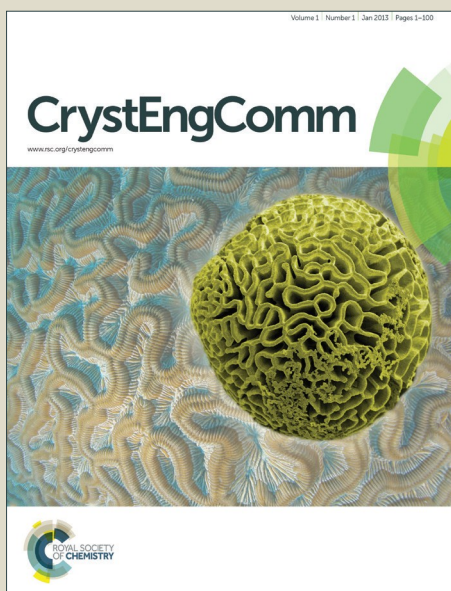


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ARTICLE

Inverted molecular cups: 1-D and 2-D Ag(I) coordination polymers from resorcinarene bis-thiacrowns

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Resorcinarene bis-thiacrown hosts **1–3** were prepared and crystallized with silver trifluoroacetate yielding one and two dimensional Ag coordination polymers. The complexation of silver in *exo*-cavity fashion folds the thiacycrown bridges inwards transforming the resorcinarene hosts into inverted molecular cups. The silver cations were coordinated to the resorcinarene ligands and trifluoroacetate anions, which act as monodentate or bidentate bridging ligands between the metal ions. Argentophilic Ag...Ag (2.93–3.38 Å) interactions supported by two bridging carboxylate anions were found in two of the structures, whereas longer Ag...Ag distances were observed if only one anion connected the silver cations. Both the anion and the resorcinarene lower rim alkyl chain had a role in the crystal packing, as indicated by the different metal coordination and packing tendencies of *C*-ethyl and *C*-pentyl bis-thiacrowns. A typical packing motif observed was a polymer chain with end-to-end joints and two Ag ions with tetrahedral coordination geometries. Solvent channels or discrete solvent pockets between the polymer layers were observed in all structures.

Introduction

Coordination polymers are solid networks composed of metal ions and organic ligands connecting the metals to continuous, polymer-like assemblies.¹ Coordination polymers form versatile functional materials, such as porous metal-organic frameworks (MOFs) for gas storage² and heterogeneous catalysis,^{1b,3} conducting and semiconducting materials,^{1a,4} and luminescent solids.⁵ Luminescence of coordination polymers may be caused by, for example, aurophilic and argentophilic interactions,⁶ which are weak attractive interactions of group 11 metal cations with closed d¹⁰ shells (Au(I) and Ag(I), respectively).⁷ These interactions are indicated by a short metal...metal contact below the van der Waals radius of two metal atoms, for example 3.40 Å for Ag.

Macrocyclic ligands are relatively rarely used in coordination polymers, even though several examples of coordination polymers have been achieved with thiacycrown ethers and mixed-donor macrocycles.^{8,9,10} Calixarenes and resorcinarenes are macrocyclic hosts which are commonly utilized for inclusion complexation of ions and other small guest molecules and as building blocks for molecular capsules.¹¹ Their inherent bowl-shape promotes the assembly into discrete metal-coordinated capsules and polyhedra¹² but occasionally the formation of coordination polymers have been observed.^{13,14} Crystalline Ag(I) coordination polymers

have been obtained with cyano-functionalized calix[4]arenes,¹⁵ as well as with thiocalix[4]arenes¹⁶ with cyano,¹⁷ pyridyl¹⁸ and carboxylate¹⁹ substituents. Resorcinarene based coordination polymers are even more rare, only a 1-D silver coordination polymer of cyano-functionalized resorcinarene,²⁰ a 1-D copper coordination polymer of pyridine functionalized resorcinarene,²¹ and the 1-D silver and gold polymers of tetraphosphinito²² and tetrakis(thiophosphinato)²³ resorcinarenes are known. In tetrakis(thiophosphinato) Au(I) coordination polymer the 1-D chains form via aurophilic interactions, whereas argentophilic interactions among calixarene-type ligands have only been seen in 1-D calix[4]arene tetracarboxylate Ag(I) polymer.²⁴

