

## Supporting Information

### Conversion of a double-tetranuclear cluster silver helicate into a dihelicate *via* a rare desulfurization process

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## Experimental Section

### Materials and Methods

All solvents, 1,3-diacetylbenzene, 4-*N*-methyl-3-thiosemicarbazide and silver metal plates (ca. 2x2 cm<sup>2</sup>) were purchased from commercial sources and were employed as received without any purification thereof.

Elemental analysis of the compounds (C, H, N and S) were carried out on a FISON EA model 1108 Analyzer. A Varian Innova 400 and a Varian Mercury 300 spectrometers were used to record the <sup>1</sup>H and <sup>13</sup>C/DEPT NMR spectra operating at room temperature. CDCl<sub>3</sub> and DMSO-d<sub>6</sub> were used as deuterated solvents and the chemical shifts are reported as δ (ppm) and expressed relative to Me<sub>4</sub>Si (δ = 0 ppm). Infrared spectra were recorded from 4000 to 500 cm<sup>-1</sup> on a BRUKER IFS-66V spectrophotometer using KBr discs. An API4000 Applied Biosystems mass spectrometer equipped with Triple Quadrupole analyzer was used to collect the electrospray ionization mass data (ESI), using standard spectroscopic-grade solvents. A Bruker Autoflex spectrometer, using DCTB as the matrix, was used to register the Matrix-Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) mass spectra.

### Synthesis and characterization of silver complex [Ag<sub>8</sub>L<sub>4</sub>]

The silver complex was synthesized by an electrochemical procedure using acetonitrile as solvent.<sup>2,3</sup> The synthetic procedure employed for the isolation of the complex [Ag<sub>4</sub>L<sub>2</sub>]<sub>2</sub> is described below:

The neutral Ag(I) complex was prepared by an electrochemical procedure. The electrochemical cell can be summarized as follows: Pt(-) | H<sub>2</sub>L + CH<sub>3</sub>CN | Ag(+). The ligand H<sub>2</sub>L (0.1 g, 0.22 mmol) was dissolved in acetonitrile (ca. 80 cm<sup>3</sup>). A tiny amount of tetraethylammonium perchlorate was incorporated to the reaction media as supporting electrolyte. The resulting mixture was electrolyzed under two different conditions: 10 mA and 19 V for 1 h 36 min to achieve the bideprotonation of H<sub>2</sub>L. The off yellow powder was isolated by filtration, washed with a small volume of diethyl ether (10 mL) and dried under vacuum. **CAUTION!** Although we have not encountered any problem so far during the electrochemical synthesis perchlorate salts must be carefully manipulated as they are potentially explosive.

**[Ag<sub>4</sub>L<sub>2</sub>]<sub>2</sub>**: Yield: 0.115 g (80%); Ef = 0.8 mol F<sup>-1</sup>; E. A. (Found: C, 30.6; H, 3.3; N, 15.3; S, 11.7; Ag<sub>4</sub>C<sub>28</sub>H<sub>36</sub>N<sub>12</sub>S<sub>4</sub> required: C, 30.6; H, 3.4; N, 15.4; S, 11.6; ESI<sup>+</sup> (*m/z*): 1100.8 [M<sub>4</sub>(L)<sub>2</sub>+H]<sup>+</sup>, 1208.7 [M<sub>5</sub>(L)<sub>2</sub>]<sup>+</sup>, 1544.8 [M<sub>5</sub>(L)<sub>3</sub>+2H]<sup>+</sup>, 1650.7 [M<sub>6</sub>(L)<sub>3</sub>+H]<sup>+</sup>, 1758.5 [M<sub>7</sub>(L)<sub>3</sub>]<sup>+</sup>, 2200.7 [M<sub>8</sub>(L)<sub>4</sub>+H]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>): ν(NH) 3365, ν(C=N + C-N) 1562, 1514, ν(C=S) 1119, 791, ν(N-N) 1047. <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>): δ 9.45 (s, 4H, H<sub>3</sub>), 7.73 (dd, *J* = 7.8, 1.9 Hz, 8H, H<sub>4</sub>), 7.52 (t, *J* = 7.8 Hz, 4H, H<sub>5</sub>), 6.92 (d, *J* = 4.5 Hz, 8H, H<sub>2</sub>), 2.73 (d, *J* = 4.5 Hz, 24H, H<sub>6</sub>), 2.47 (s, 24H, H<sub>7</sub>). <sup>109</sup>Ag-NMR (23 MHz, DMSO-d<sub>6</sub>): δ 963.9. Colorless X-ray quality crystals of [Ag<sub>4</sub>L<sub>2</sub>]<sub>2</sub> were collected after filtration of the initial precipitate obtained during the electrochemical synthesis followed by slow evaporation of the mother liquors.

