Supplementary Material for Dalton Transactions

Electronic Supplementary Information

For

Donor effect on supramolecular structures of silver(I) perchlorate complexes of macrocycles with O_2S_2X (X=S, O and NH) donor sets

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Synthesis of $[Ag(\mathbf{L^1})_2](ClO_4)$ (**1**): To a stirred solution of $\mathbf{L^1}$ (42.3 mg, 0.161 mmol) in dichloromethane (2 mL), a solution of silver perchlorate (22.3 mg, 0.161 mmol) in methanol (1 mL) was added. White precipitate was formed immediately. The solid was filtered off, and dissolved in acetonitrile (1 mL). X-ray quality crystals of **1** were obtained by diffusion of diethyl ether into the solution. MS(FAB): *m/z* = 891 ($[Ag(\mathbf{L^1})_2]^+$, $[C_{40}H_{48}AgO_4S_6]^+$), *m/z* = 499 ($[Ag(\mathbf{L^1})]^+$, $[C_{20}H_{24}AgO_2S_3]^+$). IR (KBr, cm^{-1}) 2962w, 1589m, 1496m, 1450m, 1242m, 1095vs (ClO_4^-), 941m, 779m, 617m.

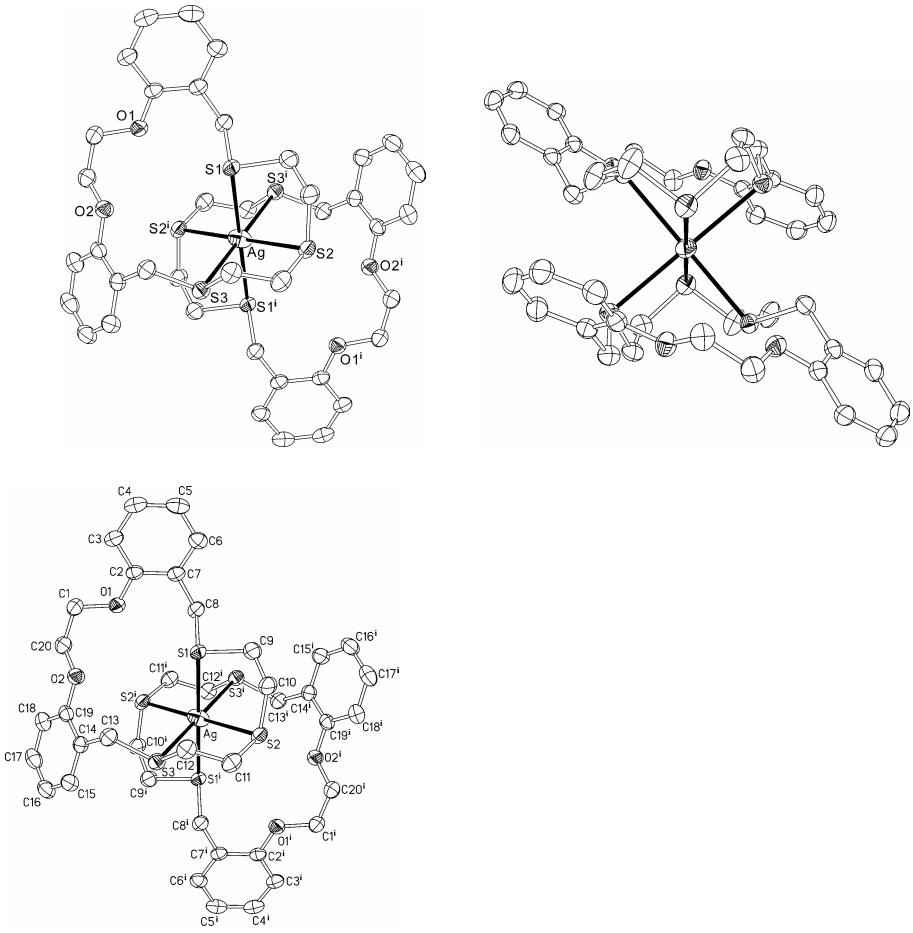
Synthesis of $\{[Ag\mathbf{L^2}(CH_3CN)](ClO_4)\}_2$ (**2a**): Silver perchlorate (33.4 mg, 0.161 mmol) and $\mathbf{L^2}$ (60.5 mg, 0.161 mmol) were stirred together in acetonitrile (3 mL). X-ray quality crystals of **2a** were obtained by slow evaporation of reaction mixture. MS(FAB): *m/z* = 483 ($[Ag(\mathbf{L^2})]^+$, $[C_{20}H_{24}AgO_3S_2]^+$). IR (KBr, cm^{-1}) 2939w, 1605m, 1497m, 1450m, 1095vs (ClO_4^-), 941m, 771m, 625m.

