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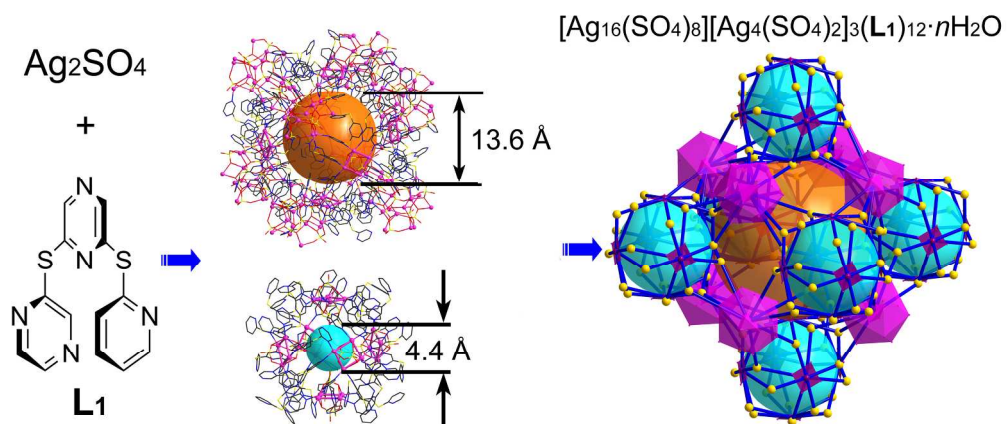www.rsc.org/dalton

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$[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(\mathbf{L_1})_{12} \cdot nH_2O$

Ag_2SO_4

+

$\mathbf{L_1}$

13.6 Å

4.4 Å

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ARTICAL

High-nuclearity Silver(I) Cluster-Based Coordination Polymers Assembled with Multidentate Oligo-α-heteroarylsulfanyl Ligands

Han Wang,[a] Chong-Qing Wan[b] and Thomas C. W. Mak*[a]

Abstract

10 Two novel coordination polymers $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(L_1)_{12} \cdot nH_2O$ ($n = 72$) (**1**) and $[Ag_{10}(SO_4)_5(L_2)_4(H_2O)_2] \cdot 8H_2O$ (**2**) based on conformationally variable oligo-α-heteroarylsulfanyl ligands 2-(pyrazin-2-ylthio)-6-(pyridin-2-ylthio)pyrazine (**L$_1$**) or 2,6-bis(pyrazin-2-ylthio)pyrazine (**L$_2$**) and sulfate-templated high-nuclearity Ag(I) clusters as structure-building units (SBUs) have been synthesized under mild conditions. Single-crystal X-ray analysis showed that complex **1** exhibits a porous three-dimensional framework containing $Ag_{16}(SO_4)_8$ and $Ag_4(SO_4)_2$ SBUs that are interconnected by **L$_1$** ligands, whereas **2** has a much denser network constructed with 15 $Ag_{10}(SO_4)_5$ SBUs and **L$_2$** linkers. To our knowledge, the $Ag_{16}(SO_4)_8$ cluster core found in **1** is the largest sulfate-based polynuclear SBU in coordination polymers, and the 14-connected $Ag_{10}(SO_4)_5$ in **2** is the highest-connectivity Ag(I) cluster SBU reported to date. These two complexes are fully characterized by infrared spectroscopy, elemental analysis, powder X-ray diffraction, thermogravimetric analysis and differential scanning calorimetry.

20

Introduction

During the past decade, rapid development in cluster chemistry has provided chemists with invaluable opportunities for crossing boundaries between major disciplines of chemistry, as well as 25 conducting integrative projects that cover the domains of physics, chemistry, and the life sciences.[1] In particular, transition-metal clusters have attracted wide attention due to their appealing ability to effectively suppress network interpenetration and function as highly-connected, secondary structure-building units 30 (SBUs) for the assembly of novel coordination architectures.[2] Cluster units formed by a judicious combination of 3d transition (Mn,[3] Fe,[4] Co,[5] Ni,[6] Cu,[7] Zn[8]) or 4f rare-earth[9] metals with anionic (carboxylate,[2] sulfonate,[10] phosphonate[11]) and/or neutral organic ligands have yielded an abundant variety of coordination 35 polymers that exhibit interesting structures and desirable properties. Notably, Ag(I) with its d^{10} electronic configuration can take variable coordination numbers in the range 2-6, and argentophilic interaction[12] between silver(I) centers is conducive to the generation of one- to three-dimensional coordination 40 networks with anionic components (such as ethynyl groups[13] and inorganic species[14]) and ancillary ligands. However, the use of high-nuclearity Ag(I) clusters for the construction of coordination polymers remain much less explored.[15]

A larger-size metal cluster with plentiful coordination sites and 45 variable bonding directions is an ideal SBU for supramolecular assembly. Of particular interest is its combination with a flexible multidentate ligand with donor sites to bind metal centers in different directions.[14-15], [16] Taking advantage of a mismatch between the number and geometry of coordination sites available 50 on a metal ion and the donor set supplied by the ligands (a 'serendipitous approach' coined by Winpenny[17]), unpredictable yet fascinating results are generally obtained, in contrast to the conventional 'designed strategy' that employs judiciously chosen ligands and metals to form predicable products.[18]