### Synthesis of the silver complex [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O

The dihelicate [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O has been obtained as a by-product during the recrystallisation process of complex [Ag<sub>4</sub>L<sub>2</sub>]<sub>2</sub> in CHCl<sub>3</sub> where the solution was exposed to light and opened to air for 3-4 weeks. The obtained compound has been studied by X-ray diffraction and ESI<sup>+</sup> spectrometry.

### Crystallographic data of complexes [Ag<sub>4</sub>L<sub>2</sub>]<sub>2</sub> and [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O

Colorless crystals of [Ag<sub>8</sub>(L)<sub>4</sub>] and [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O were obtained as indicated before. The crystals were mounted on a glass fibre and directly used for data collection. Crystal data collection was performed at a 100(2) K temperature using a BRUKER APPEX-II diffractometer with a CCD area detector, using graphite monochromated MoK(α) radiation (λ = 0.71073 Å). Data were treated with APPEX2 software.<sup>i</sup> An empirical absorption correction (SADABS)<sup>ii</sup> was applied to the collected reflections. The structure of [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O was solved by using the SIR-97 program<sup>iii</sup> and refined by full-matrix least-squares techniques against *F*<sup>2</sup> using SHELXL-97 program package.<sup>iv</sup> [Ag<sub>8</sub>L<sub>4</sub>] was solved with DIRDIF2008 program<sup>v</sup> and refined by full-matrix least-squares techniques against *F*<sup>2</sup> using SHELXL2014/7 program package.<sup>vi</sup> All non-hydrogen atoms were assigned with positional and anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions, riding on attached atoms with isotropic thermal parameters (1.2-1.5 times those of their carrier atoms). Criteria of a satisfactory complete analysis were the ratios of "rms" shift to standard deviation less than 0.001 was taken and no significant features were observed in the final difference maps. The molecular graphics include in the manuscript and the SI files were prepared with ORTEP-3<sup>vii</sup> and MERCURY<sup>viii</sup> programs. The most relevant crystal data of both crystals are listed below. Important bond distances and angles are summarized in Tables S1 and S2 while hydrogen bond parameters are listed in Table S3.

**[Ag<sub>4</sub>L<sub>2</sub>]<sub>2</sub>**: Formula: C<sub>56</sub>H<sub>72</sub>Ag<sub>8</sub>N<sub>24</sub>S<sub>8</sub>; Volume: 3544.1(3) Å<sup>3</sup>, MW, 2200.82 g·mol<sup>-1</sup>; Crystal size: 0.18 x 0.07 x 0.06 mm<sup>3</sup>; Z= 2; Spatial Group: *Pnn2*; D: 2.062 mg m<sup>-3</sup>; Crystal System: Orthorhombic; Interval  $\theta$ : 3.1–30.0 °; a= 10.7941(5) Å; b= 17.6381(9) Å, c= 18.6154(9) Å;  $\alpha$ = 90 °;  $\beta$ = 90 °;  $\gamma$ = 90 °;  $\mu$ = 2.45 mm<sup>-1</sup>; F(000)= 2160; Radiation  $\lambda$ (Mo-K $\alpha$ )= 0.7107 Å, Measured/unique reflexions: 83075/11795 (Rint= 0.060); R= 0.027; wR= 0.044; GOF= 1.041; Residues: 0.73/-0.59 e Å<sup>-3</sup>.