Synthesis of $\{[Ag_4(\mathbf{L^2})_2(CH_3OH)_2](ClO_4)_4\}_n$ (**2b**): Silver perchlorate (30.4 mg, 0.147 mmol) and $\mathbf{L^2}$ (55.3 mg, 0.147 mmol) were stirred together in methanol (5 mL). X-ray quality crystals of **2a** were obtained by slow evaporation of reaction mixture. MS(FAB): *m/z* = 499 ($[Ag_2(\mathbf{L^2})_2(CH_3OH)]^{2+}$, $[C_{41}H_{52}Ag_2O_7S_4]^{2+}$), 379 ($[Ag_3(\mathbf{L^2})_2(CH_3OH)_2]^{3+}$, $[C_{42}H_{56}Ag_3O_8S_4]^{3+}$). IR (KBr, cm^{-1}) 3487m, 2939w, 1597m, 1496m, 1450m, 1242m, 1103vs (ClO_4^-), 933m, 774m, 617m.

Synthesis of $[Ag_4(\mathbf{L^3})_4(\mu\text{-}ClO_4)_2](ClO_4)_2(CH_3CN)_2$ (**3**): To a stirred solution of $\mathbf{L^3}$ (100.3 mg, 0.266 mmol) in dichloromethane (5 mL), a solution of silver perchlorate (55.2 mg, 0.266 mmol) in methanol (2 mL) was added. White precipitate was formed immediately. The solid was filtered off, and dissolved in acetonitrile (2 mL). X-ray quality crystals of **1** were obtained by diffusion of diethyl ether into the solution. HRMS: Calcd. for $C_{40}H_{50}O_8N_2ClS_4Ag_2$: 1063.0240; Found: 1063.0249. IR (KBr, cm^{-1}) 3448s, 2931w, 1596w, 1488m, 1450m, 1250s, 1219s, 1103s, 933s, 763s, 501s.

Table S1 Crystal and experimental data for **1**, **2a**, **2b** and **3**

	1	**2a**	**2b**	**3**
Formula	$C_{40}H_{48}AgClO_8S_6$	$C_{22}H_{27}AgClNO_7S_2$	$C_{42}H_{56}Ag_4Cl_4O_{24}S_4$	$C_{84}H_{106}Ag_4Cl_4N_6O_{24}S_8$
Formula weight	992.46	624.89	1646.39	2413.51
Temperature	298(2) K	298(2) K	296(2) K	173(2) K
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$	*P*-1
Z	1	4	4	1
a (Å)	8.9985(7)	10.6319(10)	24.310(2)	11.5691(8)
b (Å)	11.6633(9)	21.039(2)	12.6134(12)	13.3821(10)
c (Å)	12.3578(9)	11.8585(11)	18.2148(18)	16.2842(12)
α (°)	116.7000(10)			85.7870(10)
β (°)	95.460(2)	107.158(2)	92.659(2)	75.2830(10)
γ (°)	106.721(2)			82.8980(10)
V (Å^3)	1070.83(14)	2534.5(4)	5579.2(9)	2417.4(3)
D_x (g/cm^3)	1.539	1.638	1.960	1.658
$2\theta_{max}$ (°)	56.62	56.72	57.16	56.64
R	0.0426	0.0419	0.0672	0.0444
wR	0.1005	0.1053	0.1725	0.1111
No. of reflection used [>2σ(*I*)]	4933	6159	13691	11330
Diffractometer	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system
Structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix	full-matrix