55 Herein, we report our successful syntheses of two novel coordination polymers, $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(L_1)_{12} \cdot nH_2O$ ($n = 72$) (**1**) and $[Ag_{10}(SO_4)_5(L_2)_4(H_2O)_2] \cdot 8H_2O$ (**2**), based on recently designed multidentate ligands 2-(pyrazin-2-ylthio)-6-(pyridin-2-ylthio)pyrazine (**L$_1$**) and 2,6-bis(pyrazin-2-60 ylthio)pyrazine (**L$_2$**), respectively. **L$_1$** and **L$_2$** can be regarded as conformationally flexible oligo-α-heteroarylsulfanyl ligands with two pendant heterocycle arms attached to a central pyrazinyl ring through C–S–C bridges[19] (Scheme 1). The former has five potential coordination sites at the pyrazinyl and pyridyl N atoms, 65 while the latter has six sites on three pyrazinyl rings. Unrestricted rotation about the C–S single bonds means that the multiple coordination sites bear no regular geometrical relationship, in contrast with ligands commonly used in the 'designed assembly' methodology. In addition, the 4-positional N atom of the central 70 pyrazinyl ring can facilely function as a peripheral donor site to generate a high-dimensional coordination framework.

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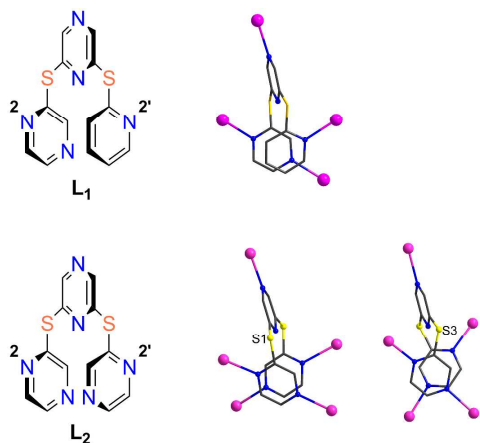
Scheme 1. Structural formula and observed configuration of L_1 (and L_2) with an *exo*-pair of 2- and 2'-positional N atoms on the pendant heteroaromatic rings, which bear a *syn* relationship with respect to the central pyrazinyl ring.

Complex **1** is built of $Ag_{16}(SO_4)_8$ and $Ag_4(SO_4)_2$ sub-units consolidated by sulfate groups,[15d, 20] and its 3-D porous framework features two kinds of cages assembled with 12-connected $Ag_{16}(SO_4)_8$ and 8-connected $Ag_4(SO_4)_2$ cluster units plus flexible L_1 connectors. In contrast, complex **2** exhibits a dense topological framework fabricated with 14-connected $Ag_{10}(SO_4)_5$ clusters and L_2 ligands. To our knowledge, the $Ag_{16}(SO_4)_8$ cluster subunits in **1** provides the first example among sulfate-based polynuclear SBUs in coordination polymers that contains more than 8 Ag(I) centers, and the 14-connected $Ag_{10}(SO_4)_5$ in **2** is the highest-connectivity Ag(I) cluster SBU reported to date.[15a-e]

Experimental Section

Materials and Physical Measurements.

All chemical reagents were obtained from commercial resources and used without further purification. 2-(Pyrazin-2-ylthio)-6-(pyridin-2-ylthio)pyrazine (L_1) and 2,6-bis(pyrazin-2-ylthio)pyrazine (L_2) were synthesized following the procedure reported by us recently.[19] IR spectra were recorded on a Perkin-Elmer Spectrum RX I FTIR spectrometer as KBr pellets in the range of 4000-400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. X-ray powder diffraction (XRD) patterns were collected on a Philips Rigaku SmartLab diffractometer using Cu $K\alpha$ radiation in the angular range of 2θ = 10-50 ° with a step size of 0.02°. Thermal gravimetry analysis (TGA) was carried out with an AutoTGA 2950 instrument in a nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was measured with a Perkin-Elmer DSC6 instrument under nitrogen atmosphere. Elemental analysis (C, H, N) was performed by the Analysis and Testing Center of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Synthesis of $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(L_1)_{12} \cdot nH_2O$ (n = 72) (1).

A mixture of 2-(pyrazin-2-ylthio)-6-(pyridin-2-ylthio)pyrazine (L_1) (30 mg, 0.1 mmol) and Ag_2SO_4 (62 mg, 0.2 mmol) were dissolved in a mixed solvent of 3 mL acetonitrile and 3 mL deionized water with stirring at room temperature. After stirring for about 3 hours, the pale-yellow solution was filtrated and

allowed to stand in the dark for slow evaporation. After about three weeks, yellow block crystals of **1** were deposited. Yield: 24.8 mg (32% based on L_1 ligand). Elem. Anal. Calcd (Found) for $C_{156}H_{256}Ag_{28}N_{60}O_{130}S_{38}$: C, 20.25 (20.49); H, 2.74 (2.64); N, 9.08 (9.20) %. IR (KBr) ν/cm^{-1}: 3435(vs), 1566(m), 1390(vs), 1358(m), 1129(vs), 1039(s), 969(m), 853(s),753(vs), 660(w).

Synthesis of $[Ag_{10}(SO_4)_5(L_2)_4(H_2O)_2] \cdot 8H_2O$ (2).

Complex **2** was synthesized in a similar way as that for **1**, except that L_1 is replaced by L_2 (30 mg, 0.1 mmol). Yellow block crystals were obtained in 35% yield (based on L_2 ligand). Elem. Anal. Calcd (Found) for $C_{48}H_{52}N_{24}S_{13}Ag_{10}O_{30}$: C, 19.61 (19.56); H, 1.78 (1.82); N, 11.43 (11.42) %. IR (KBr) ν/cm^{-1}: 3437(s), 1563(s), 1380(m), 1135(vs), 965(m), 851(vs), 662(w).

X-ray Crystallography.