**[Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>](SO<sub>4</sub>)·H<sub>2</sub>O**: Formula, C<sub>28</sub>H<sub>42</sub>Ag<sub>2</sub>N<sub>12</sub>O<sub>5</sub>S<sub>5</sub>; Volume: 3743.5(5), MW, 1002.78 g·mol<sup>-1</sup>; Crystal size: 0.08 x 0.06 x 0.06 mm<sup>3</sup>; Z= 4; Spatial Group: *I2/a*; D: 1.779 mg m<sup>-3</sup>; Crystal System: Monoclinic; Interval  $\theta$ : 1.9-25.4°; a= 16.3978(16) Å; b= 13.1041(7) Å, c= 17.5038(10) Å;  $\alpha$ = 90 °;  $\beta$ = 95.561(2) °;  $\gamma$ = 90 °;  $\mu$ = 1.38 mm<sup>-1</sup>; F(000)= 2032; Radiation  $\lambda$ (Mo-K $\alpha$ ) = 0.7107 Å, Measured/unique reflexions: 17775/3413 (Rint= 0.1); R= 0.055; wR= 0.143; GOF= 1.016; Residues: 1.46/-0.62 e Å<sup>-3</sup>.

Bond Distances (Å)		Bond Angles (°)	
Ag1–N3	2.338(3)	N9–Ag4–S1	128.46(8)
Ag3–N4	2.390(3)	N9–Ag4–S3	80.15(8)
Ag4–N9	2.385(3)	S1–Ag4–S3	147.85(4)
Ag2–N10	2.345(3)	N9–Ag4–S3	119.68(19)
Ag4–S1	2.4204(11)	N3–Ag4–S4	145.65(9)
Ag1–S1	2.4933(11)	N3–Ag1–S1	76.74(9)
Ag2–S2	2.4209(10)	S4–Ag1–S1	137.57(4)
Ag3–S2	2.5198(10)	N9–Ag4–S3	121.64(19)
Ag4–S3	2.4490(10)	N10–Ag2–S2	141.25(8)
Ag3–S3	2.4597(10)	N10–Ag2–S4	77.60(8)
Ag1–S4	2.4286(11)	S2–Ag2–S4	137.94(4)
Ag2–S4	2.5266(11)	N4–Ag3–S3	142.17(8)
Ag4–Ag1	3.0390(4)	N4–Ag3–S2	76.50(8)
Ag4–Ag3	3.1107(4)	S3–Ag3–S2	135.37(3)
Ag1–Ag2	3.0061(5)		
Ag2–Ag3	3.3155(4)		

**Table S1.** Main bond distances (Å) and angles (°) in [Ag<sub>4</sub>(L)<sub>2</sub>]<sub>2</sub>.

Bond Distances (Å)		Bond Angles (°)	
Ag1-N4	2.494(6)	S2-Ag1-S1	155.1(2)
Ag1-S1	2.428(5)	S2-Ag1-N4	76.90(18)
Ag1-S2	2.401(6)	S1-Ag1-N3	75.54(18)
Ag1-N3	2.648(6)	N3-Ag1-N4	119.68(19)
Ag1B-N3 <sup>i</sup>	2.370(6)	N4 <sup>i</sup> -Ag1B-S1B	75.82(18)
Ag1B-S2B	2.420(6)	N3 <sup>i</sup> -Ag1B-S2B	78.67(19)
Ag1B-S1B	2.416(6)	S1B-Ag1B-S2B	153.5(2)
Ag1B-N4 <sup>i</sup>	2.719(6)	N3 <sup>i</sup> -Ag1B-N4 <sup>i</sup>	121.64(19)

**Table S2.** Main bond distances (Å) and angles (°) in [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O.

D-H···A	D···A (Å)	D-H···A (°)	Symmetry Operation
N6-H6···O4	2.838(17)	161(11)	
N5-O2···O2	2.846(19)	167(14)	
O5-H5···O1	2.789(16)	150(6)	
N1-H1···O3	2.761(17)	165(28)	x, y-1, z
N2-H2···O1	2.80(2)	154(21)	-x+1/2, y-1, -z+1
N6B-H6B···O4	2.97(2)	122(4)	-x+1/2, y-1, -z+1
N2B-H2B···O2	2.765(19)	162(10)	-x+1/2, y, -z+1
NB1-H1B···O5	2.834(18)	149(6)	-x+1/2, y, -z+1

**Table S3.** Hydrogen bonds distances (Å) in [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>]SO<sub>4</sub>·H<sub>2</sub>O.