Resorcinarene bis-crowns and bis-thiacrowns have been designed to host two metal ions within their concave binding sites formed by the resorcinarene core and crown ether bridges.^{25,26} Although the resorcinarene macrocycle is permanently fixed in a *boat* conformation, there is some flexibility in the conformation seen as twisting and tilting of the macrocycle ring in a variety of crystal structures.^{25a,e,f,26} This, together with the flexibility of the bridges, enables complexation of different sized alkali metal cations (K(I), Rb(I), Cs(I))^{25a-c,f} and Ag(I)^{25d-f,26} inside the binding pockets by *endo*-cavity coordination. *Exo*-cavity coordination outside the binding pockets, which has been observed for the smallest cations Na(I)^{25a} and Ag(I),²⁶ requires the crown bridge to fold inwards transforming the resorcinarene into an inverted molecular cup (Fig. 1). Previously, *C*-ethyl resorcinarene bis-thiacrown **1** has produced an interesting dimeric 1:2 host:Ag complex with one *endo*-cavity and one *exo*-cavity bound silver cation (Fig. 1, structure 1-A).²⁶

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Electronic Supplementary Information (ESI) available: synthesis and characterization data, crystallographic figures and tables, CSD searches. See DOI: 10.1039/x0xx00000x

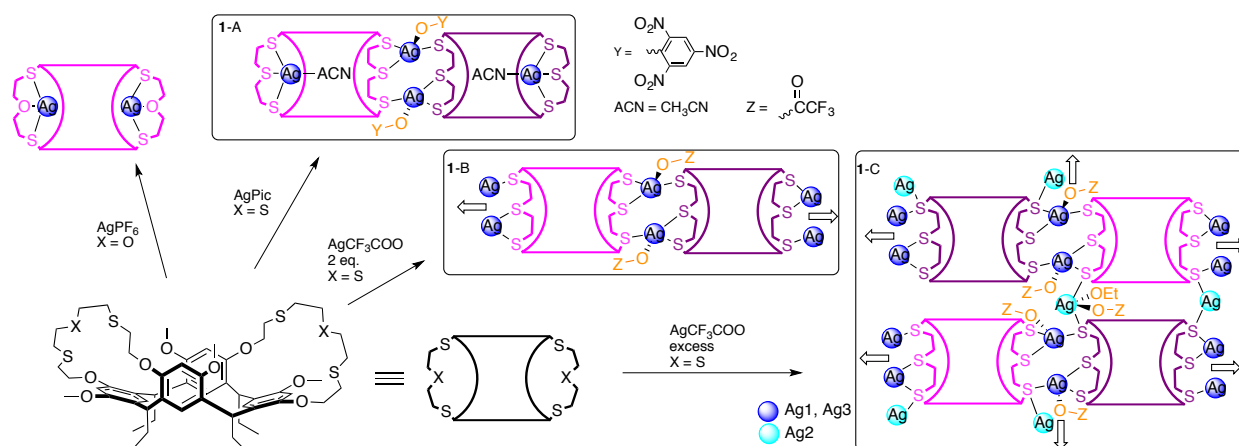


Fig. 1 Schematic presentation of the evolution from a discrete *endo*-cavity complex (top left) and *endo/exo* dimer complex (**1-A**)²⁶ into 1-D and 2-D coordination polymers (**1-B** and **1-C**, respectively) using resorcinarene bis-thiacrown ligands and silver salts (Ag1, Ag2, Ag3 refer to crystallographic numbering).

In this paper, we describe the utilization of resorcinarene bis-thiacrown (**1–3**) based inverted molecular cups as macrocyclic ligands in the construction of 1-D and 2-D Ag(I) coordination polymers. The number of the donor atoms at the thiocrown bridge as well as the lower rim alkyl chain length were varied in order to explore the effect of the host structure for the composition and packing of the polymer network. Trifluoroacetate was used as a counteranion in all experiments to investigate the effect of the coordinating anion and the resorcinarene ligands on Ag(I) coordination geometry.

Results and discussion

In order to enlighten the competitive role of metal coordination versus the self-assembly governed by the hydrophobic lower rim chains on crystal packing, amphiphilic resorcinarene bis-thiacrowns **2** and **3** with *C*-pentyl chains were prepared as a comparison to resorcinarene **1** (Fig. 2, See SI). The resorcinarene bis-thiacrowns **1** and **2** have two oxygen donors and three central sulfur donors connected by ethylene units in each bridge. The bridges of resorcinarene bis-thiacrown **3** are approximately 2 Å shorter and contain only two sulfur donors.

Resorcinarene bis-thiacrowns **1–3** were crystallized with an excess of silver trifluoroacetate from dichloromethane-ethanol solution, since excess salt enhances the crystallization and has previously produced mainly 1:2 host:metal complexes^{25,26}. The experiments yielded two different coordination polymers for resorcinarene **1**, a 1-D coordination polymer **1-B** and a two dimensional coordination polymer **1-C** (Fig. 1). Resorcinarenes **2** and **3** crystallized as 2-D coordination polymers (**2-A** and **3-A**; Fig. 3).

