)	S6-Ag7A	2.493(12)
V2-O8	1.899(9)	S6-Ag6A	2.438(8)
V2-O6	1.689(8)	Ag9-Ag12	2.909(9)
V2-O12	1.704(9)	Ag9-S7	2.638(10)
Ag11-S12	2.622(6)	Ag9-O21	2.390(3)
Ag11-S13	2.649(6)	Ag12-S7	2.213(8)
Ag11-S6	2.475(7)	Ag13-S8	2.427(9)
Ag11-Ag12	3.013(5)	Ag13-S7	2.259(12)
V3-V4	3.089(3)	S8-Ag24	2.789(11)
V3-V5	3.114(3)	S8-Ag26	2.547(13)
V3-O5	2.231(8)	S7-Ag8A	2.948(12)
V3-O3[1]	2.022(9)	S7-Ag7A	2.573(12)
V3-O8	1.967(9)	S7-Ag24	2.665(12)
V3-O7	1.838(8)	Ag8A-Ag7A	3.303(14)
V3-O13	1.826(9)	Ag8A-Ag24	2.322(13)
V3-O9	1.626(9)	Ag8A-O22A	2.400(5)
V3-V1[1]	3.078(3)	Ag7A-Ag6A	2.791(18)
Ag3-Ag2	2.972(4)	Ag7A-Ag4A	2.980(2)
Ag3-Ag4	3.041(12)	Ag6A-O9A	2.550(9)
Ag3-S10	2.405(7)	Ag-Ag27	3.320(5)
Ag3-S2	2.420(7)	O64A-Ag26	2.460(5)
Ag3-Ag	3.000(3)	Ag27-O15A	2.490(7)

[1]1-X, 1-Y, 1-Z

Table S5. Selected bond length in **2**.

Ag21-Ag6[1]	3.1957(14)	Ag5-S12	2.485(3)
Ag21-Ag12	3.2113(14)	Ag5-O26[1]	2.421(12)
Ag21-Ag22	3.1041(14)	Ag8-Ag16	3.283(15)
Ag21-S8	2.463(3)	Ag8-Ag9	3.024(10)
Ag21-S9	2.471(3)	Ag8-S6	2.438(4)
Ag21-O7	2.344(5)	Ag8-S11	2.424(5)
Ag21-Ag25	3.241(4)	Ag8-O20	2.510(2)
Ag3-Ag2	3.2580(13)	Ag18-Ag17	2.650(2)
Ag3-Ag11[1]	3.1383(15)	Ag18-S15	2.404(4)
Ag3-S3	2.474(3)	Ag18-S14	2.366(4)
Ag3-S4	2.422(3)	V3-V1[1]	3.0672(19)

Ag6-Ag7	3.3768(15)	V3-V5	3.0635(19)
Ag6-S5	2.466(3)	V3-O5[1]	2.133(5)
Ag6-S9[1]	2.590(3)	V3-O5	2.131(5)
Ag6-S1[1]	2.586(3)	V3-O8	1.894(5)
Ag6-O3	2.473(5)	V3-O13	1.678(5)
Ag12-Ag51	3.1874(18)	V3-O7	1.922(5)
Ag12-S8	2.638(3)	V3-O9	1.698(5)
Ag12-S5[1]	2.536(3)	V4-V2[1]	3.0779(19)
Ag12-O9	2.462(5)	V4-V1	3.0981(19)
Ag12-O25	2.368(10)	V4-V5	3.0963(18)
Ag19-Ag2	2.9532(15)	V4-O5	2.247(5)
Ag19-Ag20	3.0513(17)	V4-O8	1.978(5)
Ag19-Ag1	3.1298(16)	V4-O7[1]	2.042(6)
Ag19-Ag18	2.940(5)	V4-O3	1.834(6)
Ag19-S15	2.411(3)	V4-O6	1.614(5)
Ag19-S1	2.380(3)	V4-O12	1.806(5)
Ag19-Ag0L	2.947(16)	Ag16-S12	2.430(5)
Ag2-S3	2.629(3)	Ag16-S11	2.355(6)
Ag2-S15	2.594(3)	Ag16-S13	2.945(15)
Ag2-S2	2.459(3)	V2-V1	3.1028(19)
Ag22-Ag23	3.0603(18)	V2-V5	3.073(2)
Ag22-S9	2.613(3)	V2-O5	2.220(5)
Ag22-S10	2.479(3)	V2-O8[1]	1.979(5)
Ag22-S14	2.565(3)	V2-O7	2.025(5)
Ag15-Ag7	2.9897(15)	V2-O2	1.801(5)
Ag15-Ag8	3.023(11)	V2-O4	1.604(5)
Ag15-Ag16	3.115(12)	V2-O11	1.834(6)
Ag15-S12	2.485(3)	V1-V5	3.026(2)
Ag15-S6	2.526(4)	V1-O5	2.292(5)
Ag15-O18	2.530(2)	V1-O2	1.909(6)
Ag15-O19	2.418(11)	V1-O9[1]	2.049(6)
Ag4-Ag5	3.1966(19)	V1-O3	1.845(5)
Ag4-Ag16	3.242(5)	V1-O10	1.830(6)
Ag4-S4	2.406(3)	V1-O1	1.606(5)
Ag4-S12	2.482(3)	Ag9-S7	2.601(4)
Ag4-Ag0O	3.072(8)	Ag9-S2[1]	2.556(4)
Ag7-Ag5	3.0020(19)	Ag9-S11	2.966(8)
Ag7-S5	2.500(3)	Ag9-O21	2.330(3)
Ag7-S6	2.480(3)	V5-O5	2.276(5)
Ag7-O17	2.230(3)	V5-O13	2.069(5)
Ag11-Ag10	3.0838(17)	V5-O10	1.826(6)
Ag11-Ag13	3.059(3)	V5-O12	1.913(5)
Ag11-S8	2.548(3)	V5-O11	1.861(6)