## 2. Additional Figures

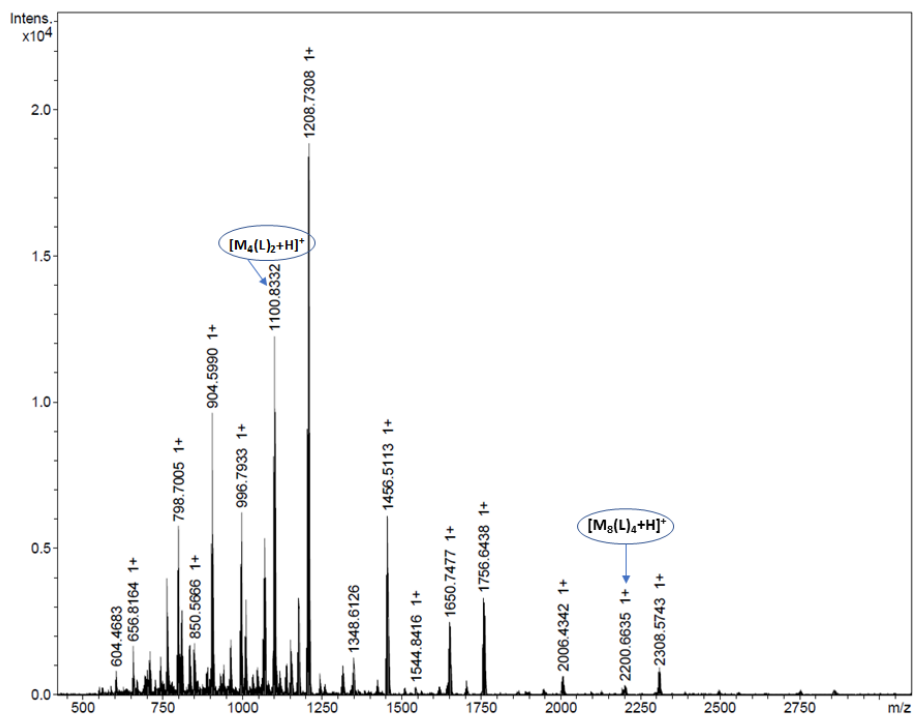


Figure S1. ESI-MS spectrum of complex  $[Ag_4L_2]_2$ .