(a) (b)

Fig. S1 Sandwich structure of **1**, $[Ag(\mathbf{L}^1)_2](ClO_4)$ (a) top view and (b) side view. Hydrogen atoms and noncoordinating anions are omitted. Ellipsoids are drawn at the 30 % probability level. Selected bond lengths (Å) and angles (deg): Ag-S(1) 2.730(1), Ag-S(2) 2.860(1), Ag-S(3) 2.792(1). S(1)-Ag-S(2) 76.00(2), S(1)-Ag-S(3) 89.85(2), S(2)-Ag-S(3) 76.35(2), S(1)-Ag-S(2′) 104.00(2), S(1)-Ag-S(3^i) 90.15(2). O(1)-C-C-O(2) 65.71(33), S(1)-C-C-S(2) 61.22(39), S(2)-C-C-S(3) 67.10(31) [symmetry operation: $-x + 1, -y + 1, -z + 1$].

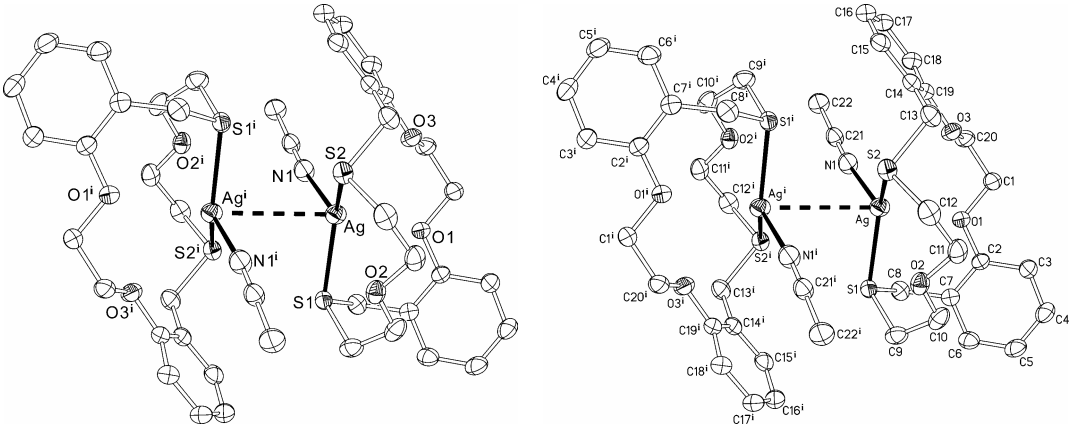


Fig. S2 Dimeric structure of **2a**, $\{[Ag\mathbf{L}^2(CH_3CN)](ClO_4)\}_2$. Hydrogen atoms and noncoordinating anions are omitted. Ellipsoids are drawn at the 30 % probability level. Selected bond lengths (Å) and angles (deg): Ag-S(1) 2.512(1), Ag-S(2) 2.485(1), Ag-N(1) 2.321(3), Ag-O(2) 2.946(2), Ag-Ag^{i} 3.329(1). S(1)-Ag-S(2) 134.28(3), S(1)-Ag-N(1) 101.76(9), S(2)-Ag-N(1) 119.05(9), S(1)-Ag-Ag^{i} 85.83(2), S(2)-Ag-Ag^{i} 86.64(2), N(1)-Ag-Ag^{i} 73.73(8). O(1)-C-C-O(3) 76.92(37), S(1)-C-C-O(2) 62.21(34), S(2)-C-C-O(2) -66.27(34) [symmetry operation: -*x*, -*y* + *2*, -*z* + 1].