Diffraction data of **1** and **2** were collected on a Bruker Kappa APEX II CCD diffractometer operating at 50 kV and 0.9 mA using Cu-$K\alpha$ radiation (λ = 1.5406 Å) and 50 kV and 30 mA using Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 173 K respectfully. The structures were solved by direct methods with SHELX-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX.[21] The ordered atoms in each structure were refined with anisotropic displacement parameters, while the hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atoms. Some lattice water molecules of complex **1** were located from Fourier maps. The lattice O1W and O2W are normal, O3W, O4W and O6W all exhibit fractional site occupancy ratio of 0.5, while O5W has a quarter of site occupancy. All the H atoms of these lattice water molecules could not be located from Fourier maps, and thus were not included in the final refinement. In complex **2,** O4W is refined with a site-occupancy of 0.5; O6W and O12 are located at the same site, both being assigned half occupancy. Hydrogen atoms of O1W, O2W and O4W were obtained from Fourier-difference maps, while those of O3W, O5W and O6W could not be located.

Result and Discussion

Crystal structure of $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(L_1)_{12} \cdot nH_2O$ (n = 72) (1)

Complex **1** crystallizes in chiral cubic space group $F432$ (No. 209), which is rarely reported in the literature. Just twenty-one hits were found through a thorough CSD (Cambridge Structure Database) search[22] with no filter or restriction imposed. We have taken particular care regarding the correct choice of space group, as other assignments such as $Fm3m$ or F-$43m$ could not lead to an acceptable crystal structure or improvement on the merging R value. In the asymmetric unit of **1**, the S1-containing L_1 ligand and two independent Ag(I) ions (labeled Ag2 and Ag3) occupy general equivalent positions, and one Ag(I) ion (designated as Ag1) lies on a crystallographic 3-fold axis. The S3- and S4-containing sulfate groups are each located on a site of symmetry 3, but the latter exhibits orientational disorder with only its S atom lying on the 3-axis (Fig. 2). The S5- and S6-containing sulfates each has a S–O bond lying in opposite directions on the same 4-fold axis (Fig. 2). Consequently, the S4···Ag1···S3c and the O7–S5···S6–O11 systems lie on 3-fold and 4-fold axes,

respectively. As shown in Fig. 1 and 2, the disordered S4- to S6-containing sulfates have Ag–O$_{disordered}$ bond lengths (2.18(8)-2.63(4) Å) lying within an acceptable range. The binding modes of the sulfate ions are described according to the "Harris
[5] Notation" as X.Y$_1$Y$_2$Y$_3$...Y$_n$, where X is the overall number of metal ions bound by the whole ligand, and each value of Y refers to the number of metal ions attached to sequential donor atoms. Hence for each sulfate ion there will be four values of Y ordered following the Cahn–Ingold–Prelog priority rules, i.e. O before

[10] N.[23] The Ag1 center is tetrahedrally coordinated by three coplanar O1 atoms of symmetry-related sulfates (S3-containing) and one O atom from a S4-containing sulfate. On the other hand, both Ag2 and Ag3 exhibit distorted tetrahedral N$_2$O$_2$-coordination geometry: Ag2 is surrounded by O atoms of the S3- and S4-
[15] containing sulfates and N atoms from separate **L$_1$** ligands, and Ag3 is likewise bound by O atoms from the S5- and S6-containing sulfates and N atoms from separate **L$_1$** ligands (Fig. 1).

Table 1 Crystallographic data of complex **1** and **2**.

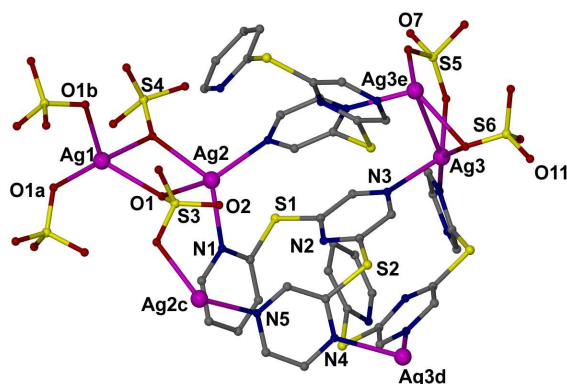| Compound reference	**1**	**2**
Chemical formula	C$_{156}$H$_{252}$Ag$_{28}$N$_{60}$O$_{128}$S$_{38}$	C$_{48}$H$_{44}$Ag$_{10}$N$_{24}$O$_{30}$S$_{13}$
Formula Mass	9254.82	2932.55
Crystal system	Cubic	Monoclinic
a/Å	39.2220(2)	11.6523(6)
b/Å	39.2220(2)	17.9655(9)
c/Å	39.2220(2)	21.6837(8)
α/°	90.00	90.00
β/°	90.00	115.696(2)
γ/°	90.00	90.00
Unit cell volume/Å^3	60337.8(5)	4090.4(3)
Temperature/K	173(2)	173(2)
Space group	F432 (No. 209)	$P2_1/c$ (No. 14)
No. of formula units per unit cell, Z	8	2
Density, ρ_c/g · cm^{-3}	2.038	2.381
Radiation type	CuKα	MoKα
Absorption coefficient, μ/mm^{-1}	17.527	2.765
No. of reflections measured	162810	58355
No. of independent reflections	4459	7199
R_{int}	0.2343	0.0781
Final R_1 values ($I > 2\sigma(I)$)	0.0549	0.0432
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1481	0.1149
Goodness of fit on F^2	1.046	1.031
Flack parameter	-0.02(2)	

[20]