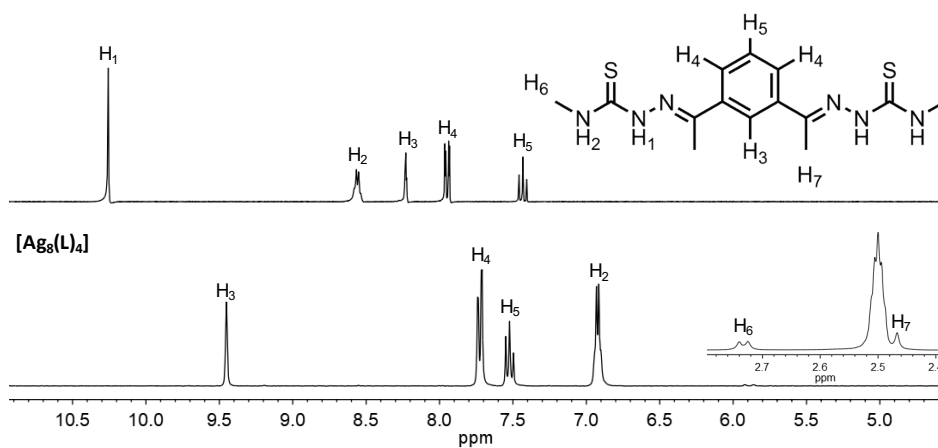
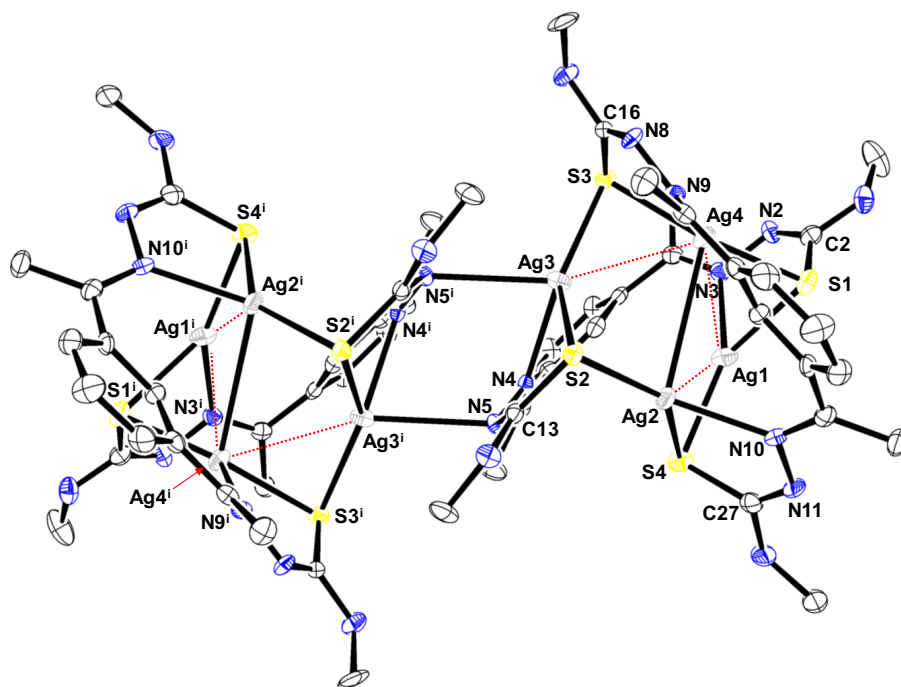
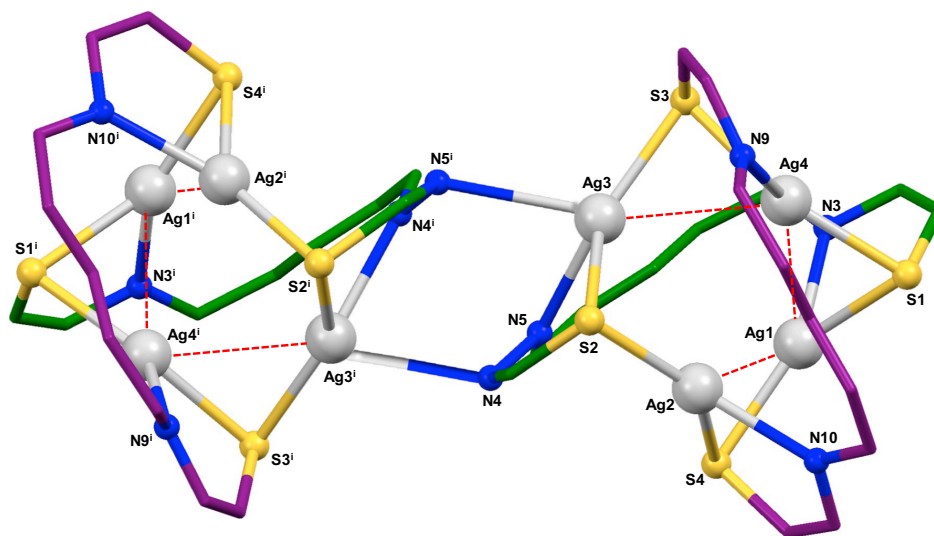


Figure S2.  $^1H$ -RMN spectra superposition of  $[Ag_4(L)_2]_2$  complex and  $H_2L$  bithiosemicarbazone ligand.