Ag11-S31	2.508(3)	V5-O14	1.594(6)
Ag11-O25	2.597(10)	Ag17-S4	2.359(6)
Ag11-O24	2.532(13)	Ag17-S14	2.429(5)
Ag10-Ag13	3.050(3)	S8-Ag25	2.725(6)
Ag10-S3[1]	2.509(3)	S4-Ag0T	2.686(15)
Ag10-S7	2.498(3)	S7-Ag25	2.692(6)
Ag10-Ag0R	3.185(14)	S7-Ag0R	2.440(5)
Ag10-O23	2.350(15)	S7-Ag27	2.146(6)
Ag10-O4A	2.310(6)	S15-Ag0L	2.403(11)
Ag10-O22	2.528(17)	S12-Ag0O	2.661(12)
Ag10-O22A	2.521(19)	S10-Ag24	2.359(5)
Ag20-Ag18	3.040(7)	S10-Ag25	2.524(8)
Ag20-S9	2.491(3)	S2-Ag0R[1]	2.415(6)
Ag20-O16	2.360(2)	S2-Ag26[1]	2.850(3)
Ag20-O12A	2.100(4)	S6-Ag26	2.790(3)
Ag20-Ag0L	2.950(15)	S14-Ag0T	2.609(9)
Ag1-Ag8[1]	3.149(9)	S14-Ag0L	2.549(14)
Ag1-S1	2.525(3)	S11-Ag24	2.660(6)
Ag1-S2	2.473(4)	S11-Ag27	2.078(6)
Ag1-S6[1]	2.741(3)	S11-Ag26	2.522(10)
Ag1-Ag26[1]	2.844(9)	S11-Ag0O	2.616(12)
Ag13-Ag14	2.983(3)	S13-Ag0O	2.300(2)
Ag13-S8	2.354(3)	S13-Ag0T	2.410(17)
Ag13-S7	2.384(3)	Ag24-Ag27	2.832(9)
Ag14-Ag23	2.951(2)	Ag24-Ag0O	2.775(12)
Ag14-S7	2.767(3)	Ag25-Ag27	3.028(7)
Ag14-S10	2.551(3)	Ag0R-Ag27	2.720(15)
Ag14-S11	2.519(3)	Ag0R-Ag26	3.250(4)
Ag14-O11	2.521(5)	Ag27-Ag26	3.260(3)
Ag23-S10	2.403(3)	Ag26-O27	2.080(5)
Ag23-S13	2.384(5)	O11A-Ag0L	2.570(4)
Ag5-S5	2.506(3)		

[1]1-X, 1-Y, 1-Z

Table S6. Selected bond length in **3**.

Ag3-Ag2	2.9809(18)	Ag8-S2	2.388(4)
Ag3-Ag4	2.9718(19)	Ag8-S6	2.390(5)
Ag3-Ag7[1]	3.164(6)	Ag8-O2	2.560(2)
Ag3-S6[1]	2.600(5)	Ag6-Ag5	2.847(7)
Ag3-S3	2.547(5)	Ag6-Ag1[1]	3.146(3)
Ag3-O7	2.321(12)	Ag6-S2[1]	2.505(5)
Ag3-O6	2.350(2)	Ag6-S5	2.429(5)

Ag3-Ag0B[1]	3.341(10)	Ag6-O10	2.278(11)
Ag3-O6A	2.410(4)	Ag6-Ag	3.170(5)
Ag9-Ag10	3.109(2)	Ag5-S4	2.532(9)
Ag9-Ag6[2]	3.283(2)	Ag5-S2[1]	2.652(14)
Ag9-Ag5[2]	3.131(6)	Ag5-O9	2.261(15)
Ag9-Ag7[2]	3.290(4)	Ag1-S2	2.424(5)
Ag9-S4[2]	2.486(4)	Ag1-S3	2.416(4)
Ag9-S5[2]	2.506(5)	Ag7-S6	2.393(5)
Ag9-O11	2.343(15)	Ag7-S5	2.475(6)
Ag9-Ag[2]	3.123(18)	Ag7-O3[1]	2.580(3)
Ag2-Ag6[1]	3.199(2)	S4-Ag	2.340(16)
Ag2-Ag1	3.040(2)	S1-O2	1.409(17)
Ag2-Ag7[1]	3.083(5)	S1-O2[1]	1.409(17)
Ag2-S3	2.515(5)	S1-O1	1.600(3)
Ag2-S5[1]	2.510(5)	S1-O1[1]	1.600(3)
Ag2-O5	2.370(3)	S1-O4	1.200(3)
Ag2-Ag0B[1]	3.199(9)	S1-O4[1]	1.200(3)
Ag2-O5A	2.190(6)	S1-O3	1.380(2)
Ag4-Ag8[1]	3.047(2)	S1-O3[1]	1.380(2)
Ag4-Ag5	3.374(6)	S6-Ag0B	2.555(14)
Ag4-S4	2.449(4)	S5-Ag0B	2.452(8)
Ag4-S6[1]	2.544(5)	O9-Ag	2.010(3)
Ag4-O8	2.310(11)	O2-O4[1]	1.370(3)
Ag10-S4[2]	2.531(4)	O2-O3[1]	1.340(3)
Ag10-S3[2]	2.540(5)	O1-O4[1]	1.680(4)
Ag10-O12	2.349(15)	O4-O3[1]	1.430(4)
Ag8-Ag5[1]	3.270(12)		

[1]3/2-X, 3/2-Y,1-Z; [2]3/2-X, -1/2+Y, 1/2-Z; [3]2-X, 1-Y, 1-Z