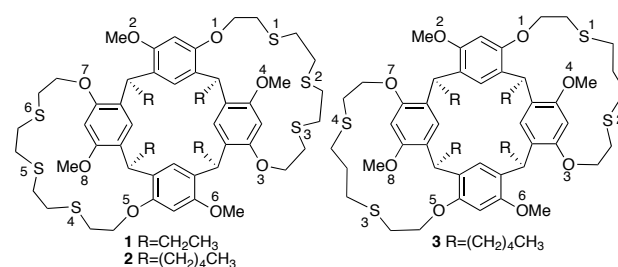


Fig. 2 Resorcinarene bis-thiacrowns **1–3** showing selected crystallographic numbering for the right-handed enantiomer.

Structure 1-B

The crystallization of *C*-ethyl bis-thiacrown **1** with an excess of silver trifluoroacetate produced 1-dimensional coordination polymer **1-B** (in P-1, Fig. 4) with 1:2 resorcinarene to silver ratio as in the previously published structure **1-A**²⁶. In the structure **1-A** the propagation of a coordination polymer was blocked by the *endo*-cavity complexation of half of the Ag(I) cations. In **1-B**, all of the silver cations are coordinated tetrahedrally by *exo*-cavity binding mode to the inverted molecular cup, which connects the resorcinarenes to polymeric (Ag₂(μ-L₁)(CF₃COO)₂)_n (L₁ = resorcinarene **1**) chains with direct end-to-end joints between the resorcinarene hosts (Fig. 1).

The asymmetric unit of the structure **1-B** contains four silver trifluoroacetates and two molecules of **1** with slightly different thiocrown bridge and resorcinarene macrocycle conformations. The coordination to Ag1 is essentially identical to the tetrahedral *exo*-cavity binding in **1-A**. Three coordination bonds are formed to the bridge sulfurs S1, S2 and S3¹ of the neighbouring host (2.55–2.63 Å, ¹2-*x*,3-*y*,_{-z}, Table S-

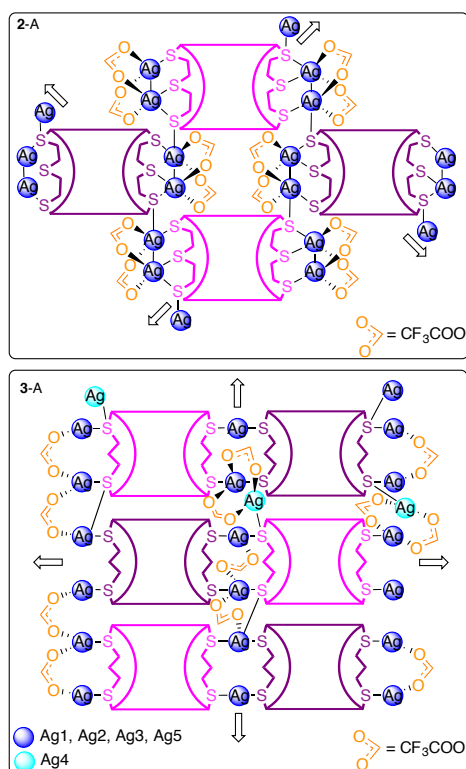


Fig. 3 Schematic presentation of the 2-D coordination polymers **2-A** (top) and **3-A** (bottom) showing the zigzag arrangement of resorcinarene ligands in **2-A** and a direct end-to-end arrangement of ligands in **3-A**. Ag1–Ag5 refer to crystallographic numbering.

4). The fourth bond forms to the trifluoroacetate anion (O9...Ag1 2.421(8) Å). The dihedral angles of the S-C-C-S units in the bridge from S1 to S2 and from S2 to S3 are close to optimal *gauche* (staggered) and *anti* conformations, respectively, and the Ag1...Ag1¹ distance of 6.24 Å is also close to the Ag...Ag distance in **1-A** (6.18 Å).

The coordination of Ag2, Ag3 and Ag4 is also tetrahedral with three coordination bonds to the bridge sulfurs and one to the anion. The torsion angles of the coordinating S-C-C-S units are close to an ideal *gauche* conformation leading to Ag3...Ag3 (1-x,-y,1-z) distance of 5.32 Å, and Ag2...Ag4 distance of 4.78 Å, which is the shortest Ag...Ag distance found in this structure. The differences in the thiocrown bridge conformation (*gauche* and *anti* or only *gauche*) indicate that the resorcinarene bis-thiocrowns have some degree of flexibility in their binding site, which leads to the variation of Ag...Ag distances.

Structure 1-C

The crystallization of **1** with a tenfold excess of silver trifluoroacetate produced the structure **1-C** (P-1) with a 1:3 host:Ag ratio (Fig. 5). The coordination to Ag1 and Ag3 repeat the tetrahedral geometry observed in structure **1-B**, which connects the bis-thiocrowns into polymeric chains (Ag₂(μ-L₁)(CF₃COO)₂)_n (L₁ = resorcinarene **1**) with direct end-to-end joints. In **1-C**, however, both bridges have symmetrical conformation with one S-C-C-S unit in a *gauche* and the other in an *anti* conformation, respectively.