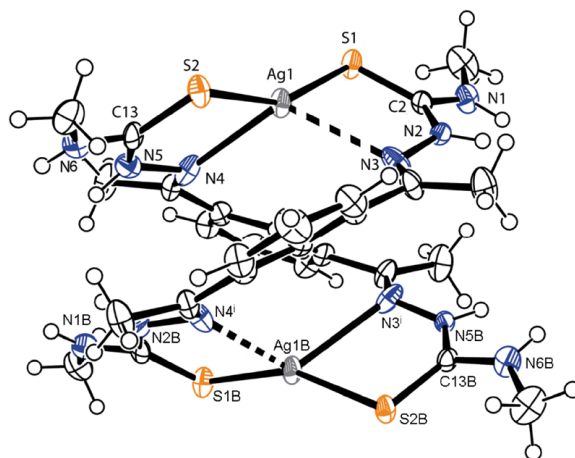


**Figure S3.** ORTEP representation of the double tetranuclear cluster helicate  $[Ag_4L_2]_2$ .

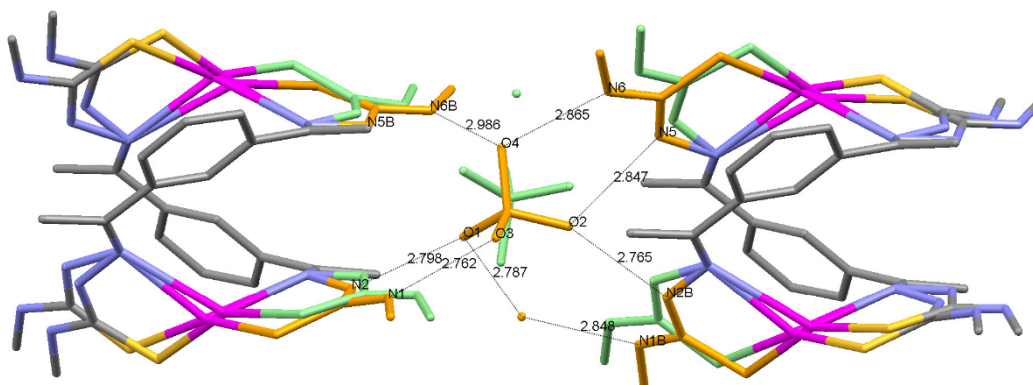


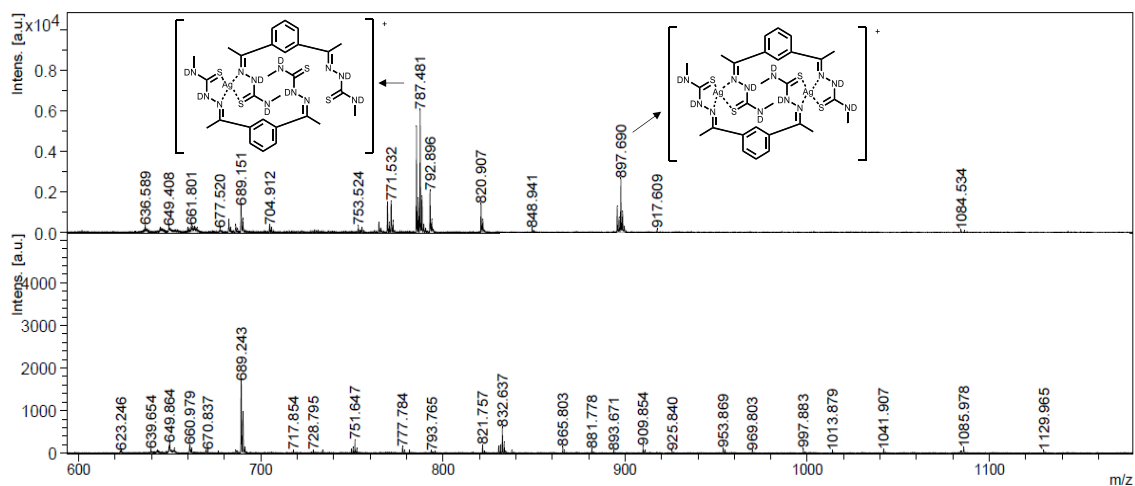
**Figure S4.** Coordination environment of metal centers in the cluster  $[Ag_4(L)_2]_2$ .