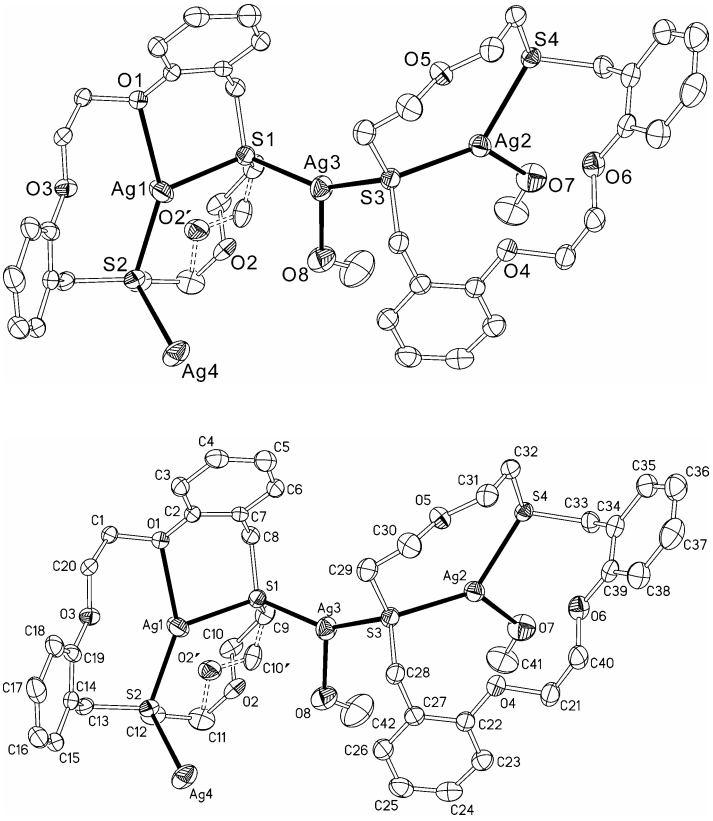


Fig. S3 1-D polymeric structure of **2b**, $\{[Ag_4(\mathbf{L}^2)_2(CH_3OH)_2](ClO_4)_4\}_n$. Hydrogen atoms and noncoordinating anions are omitted. Ellipsoids are drawn at the 30 % probability level. O2 and C10 atoms are disordered occupying two positions (65.6:34.4). Selected bond lengths (Å) and angles (deg): Ag(1)-S(1) 2.470(2), Ag(1)-S(2) 2.465(2), Ag(1)-O(1) 2.516(5), Ag(2)-S(3) 2.508(2), Ag(2)-S(4) 2.561(2), Ag(2)-O(7) 2.398(7), Ag(3)-S(1) 2.497(2), Ag(3)-S(3) 2.476(2), Ag(3)-O(8) 2.358(8), Ag(4)-S(2) 2.433(2), Ag(4)-S(4′) 2.476(2). S(1)-Ag(1)-S(2) 126.28(7), S(1)-Ag(1)-O(1) 84.05(12), S(2)-Ag(1)-O(1) 149.29(13), S(3)-Ag(2)-S(4) 136.40(7), S(3)-Ag(2)-O(7) 128.70(20), S(4)-Ag(2)-O(7) 91.90(20), S(1)-Ag(3)-S(3) 149.59(7), S(1)-Ag(3)-O(8) 90.57(20), S(3)-Ag(3)-O(8) 119.81(20), S(2)-Ag(4)-S(4′) 148.56(7). O(1)-C-C-O(3) -72.98(75), S(1)-C-C-O(2) -58.58(2.15), S(1)-C-C′-O(2′) 53.81(5.46), O(2)-C-C-S(2) -46.23(1.29), O(2′)-C-C-S(2) -74.95(1.69), O(4)-C-C-O(6) -79.05(85), S(3)-C-C-O(5) 67.93(86), O(5)-C-C-S(4) -61.47(75) [symmetry operation: *x*, -*y*, *z*].