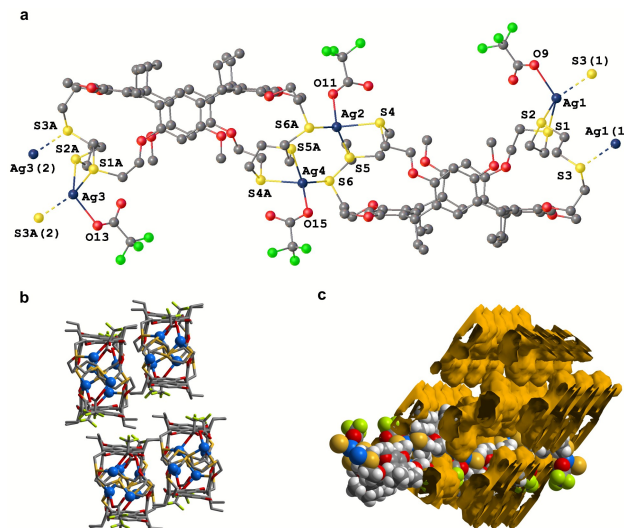


Fig. 4 The asymmetric unit of 1-D coordination polymer **1-B** (a), dashed bonds indicate the continuation of the coordination polymer chains (b) and a coordination polymer chain showing solvent filled channels (c). Hydrogen atoms, disorder and solvents are excluded for clarity. Symmetry operations: $2-x,3-y,-z$; $1-x,-y,1-z$; $+x,1+y,-1+z$; $+x,1+y,+z$.

The third silver, Ag2, connects the polymer chains into two dimensional stepped sheets, as it is coordinated to S3 (2.600(2) Å) on both sides of the polymer chain with a relatively short Ag2...Ag1 (1-x,1-y,-z) distance of 4.03 Å and to S4 of the adjacent inverted molecular cup (2.620(2) Å, -x,2-y,1-z; Fig. 1, Fig. 5c). Bonds to trifluoroacetate (O11, 2.287(6) Å) and solvent ethanol (O100, 2.358(10) Å) complete the tetrahedral coordination sphere.

Structure 2-A

Structure **2-A** (P₂₁/n) was obtained by crystallizing *C*-pentyl bis-thiacrown **2** with excess (approximately 5 eq) of silver trifluoroacetate. Repeated experiments with varying, yet always excess amount of silver salt produced consistently the same structure. The asymmetric unit constitutes of one molecule of **2** and four silver trifluoroacetates forming a two-dimensional coordination polymer (Fig. 6). In addition, a partially occupied AgCF₃COO is located inside the resorcinarene cavity, which shows that despite the *exo*-binding to the inverted cup, the flexibility of the macrocycle allows simultaneous guest inclusion into the resorcinarene cavity.

The coordination to silver differs remarkably from the structures of resorcinarene **1**. Instead of a tetragonal geometry, each network forming silver cation (Ag1–Ag4) has distorted trigonal bipyramidal coordination geometry. Silver cations Ag1 and Ag2 are coordinated by S...Ag bonds (2.46–2.70 Å) to S1, S2 and S3 and additionally to two bridging trifluoroacetate anions (2.23–2.41 Å), and to a sulfur of an adjacent bis-thiacrown (S6; 1/2-x,1/2+y,1/2-z). A short argentophilic metal...metal contact of 2.9341(9) Å between Ag1 and Ag2 completes the coordination sphere of the cations (Fig. 3, Fig. 6a). The dihedral angle of the crown bridge S1-C35-C36-S2 unit is only -26(2)° whereas the S2-C37-C38-S3 torsion of -66.5(8)° is close to an ideal *gauche* conformation.