Fig. 1. Coordination geometries of independent Ag(I) centers in complex **1**. Symmetry codes: a −y + 0.5, z, −x + 0.5; b −z + 0.5, −x + 0.5, y; c y, z, x;
[25] d z, −y + 1, x; e x, z, −y + 1.
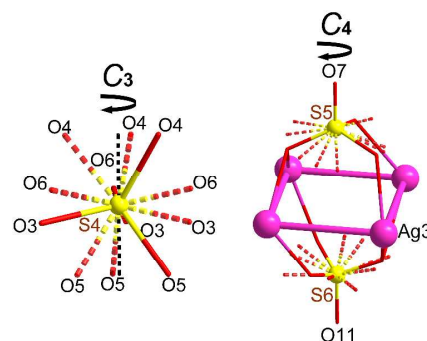

Fig. 2 Illustration of the S4-containing sulfate (left part) that is orientationally disordered about a 3-axis, and the Ag$_4$(SO$_4$)$_2$ cluster containing Ag3 ions and orientationally disordered S5- and S6-containing
[30] sulfates arranged around a 4-axis (right part) in complex **1**. Only one possible orientation of each sulfate ligand is shown by solid bonds.

The S4-containing sulfate lying on a 3-axis links to three symmetry-related Ag2 atoms and one Ag1 on the same axis to form a Ag$_4$ unit (Fig. 3a), and four such units are arranged
[35] tetrahedrally and interconnected through four S3-containing sulfates on 3-axes to furnish a large Ag$_{16}$(SO$_4$)$_8$ cluster (Fig. 3b), considered as the first secondary-building unit (SBU) in complex **1**. Furthermore, four Ag3 atoms arranged around a 4-axis exhibit argentophilic interactions (Ag···Ag = 3.360(2) Å), being
[40] sandwiched by two sulfates (S-5 and S6-containing) through Ag–O bonding to form a Ag$_4$(SO$_4$)$_2$ cluster, regarded as a second

cluster SBU (Fig. 3c). Notably, the 2-pyridyl and the 2-pyrazinyl N atoms of the pendant rings on L_1 are in an *anti* relationship (Scheme 1 and Fig. 4a). L_1 displays a μ_4-bridging mode without participation of the 1-pyrazinyl N atom of the center ring, being

5 bound to Ag2, Ag2c, Ag3 and Ag3d (see Fig. 1) on one $Ag_{16}(SO_4)_8$ and two $Ag_4(SO_4)_2$ SBUs, hence functioning as a 3-connected linkage. Each tetrahedral $Ag_{16}(SO_4)_8$ cluster containing four Ag_4 units at its vertices (Fig. 3b) is surrounded by twelve L_1 ligands, with each Ag_4 holding three L_1 ligands. Thus each

10 $Ag_{16}(SO_4)_8$ can be viewed as a 12-connected node through the 3-connected L_1 peripherally linking to a total of twelve $Ag_4(SO_4)_2$ units around it (Fig. 4). The $Ag_4(SO_4)_2$ SBU is surrounded by eight L_1 that peripherally bridge four $Ag_4(SO_4)_2$ and four $Ag_{16}(SO_4)_8$ units, acting as an 8-connected node. Based on the

15 $Ag_4(SO_4)_2$ and $Ag_{16}(SO_4)_8$ SBUs and the 3-connected L_1, a 3-D framework featuring two kinds of cages is constructed; after subtraction of the van der Waals radii of interior atoms, the small cage $(4.4 \times 4.4 \times 4.4 \text{ Å}^3)$ can be viewed as an octahedral skeleton with six $Ag_4(SO_4)_2$ units at its vertices, while the larger cage

20 $(13.6 \times 13.6 \times 13.6 \text{ Å}^3)$ can be regarded as a cubic framework with eight $Ag_{16}(SO_4)_8$ at its corners (Fig. 4, and Fig. 5). Additionally, each octahedron assembled with $Ag_4(SO_4)_2$ units lies on a 4-axis with a vertex located 2.3 Å above a face of the cube. Taking the $Ag_4(SO_4)_2$ nodes/units capping the six cube

25 faces as new lattice points, the cage composed of the $Ag_{16}(SO_4)_8$ and $Ag_4(SO_4)_2$ nodes can be regarded as a tetrakishexahedron (Fig. 7). In other words, the two types of cages are packed in a NaCl-like lattice, with the small cage at each lattice point of a face-centered cubic (fcc) unit cell, and the large cage placed half

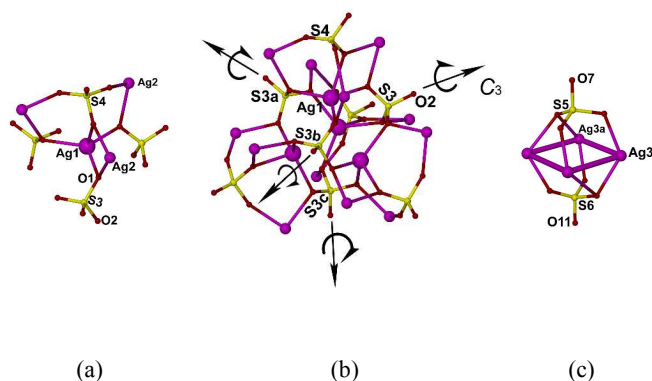30 way between lattice points along an unit-cell edge.