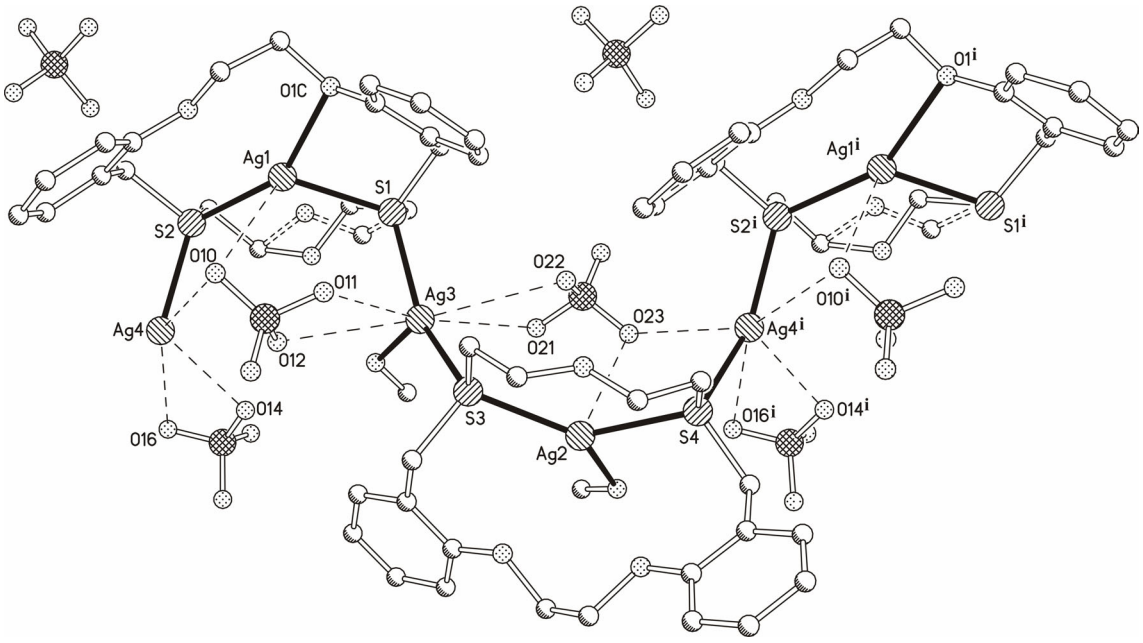


Fig. S4 1-D polymeric structure of **2b**, $\{[Ag_4(\mathbf{L}^2)_2(CH_3OH)_2](ClO_4)_4\}_n$ showing anion interactions (dashed lines). Hydrogen atoms anions are omitted. Selected interatomic distances (Å): Ag(1)···O(10) 3.260(12), Ag(2)···O(23) 3.193(22), Ag(3)···O(11) 2.922(11), Ag(3)···O(12) 3.049(11), Ag(3)···O(22) 3.200(11), Ag(3)···O(21) 2.922(10), Ag(4)···O(10) 3.450(11), Ag(4)···O(16) 3.175(26), Ag(4)···O(14) 2.691(11), Ag(4^i)···O(23) 2.911(14) [symmetry operation: x, y-1, z].