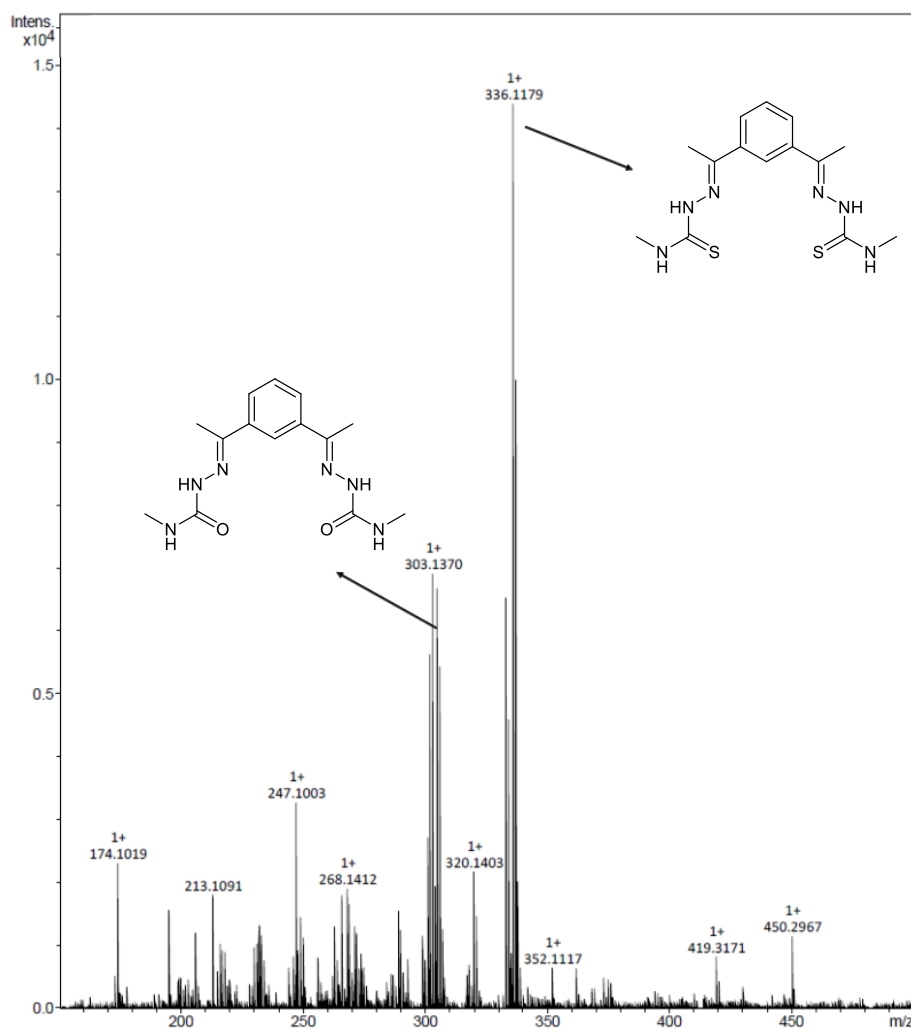


**Figure S5.** ORTEP representation of the dihelicate  $[Ag_2(H_2L)_2](SO_4) \cdot H_2O$ . Sulfate ion and the water molecule have been eliminated for clarity.