Fig. 3 (a) Cutout showing the Ag_4 unit bridged by a S4-containing sulfato group (4.2110 mode) in complex **1**. (b) Four symmetry-related Ag_4 units bridged by S3-containing sulfates (6.2220 mode) to form the $Ag_{16}(SO_4)_8$ entity (larger purple balls represent Ag1, small ones indicate Ag2.
35 Symmetry codes: a $-x + 0.5, y, -z + 0.5$; b $-x + 0.5, -y + 0.5, z$; c $x, -y + 0.5, -z + 0.5$. (c) $Ag_4(SO_4)_2$ cluster locate on a 4-fold axis consolidated by S5- and S6-containing disordered sulfato groups acting in the 4.2110 mode. Note that each disordered sulfato group is shown in one possible orientation for clarity. Symmetry code: a $x, z, -y +1$
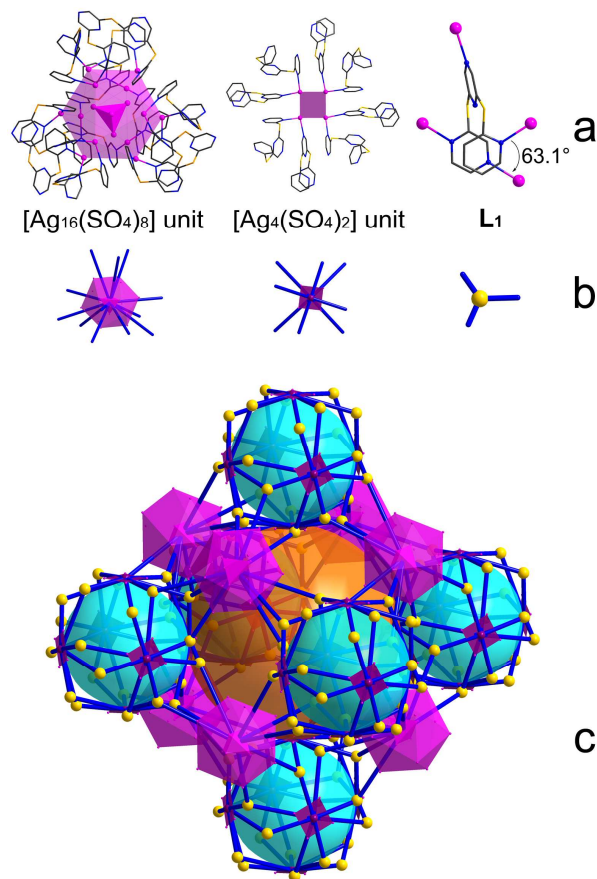

40 **Fig. 4** (a) Two types of SBUs $[Ag_{16}(SO_4)_8, Ag_4(SO_4)_2]$ and the L_1 ligand in complex **1**. All sulfate groups are omitted for clarity. (b) The correspondingly rationalized symbols of the building blocks in part (a). (c) Illustration of the 3-D framework assembled with the building blocks 45 of part (b).
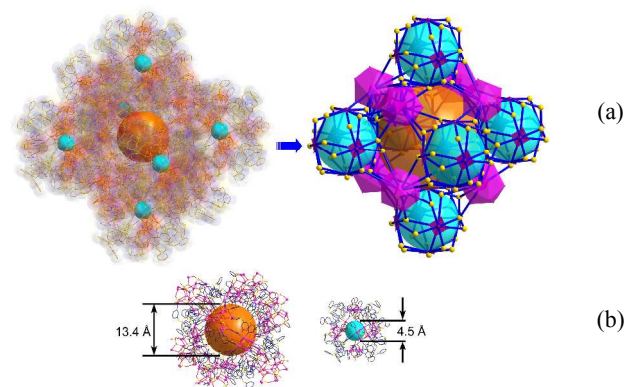

Fig. 5 (a) Illustration of porous framework of complex **1**, which features a large spherical cavity of diameter *ca.* 13.6 Å (light brown ball) symmetrically surrounded by six small spherical cavities of diameter *ca.* 4.4 Å (turquoise ball), and the rationalized framework described in the 50 main text. (b) Size comparison of the two kinds of cavities

Calculations with PLATON showed that the effective solvent-accessible volume in **1** is 18383.3 Å^3 per unit cell, being 30.5 % of the crystal volume.[24] Full-matrix least-squares refinement (R_1 = 0.0549, wR_2 = 0.1480 for 3319 observed reflections $I > 2\sigma(I)$) 55 and Fourier difference maps led to the location of 3.75 water molecules in the asymmetric unit: O1W to O2W are normal,

whereas O3W, O4W and O6W each has ½ site occupancy, and O5W has ¼ site occupancy. Guest water molecule O6W is located inside the small cage, and all others are accommodated within the large cage (Table 2 and Fig. 6).   On the other hand, the TGA weight loss of 14.39% at 116.7 °C (see Supporting information Figure S1) attributed to the release of guest water molecules indicates a hydration number of 74.24 in the structural formula, or (74.24 x 8)/96 $\cong$ 6.19 water molecules in the asymmetric unit. Taking the structural formula as $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(L_1)_{12} \cdot n H_2O$ (n = 72), the calculated and observed elemental analysis results are C, 20.25 (20.49); H, 2.74 (2.64); N, 9.08 (9.20) %. Furthermore, structure refinement with the squeeze procedure[24] (R_1 = 0.0544, wR_2 = 0.1107 for $I >$ $2\sigma(I)$) indicated the presence of 6.32 independent guest water molecules in the asymmetric unit, which is also in good agreement with the value of 72 in the structural formula of complex **1**. The fact that only part of the guest water molecules per asymmetric unit (3.75 out of 6) could be located from least-squares structural refinement can be ascribed to positional disorder and/or high thermal vibration. A sample of complex **1** tested for N_2 sorption showed that its nano-porous host framework is not stable enough to withstand the removing of guest water molecules, and no uptake occurred during activation (see Figure S2).