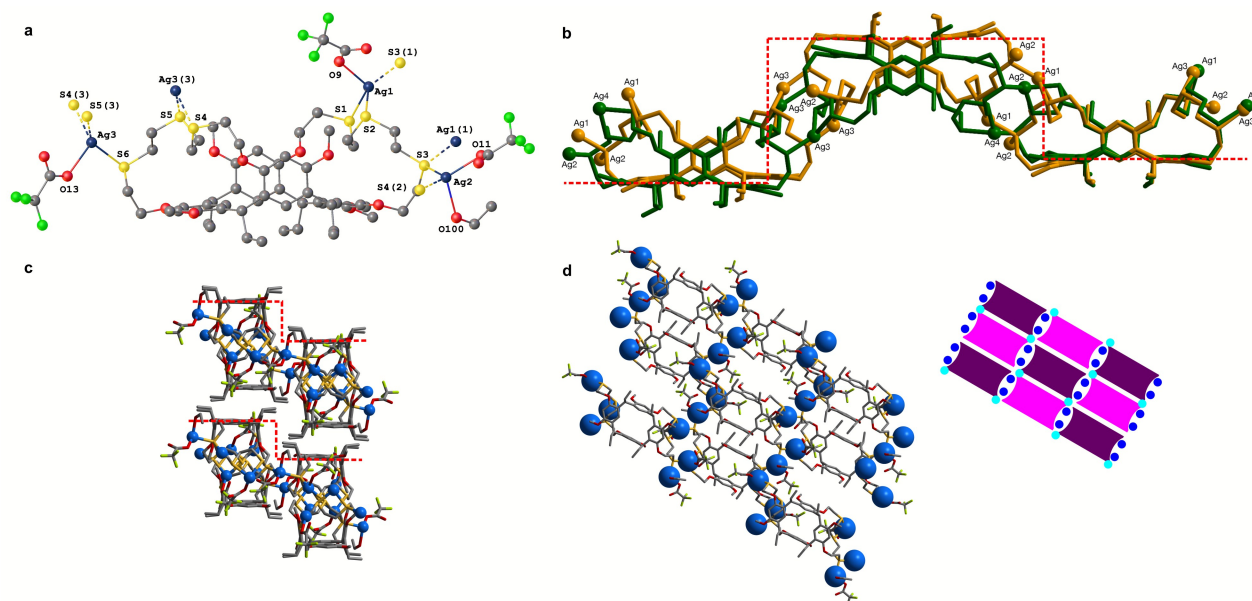


Fig. 5 The asymmetric unit of **1-C** (a), dashed bonds indicate the coordination network. A structure overlay of **1-C** (yellow) with **1-B** (green) highlights the stepped front view of polymer chains (b). A side view of packing shows the stepped shape of the polymer sheets (c). A 2-D sheet with Ag as blue spheres and a diagram showing the left-handed and right-handed resorcinarenes with light and dark purple, respectively, and Ag2 as turquoise spheres (d). Hydrogen atoms, disorder and solvents are excluded for clarity. Symmetry operations: $1-x, 1-y, -z$; $1-x, 2-y, -z$; $3-x, 2-y, 1-z$; $-x, 2-y, 1-z$.

The coordination of Ag3 and Ag4 to the second thiocrown bridge (S4, S5, S6) is similar resulting in a Ag3...Ag4 contact of 2.9643(9) Å. The crown bridge is disordered over two positions, which allows partially occupied Ag5 to be bound inside the resorcinarene cavity by S5...Ag5 (2.540(6) Å) and η^2 metal...arene coordination (2.49–2.65 Å). Additionally, Ag5 is coordinated to the counter anion (Ag5...O17 2.19(4) Å). The dihedral angle of S4-C43-C44-S5, 45.8(16)°, is less strained than in the first bridge. The core of the resorcinarene is pronouncedly twisted from an ideal boat conformation with twist and tilt angles of 22.4° and 28.0°, respectively (Fig. 6b). The reason for this is likely the high Ag:host ratio and simultaneous *endo*- and *exo*-cavity binding.

The crystal packing of two dimensional sheets consists of polymeric (Ag₂[μ -L₂][μ -(CF₃COO)₂])_n chains (L₂ = resorcinarene **2**), which continue along the crystallographic *a* axis. The second polymer dimension consists of (Ag₂[μ -L₂])_n chains forming a zigzag pattern along the *b* axis (Fig. 3, Fig. 6c). In contrast to other bis-thiacrown structures, the polymer sheets consist of a single resorcinarene enantiomer.

Structure 3-A

The binding site of *C*-pentyl resorcinarene bis-thiacrown was modified in order to test the effect of a smaller cavity and fewer sulfur donors for silver coordination and further to the coordination polymer formation. Bis-thiacrown **3** was crystallized with excess of silver trifluoroacetate (5 or 10 eq), which gave a two dimensional coordination polymer **3-A** (P-1) with 2:5 host:Ag ratio. The asymmetric unit contains two molecules of **3**, one of which is pronouncedly twisted, five silver trifluoroacetates, and ethanol and water solvents (Fig. 7a-b). Despite the difference in the number of sulfur donors, exclusive *exo*-cavity binding of Ag(I) to the inverted molecular

cups is observed. The crown bridges of **3-A** are fully extended to *anti* conformation between S-C-C-C-S units and the opposing vertical aryl rings are leaning inwards with angles of -2.1 and -12.4°, respectively, which blocks the resorcinarene cavity.