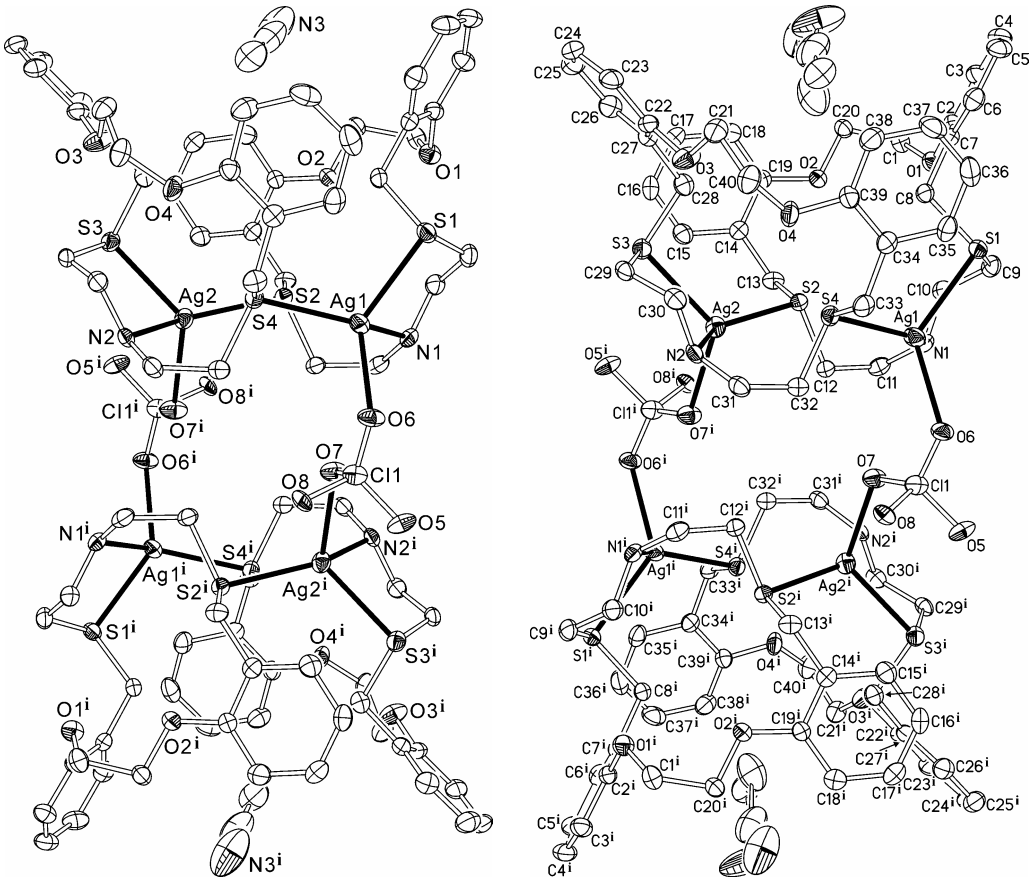


Fig. S5 Tetrameric bowl-type structure of **3**, $[Ag_4(\mathbf{L}^3)_4(\mu\text{-}ClO_4)_2](ClO_4)_2(CH_3CN)_2$. Hydrogen atoms and noncoordinating anions are omitted. The acetonitrile solvent is disordered (85.5:14.5) with C44-C43-N3 and C44′-C43-N3′ units occupying two positions. Selected bond lengths (Å) and angles (deg): Ag(1)-S(1) 2.578(1), Ag(1)-S(4) 2.530(1), Ag(1)-N(1) 2.379(4), Ag(1)-O(6) 2.415(3), Ag(2)-S(3) 2.575(1), Ag(2)-S(2) 2.499(1), Ag(2)-N(2) 2.369(4), Ag(2)-O(7^i) 2.421(3). S(1)-Ag(1)-N(1) 82.53(9). S(1)-Ag(1)-S(4) 111.14(4), N(1)-Ag(1)-S(4) 134.57(9), S(1)-Ag(1)-O(6) 128.08(8), N(1)-Ag(1)-O(6) 102.72(12), S(4)-Ag(1)-O(6) 101.19(8), S(3)-Ag(2)-N(2) 82.32(9), S(3)-Ag(2)-S(2) 118.25(4), N(2)-Ag(2)-S(2) 137.06(9), S(3)-Ag(2)-O(7^i) 121.61(8), N(2)-Ag(2)-O(7^i) 95.53(12), S(2)-Ag(2)-O(7^i) 102.47(9). O(1)-C-C-O(2) -67.28(45), S(1)-C-C-N(1) -63.09(45), N(1)-C-C-S(2) 61.79(47), O(3)-C-C-O(4) 54.90(53), S(3)-C-C-N(2) -62.72(42), N(2)-C-C-S(4) 62.31(45) [symmetry operation: $-x + 1, -y + 2, -z + 1$].