Treating each L_1 as a 3-connected node, the $Ag_4(SO_4)_2$ and $Ag_{16}(SO_4)_8$ as an 8-connected and 12-connected node, respectively, the 3-D framework of **1** can be rationalized as an unprecedented trinodal (12,8,3)-connected topological structure (Fig. 7) with a Schläfli vertices symbol of $\{4^{12}.8^{54}\}\{4^3\}_{12}\{4^8.6^{12}.8^8\}_3$.[25]

Table 2 Location of lattice water molecules and their intermolecular distances with neighboring water molecules and sulfate ions.

Atom label	Atomic coordinates (× 10^4) and Thermal parameters (Å² × 10^3)				Site occupancy	D(O$_W$···O$_W$') (Å)		D(O$_W$···O) (Å)	
	x	y	z	U_{eq}					
O1W	3389(4)	3622(4)	9220(4)	139(6)	1.00	O2W#4 O3W#5	3.043(3) 2.848(2)	O4#1 O4#2 O6#3	2.901(3) 2.432(3) 2.860(3)
O2W	6233(6)	7921(6)	4822(6)	194(9)	1.00	O1W#6 O4W#3 O5W O3W#7	3.043(3) 3.072(5) 2.458(5) 2.616(3)		
O3W	3858(9)	4578(9)	1801(9)	144(11)	0.50	O1W#10 O2W#7 O4W#7 O5W#10	2.848(2) 2.616(3) 2.644(3) 2.763(3)		
O4W	5480(20)	8207(16)	5571(18)	300(30)	0.50	O2W#9 O3W#7	3.072(5) 2.644(3)	O7#8	3.181(4)
O5W	6700(20)	8300(20)	5000	410(60)	0.25	O2W O3W#7	2.458(5)[26] 2.763(3)		
O6W	4206(6)	5000	4206(6)	241(15)	0.50			O11 O13	3.050(4) 3.171(4)

Symmetry codes: #1 y, –x + 0.5, z + 0.5; #2 –x + 0.5, z, y + 0.5; #3 z, y, –x + 1; #4 y – 0.5, –x + 1, z + 0.5; #5 x, –z + 0.5, y + 0.5; #6 –y + 1, x + 0.5, z – 0.5; #7 –x + 1, –z + 1, –y + 1; #8 z, –x + 1, –y + 1; #9 –z + 1, y, x; #10 x, z – 0.5, –y + 0.5.
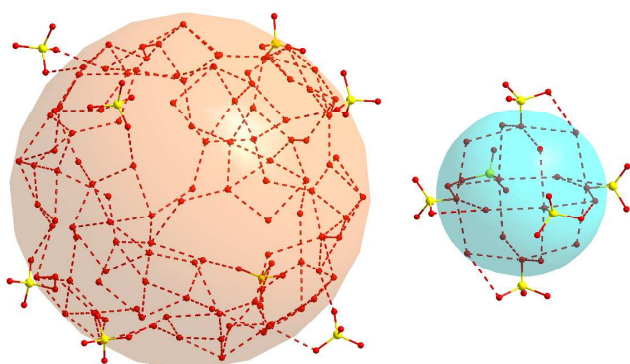

Fig. 6 Water clusters located within the large cavity (left) and small cavity (right) within the coordination framework of complex **1**. Hydrogen bonds involving water molecules and sulfate ions are indicated by broken lines.
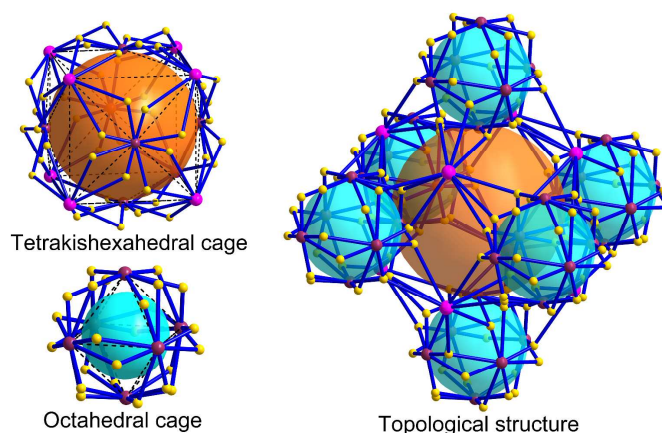

Tetrakishexahedral cage

Octahedral cage

Topological structure

Fig. 7 Cutout showing the rationalized tetrakishexahedral and octahedral cages in **1** by treating the $Ag_{16}(SO_4)_8$ unit as a 12-connected node (Ag represented by large purple ball), the $Ag_4(SO_4)_2$ unit as an 8-connected node (Ag represented by medium plum ball) and the L_1 ligand as a 3-connected node (small yellow ball) in **1**, and the rationalized 3-D topological structure corresponding to Fig. 4 and Fig. 5.