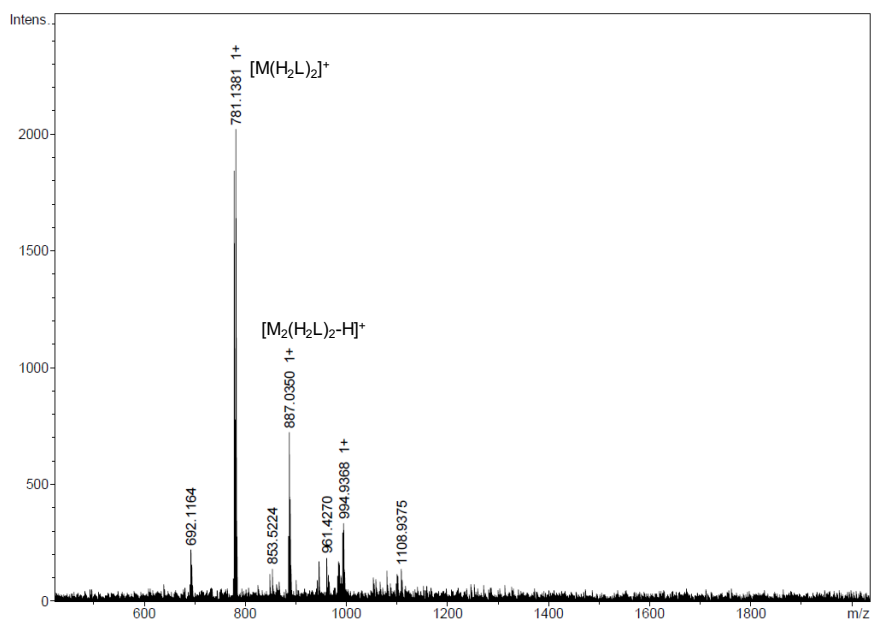




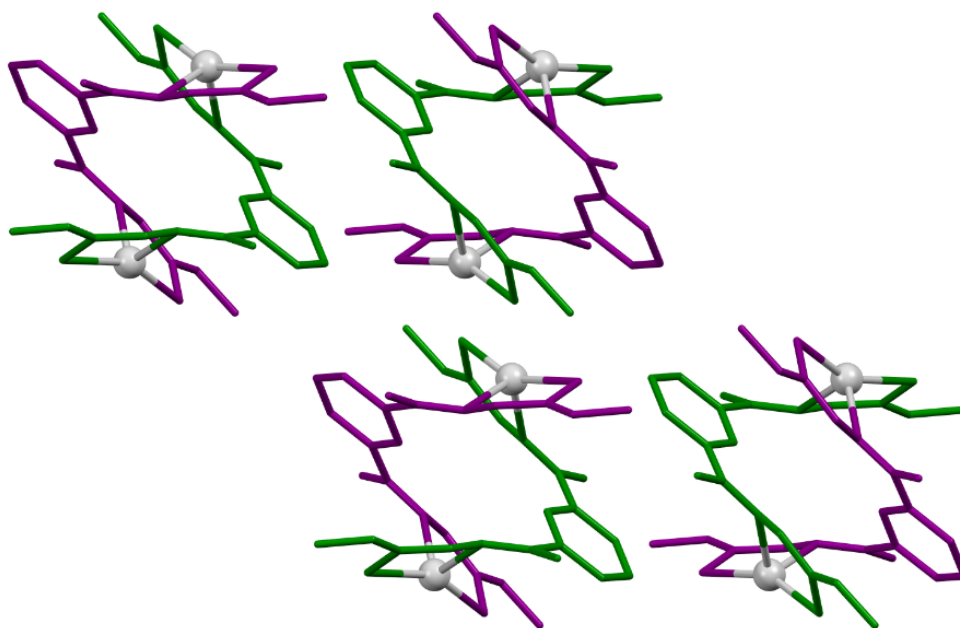
**Figure S7.** MALDI spectrum of the  $\text{CDCl}_3$  solution resulting for the NMR experiments depicted in Figure 3.



**Figure S8.** ESI<sup>+</sup> spectrum of organic side-products in the chloroform recrystallization solution.



**Figure S9.** ESI<sup>+</sup> spectra of  $[Ag_2(H_2L)_2](SO_4) \cdot H_2O$ .



**Figure S10.** Crystal lattice of  $[Ag_2(H_2L)_2]SO_4 \cdot H_2O$  in which both enantiomers,  $\Delta\Delta$  and  $\Lambda\Lambda$  can be observed into a racemic mixture.

### 3. References

- (<sup>i</sup>) BRUKER, AXS. D8 ADVANCE, **2005**.
- (<sup>ii</sup>) Sheldrick, G. M.; SADABS, Program for Scaling and Correction of Area Detector Data, University of Göttingen, Germany, **1996**.
- (<sup>iii</sup>) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R., SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.*, **1999**, 32, 115-119.
- (<sup>iv</sup>) Sheldrick, G. M. A short history of SHELX. *Acta Cryst.*, **2008**, A64, 112–122.
- (<sup>v</sup>) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M.; The DIRDIF2008 Program System, Crystallography Laboratory, University of Nijmegen, The Netherlands, **2008**.
- (<sup>vi</sup>) Sheldrick, G. M. SHELXT: Integrating space group determination and structure solution. *Acta Crystallogr., Sect. A: Found. Adv.*, **2014**, 70, C1437.
- (<sup>vii</sup>) L. J. Farrugia, *J. Appl. Cryst.*, **1997**, 30, 565; b) L. J. Farrugia, *J. Appl. Cryst.*, **2012**, 45, 849.
- (<sup>viii</sup>) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodríguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A.; MERCURY CSD 2.0 – new features for the visualization and investigation of crystal structures. *J. Appl. Cryst.* **2008**, 41, 466–470.