The coordination pattern of the tetrahedrally coordinated silver cations is relatively complex (Fig. 3, Fig. 7). Ag1, Ag2 and Ag5 connect two bis-thiacrown enantiomers into a chain with direct end-to-end joints as in **1-B** and **1-C**. The role of the anion in coordination, however, is different with each cation. Ag1 and Ag2 form two coordination bonds to the crown bridge sulfurs (2.46–2.57 Å) and two coordination bonds with altogether three trifluoroacetate anions, one of which acts as a bridging ligand between the cations inducing Ag1...Ag2 distance of 4.92 Å. Ag5 is coordinated to three sulfur donors in three different ligands (2.49–3.02 Å) and via a bridging anion (O17...Ag5 2.362(6) Å) to Ag2 (1+x,+y,+z) of the adjacent chain Ag2...Ag5 distance being 4.09 Å. Ag3 is coordinated between two resorcinarene ligands in a chain adjacently to a symmetry generated Ag3 (1-x,-y,1-z). The tetrahedral coordination geometry of Ag3 is completed with two Ag...S and two Ag...O bonds (Ag...O 2.26–2.42 Å) to two bridging anions, which connect Ag3 to a second silver cation Ag4 forming a long argentophilic interaction between Ag3...Ag4, 3.3837(7) Å (Fig. 3). The remaining coordination bonds of Ag4 are to S1 (2.4552(18) Å) and O4 (2.598(5) Å) of the resorcinarene ligand. Thus, each sheet in **3-A** has both direct end-to-end joints as in structures **1-B** and **1-C**, and argentophilic interactions formed by two bridging trifluoroacetate and bis-thiacrown ligands as in structure **2-A**.

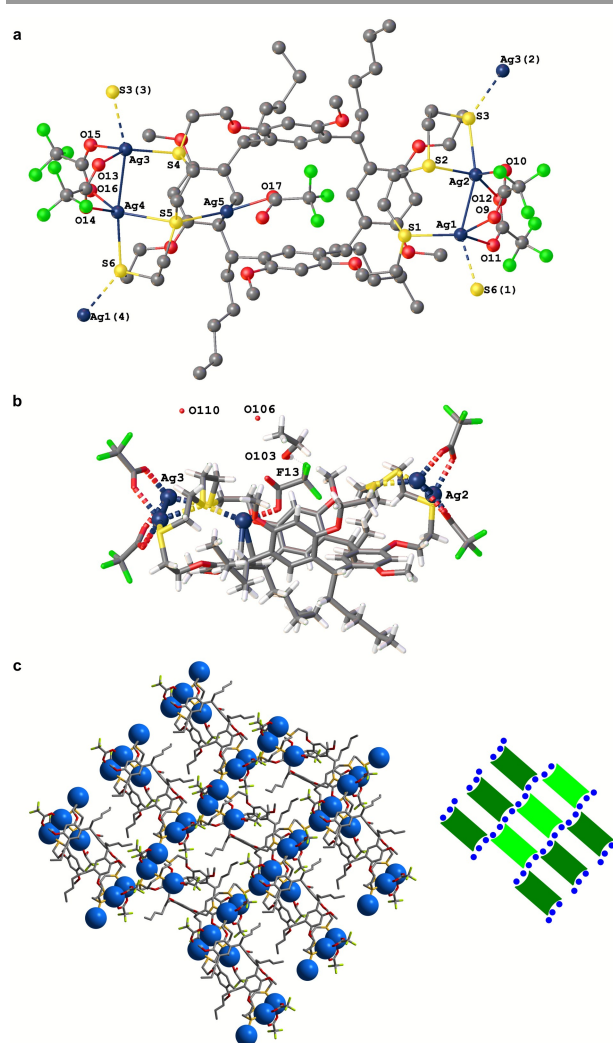


Fig. 6 The asymmetric unit of **2-A** with hydrogen atoms, disorder and solvents excluded (a). Dashed bonds indicate the coordination network. A front view of the structure indicates twisting of the resorcinarene macrocycle (b). Packing of the 2-D sheets with Ag shown as blue spheres (c). A packing diagram shows up and down facing resorcinarenes (same enantiomer) with light and dark green, respectively. Symmetry operations: $1/2-x, 1/2+y, 1/2-z$; $3/2-x, -1/2+y, 1/2-z$.

Void space and solvates

Crystal packing of the polymer chains or sheets in all structures creates voids, which are filled by disordered solvents and crown bridges or alkyl chains of the resorcinarene bis-thiacrowns. The resorcinarene chains and sheets in the structures **1-B** and **1-C** have a stepped pattern when viewed from the front (Fig. 5b). The void space on top of each resorcinarene in **1-B** is filled by a dichloromethane and an ethanol, or two molecules of ethanol forming hydrogen bonds to anions (O100...O16, O123...O12, 2.78–2.91 Å). In **1-C**, the resorcinarene cavity is more open and a disordered ethanol molecule (O109) is located deeper in the cavity of the resorcinarene. In **1-B** the solvents (dichloromethane, water and a severely disordered solvent, which most likely is ethanol) fill also the lower rim interface of the resorcinarene bis-thiacrowns forming solvent channels running diagonally relative to the polymer chain direction (Fig. 4c), and comprising 23.8 % of the unit cell volume. In **1-C**, the ethanol and water solvents are confined to smaller pockets between

the polymer sheets reducing the solvent filled space to 15.1 % of the unit cell volume.