Crystal structure of $[Ag_{10}(SO_4)_5(L_2)_4(H_2O)_2] \cdot 8H_2O$ (2)

Ligand L_2 is a structural analogue of L_1 with the lone pyridyl ring of the latter replaced by a pyrazinyl ring. Interestingly, a new framework based on an unexpected 14-connected decanuclear

5 Ag(I) cluster $Ag_{10}(SO_4)_5$ was obtained in 2 through reaction of L_2 with silver(I) sulfate in a similar procedure as that for complex 1. In crystal structure of 2, the asymmetric unit contains five independent Ag(I) ions (labeled Ag1 to Ag5) that exhibit different coordination geometries. As shown in Fig. 8a, Ag1 is

10 coordinated by two N atoms of separate L_2 ligands and one sulfate O atom, Ag4 is surrounded by three sulfate O and two N atoms, adopting a distorted pyramidal N_2O_3-coordination geometry, while Ag2, Ag3 and Ag5 are all in distorted tetrahedral coordination environments involving sulfate groups: N_3O- ligand

15 set for Ag2, NO_3-set for Ag3, and N_2O_2-set for Ag5 with one η^1-O from an aqua ligand. The oxygen site coordinated to Ag2 is equally populated by aqua molecule O6W and the O12 atom of the S7-containing sulfate. Notably, sulfate ligand S7 displays offset two-fold positional disorder to bridge two Ag_5 subunits

20 across an inversion center (Fig. 8b). Herein the sulfate anions exhibit 2.1100 (S5-), 3.2110 (S6-) and 3.1110 (S7-containing) bridging modes to connect ten Ag(I) ions to form a new $Ag_{10}(SO_4)_5$ cluster differing from the Ag_{16} and Ag_4 units in 1.
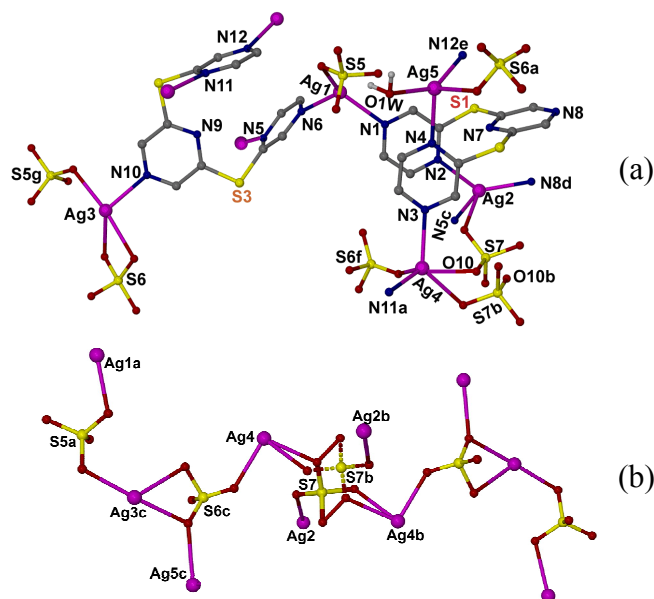
Treating the $Ag_{10}(SO_4)_5$ aggregation as a SBU, the S1- and S3-containing L_2 respectively function as a 4- and a 3-connected

35 linkage between the Ag_{10} cluster units. Each $Ag_{10}(SO_4)_5$ cluster is surrounded by fourteen L_2 (eight S1- and six S3-containing L_2, Fig. 9), which peripherally link to 14 adjacent $Ag_{10}(SO_4)_5$ units to furnish an unprecedented trinodal (3,4,14)-connected topological

structure with a Schläfli vertices symbol of

40 $\{4^{32}.6^{46}.8^{13}\}\{4^3\}_2\{4^6\}_2$ (Fig. 10).[25] Additionally, a total of 4 lattice water molecules per asymmetry unit are embedded within the interstice of the 3-D framework in **2**, being consistent with the value of 5 calculated from TGA measurement (6.12% weight lost at 123.7℃, supporting information Figure S1), which is further

45 supported by elemental analysis (see experimental section). Herein, the $Ag_{10}(SO_4)_5$ SBU can be viewed as a 14-connected node that has a higher rank than the 8- and 12-connected ones in **1**.
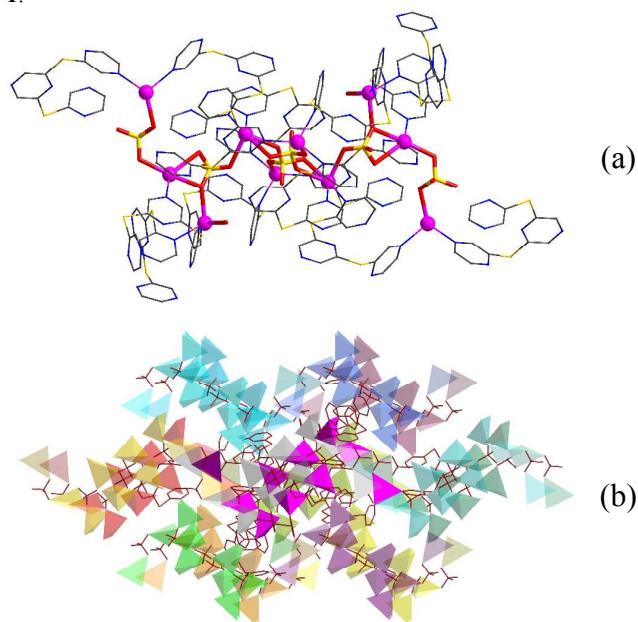
Both independent L_2 ligands (S1- and S3-containing) in complex

55 **2** adopt a similar configuration with slightly different dihedral angles [21.79(2)° and 29.74(3)°, respectively] between each pair of pendant pyrazinyl rings. Like L_1 in complex **1**, the 1-pyraziny N atom of the central ring in both independent L_2 ligands does not partake in coordination, but all other pyrazinyl N atoms