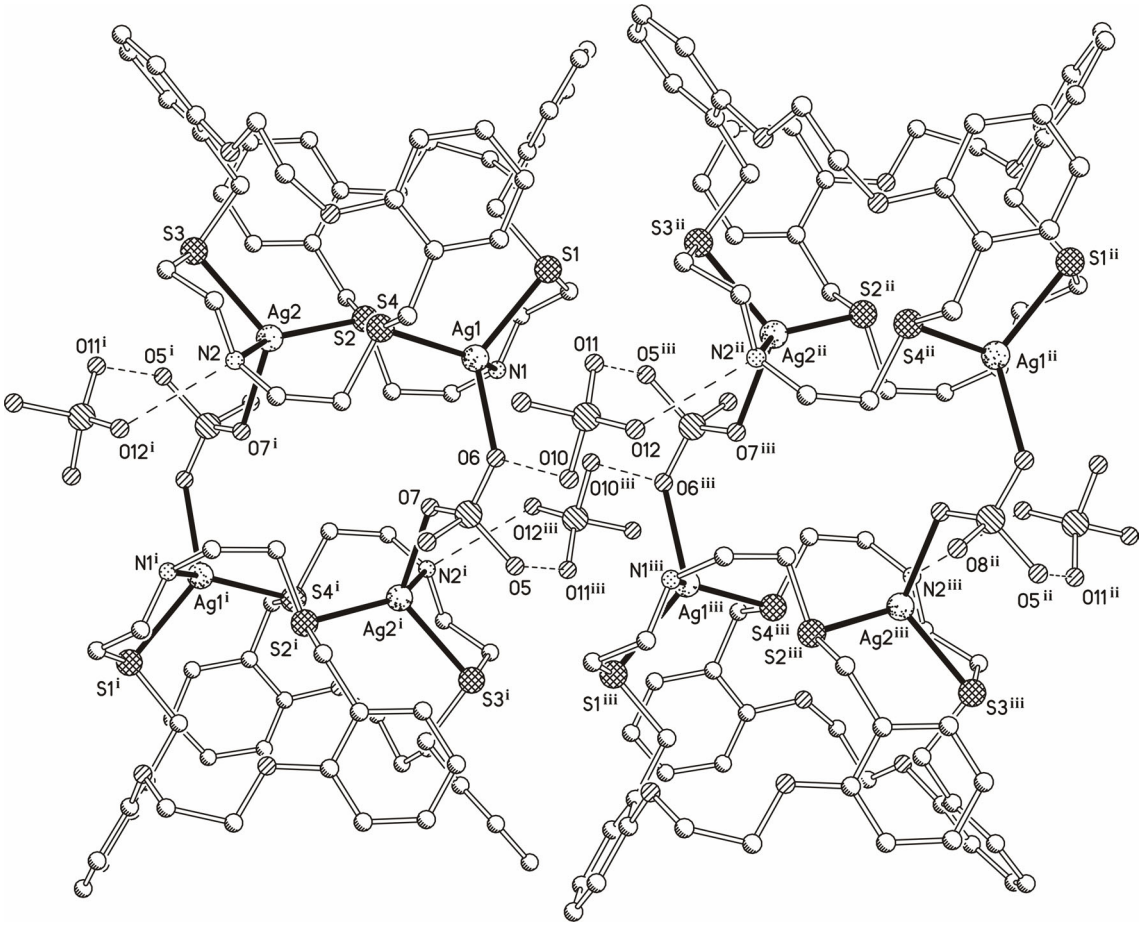


Fig. S6 Tetrameric bowl-type structure of **3**, $[Ag_4(\mathbf{L}^3)_4(\mu\text{-}ClO_4)_2](ClO_4)_2(CH_3CN)_2$ showing anion interactions (dashed lines). Hydrogen atoms are omitted. Selected interatomic distances (Å): O(6)···O(10) 2.560(4), O(11)···O(5^{iii}) 2.529(5), O(12)···N(2^{ii}) 2.920(4) [symmetry operations: i) -*x*+1, -*y*+2, -*z*+1; ii) *x*+1, *y*, *z*; iii) -*x*+2, -*y*+2, -*z*+1].

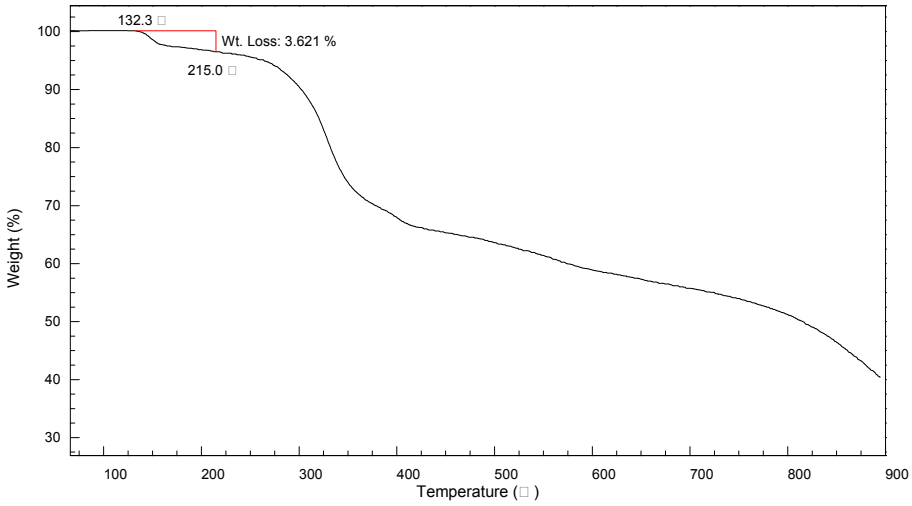


Fig. S7 TGA diagram of $[Ag_4(\mathbf{L}^3)_4(\mu\text{-}ClO_4)_2](ClO_4)_2(CH_3CN)_2$ (**3**), recorded 10 °C/min.

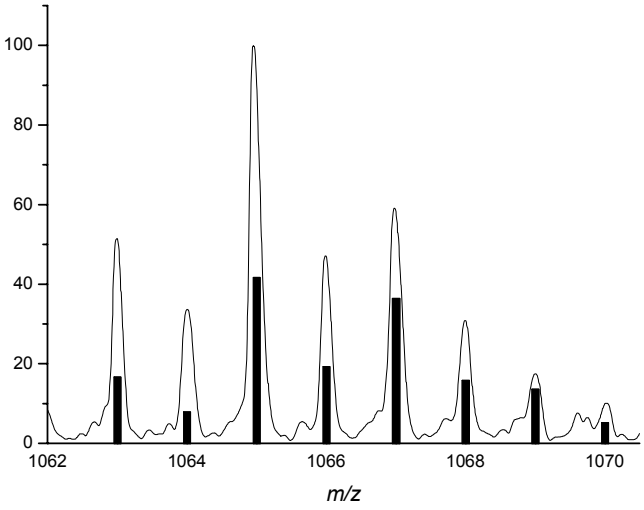


Fig. S8 Isotope pattern (FAB mass) of **3**. Bar-graph indicates the half-height of calculated values.