The polymer sheets in the structure **2-A** are relatively flat, since the resorcinarenes are in a staggered alignment and adopt a twisted conformation (Fig. 6b). The solvent filled space is relatively small as the lower rim C-pentyl chains bend to fill the voids between the resorcinarene molecules. The solvents, disordered water and ethanol, are confined in the pockets between the polymer layers formed by the cavity of resorcinarene with partially occupied AgCF_3COO and the lower rim of the resorcinarene of the next layer (12.4% of the unit cell volume).

In the structure **3-A** the resorcinarenes are more densely packed, whereas the silver cations are arranged in a looser assembly. The alkyl chains of the resorcinarenes are partly interdigitated, and form a lower rim interface between the polymer layers (Fig. 7d) to which one of the anions coordinated to Ag1 points as well. Ethanol and water are located within the interface as long hydrogen bonded chains composed of ten ethanol and two water molecules (14.5 % of the unit cell volume), and are confined by hydrogen bonds to the mono-coordinated anions (Fig. 7b, O10...O109, 2.847(12) Å, <DHA 127.5°).

Conclusions

Resorcinarene bis-thiacrowns form willingly coordination polymers with silver trifluoroacetate. The sulfur donors in each thiacycrown bridge are favourably arranged to allow the formation of so called inverted molecular cups, which can coordinate up to four silver cations in *exo*-cavity fashion creating various metal-organic frameworks. The structures are unique among resorcinarene and calixarene complexes and present the first examples of resorcinarene based coordination polymers with argentophilic contacts (**2-A**, **3-A**). The formation of 1-D and 2-D coordination polymers with short Ag...Ag contacts depends on the structure and conformational properties of the resorcinarene ligand, such as twisting of the thiacycrown core and conformation of the thiacycrown bridges. In addition, bidentate coordination to the carboxylate anion seems to be important for inducing the argentophilic contacts as the structure searches from the Cambridge Structural Database indicated that bridging carboxylate anion is often associated with short Ag...Ag contacts (see SI). The S-C-C-S ligands, on the other hand, have rarely produced short Ag...Ag contacts below 3.4 Å.^{9,27}

The shorter alkyl chain *C*-ethyl bis-thiacrown **1** formed 1-D and 2-D coordination polymers (**1-B** and **1-C**) with host:metal ratios of 1:2 and 1:3, respectively. In both structures direct end-to-end arranged polymer chains with tetrahedrally coordinated silver cations and monodentate carboxylate anions were present. In the 2-D polymer structure **1-C**, the adjacent chains are connected by a third Ag cation. *C*-pentyl bis-thiacrown **2** had interesting ligand properties, since the longer alkyl chains allowed the organization of the resorcinarenes into staggered 2-D sheets, in which the space