60 involve Ag–N bonding, exhibiting a similar μ_5-bridging mode. The pair of 2-posional pyrazinyl N atoms on the pendant rings are in an *anti* relationship (Scheme 1), but the angle between two Ag–N···N–Ag vectors on each pair of pendant pyrazinyl rings is much different [55.2(2)° for S1-containing L_2, 92.1(3)° for S3-
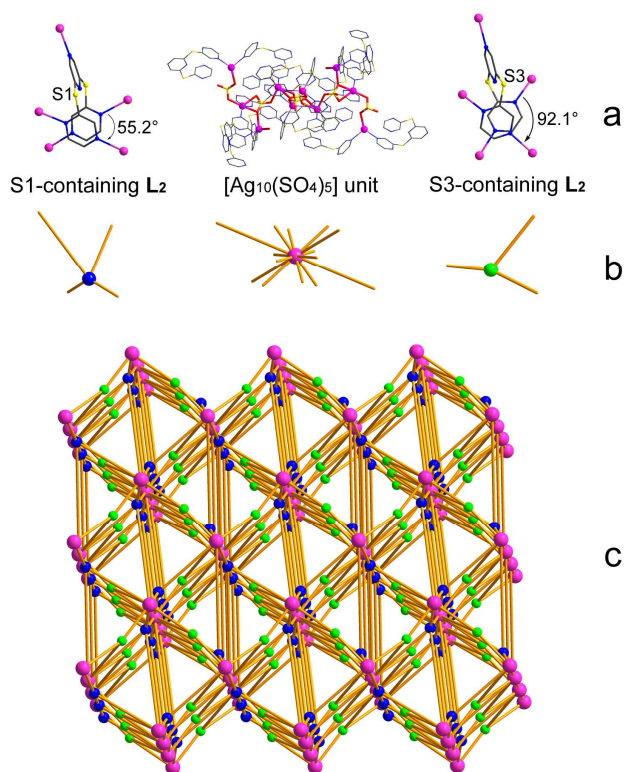
65 containing L_2] (see Fig. 10).

Fig. 10 (a) $Ag_{10}(SO_4)_5$ SBU and coordination modes of two independent L_2 ligands in complex **2**. (b) Rationalized connective nodes corresponding to part (a). (c) Topological 3-D net of complex **2**.

High-nuclearity Ag(I) cluster formation and self-assembly in complexes 1 and 2

The high charge density, tetrahedral geometry and flexible ligation modes of SO_4^{2-} account for its wide use as a versatile bridging co-ligand in the construction of a large variety of metal coordination complexes.[20] In this study the sulfate anions exhibit variable 4.2110 and 6.2220 modes in **1** and 2.1100, 3.2110 and 3.1110 modes in **2**, while the oligo-α-heteroarylsulfanyl ligands L_1 and L_2 display μ_4- and μ_5-bridging modes, respectively, to link Ag(I) ions in different directions. The coordination geometries of Ag(I) in **1** and **2** can be designated by a simplified AgN_xO_y symbol involving up to four sulfates and/or two L_1/L_2 ligands around a metal center (O_4-, N_3O-, N_2O_2-, N_2O-, NO_3- and N_2O_3-, see Fig. 1 and 5a). With those flexible ligands and anionic co-ligands, a 3-D nano-porous framework is assembled with 12-connected $Ag_{16}(SO_4)_8$ and 8-connected $Ag_4(SO_4)_2$ clusters in complex **1**, and a dense topological framework is fabricated with the 14-connected $Ag_{10}(SO_4)_5$ in complex **2**. Chen *et al.* reported a large Ag_8 cluster stabilized by sulfates that combines with 2,2'-bis(2-pyridyl)ethane to give a 2D coordination framework $\{[Ag_8(SO_4)_4(2,2'-bpe)_5] \cdot 10H_2O\}_n$.[15d] Ma *et al.* generated a Ag_7 cluster consolidated by a polycarboxylate anion and a multidentate pyridyl-based ligand, which functions as a 12-connected node to form 3D coordination polymer $[Ag_7(4,4'-tmbpt)(HL)_2(L)(H_2O)]_n$ (4,4'-tmbpt = 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole, H_3L = 5-(4-carboxybenzyloxy)isophthalic acid).[15e] To date, there is no example of any coordination polymer built with sulfate-based Ag(I) cluster SBUs having a nuclearity larger than 8 in the literature.[7e, 15] A thorough CSD search[22] also showed that just

thirty-one hits of silver(I) sulfato complexes were found, and complex **1** is the first sample that crystallizes in the rare chiral $F432$ space group.

The pair of pendant heteroaromatic rings of L_1 in **1** bear a *syn* relationship with respect to the central pyrazinyl ring, such that the 2-positional N atoms adopt *exo* orientations to coordinate to surrounding silver(I) centers, thereby generating a centroid-scattered, nano-porous supramolecular architecture assembled with $Ag_{16}(SO_4)_8$ and $Ag_4(SO_4)_2$ SUBs. In contrast, replacing the pyridyl ring on L_1 by a pyrazinyl ring provides more bonding sites for L_2, which accounts for the relatively dense 3D coordination framework in **2**.

Conclusions

In summary, three novel sulfate-based Ag(I) clusters units, namely $Ag_{16}(SO_4)_8$, $Ag_4(SO_4)_2$ and $Ag_{10}(SO_4)_5$, have been identified as structure-building blocks in two coordination polymers $[Ag_{16}(SO_4)_8][Ag_4(SO_4)_2]_3(L_1)_{12} \cdot nH_2O$ ($n = 72$) (**1**) and $[Ag_{10}(SO_4)_5(L_2)_4(H_2O)_2] \cdot 8H_2O$ (**2**) synthesized from the reaction of silver(I) sulfate under mild conditions with conformationally variable oligo-α-heteroarylsulfanyl ligands L_1 and L_2, respectively.

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