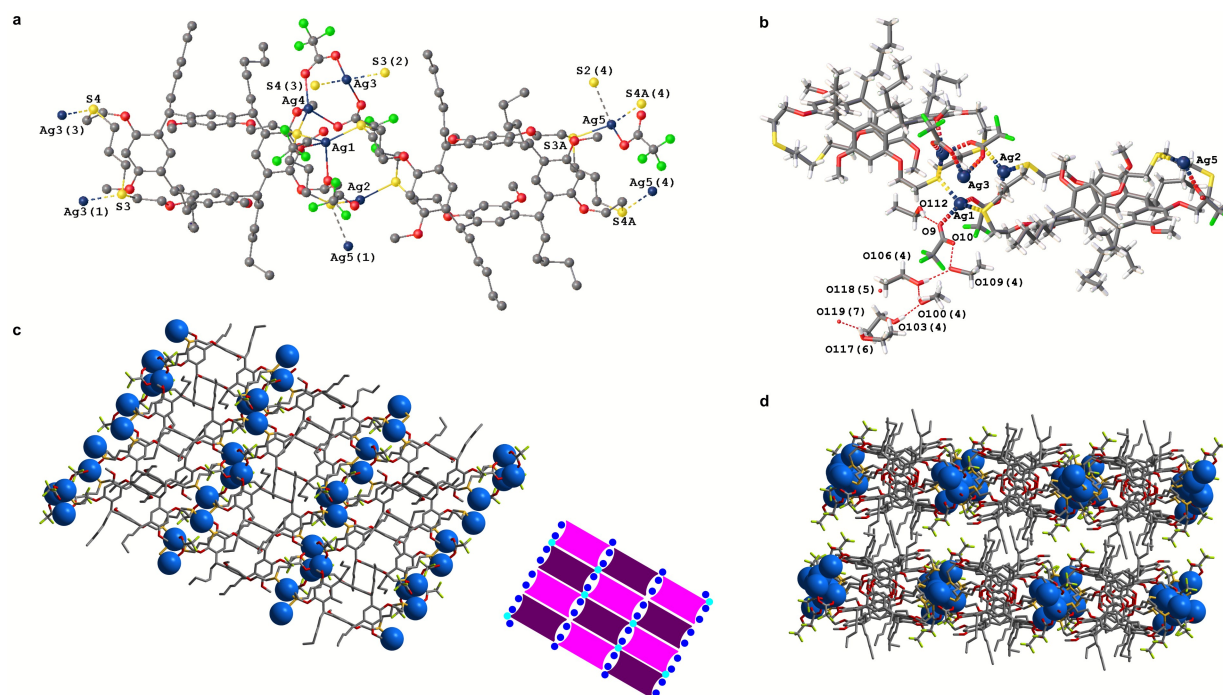


Fig. 7 The asymmetric unit of **3-A** with hydrogen atoms, disorder and solvents omitted (a). Dashed bonds indicate the coordination network. A side view of the structure with hydrogen bonds shown as dotted lines (b). Packing of the 2-D sheet with Ag shown as blue spheres (c, d). A packing diagram shows left-handed and right-handed resorcinarenes with light and dark purple, respectively, and Ag4 as a turquoise sphere. Symmetry operations: $-1+x, +y, +z$; $1+x, +y, +z$; $-x, -y, 1-z$; $3-x, 1-y, 2-z$; $+x, -1+y, +z$; $1-x, 1-y, -z$; $+x, -1+y, -1+z$.

between the inverted molecular cups are filled by the backbending alkyl chains. This also allowed two carboxylate anions to coordinate to the Ag...Ag dimer in a trigonal bipyramidal geometry at the end of each resorcinarene with 1:4.5 host:metal ratio. The resorcinarenes in **3-A** are arranged in direct end-to-end joints similarly to **1-B** and **1-C** but due to fewer sulfur donors, Ag(I) cations are coordinated by bridging carboxylate anions. Again, a weak argentophilic interaction supported by two bridging carboxylate anions was found. The tighter alignment of the resorcinarene ligands compared to **2-A** lead to the formation of interdigitated alkyl chains at the lower rim interface.

Structure **1-B** had the largest solvent accessible voids as solvent filled continuous channels instead of isolated solvent pockets are seen in the structure. The second largest fraction of solvent filled space was in structure **1-C**, in which the larger step size within the end-to-end polymer chains leads to larger voids. In the structures **2-A** and **3-A** the solvent pockets are located between polymer sheets.

Experimental

All chemicals and solvents were ordered from commercial suppliers (Sigma-Aldrich and VWR) and used as received. Synthesis and characterization data of the resorcinarene bis-thiacrowns **2** and **3** are reported in the supporting information.

Crystallizations

Approximately 1 mg of the resorcinarene bis-thiacrowns **1-3** were dissolved in 0.2 ml of dichloromethane and cooled down

to $-20\text{ }^{\circ}\text{C}$. A few milligrams (5–10 molar equivalents) of silver trifluoroacetate (AgCF_3COO) was dissolved in 0.2 ml of ethanol and cooled. AgCF_3COO solution was carefully added on top of the solution of bis-thiacrown. Crystals grew at room temperature in a few days.

Crystallography

Single crystal X-ray data for the structure **1-B** were recorded on a Nonius Kappa CCD diffractometer with Apex II detector using graphite monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71070\text{ \AA}$) radiation. The data was processed and absorption correction was made with Denzo-SMN v.0.97.638.²⁸ Single crystal X-ray data for the structures **1-C**, **2-A** and **3-A** were collected on an Agilent Supernova Dualsource diffractometer using an Agilent Atlas CCD detector with mirror monochromatized $\text{CuK}\alpha$ ($\lambda = 1.54180\text{ \AA}$). The data were processed and empirical absorption correction was made with CrysAlisPro.²⁹ The structures were solved using a charge flipping method of Superflip program³⁰ in Olex2³¹. The structure refinement was made with Olex2 using SHELXL refinement package³² with least squares minimization. The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms. Hydrogen atoms for water molecules were not determined but were added to the formula. EADP and EXYZ constrains and SADI, DFIX, DELU, SIMU, and ISOR restrains were used in the refinement of disordered fragments. Solvent occupied volumes were calculated using Mercury CSD 3.5.1. A crystallographic file without solvent molecules was prepared and the void space was calculated with a 1.2 \AA probe radius

Table 1. Crystal data and data collection parameters.

	1-B ^a	1-C	2-A	3-A
Formula	C ₁₃₅ H ₂₀₂ Ag ₄	C ₇₂ H ₁₀₇ Ag ₃	C ₇₉ H ₁₁₁ Ag _{4.5}	C ₁₅₃ H ₂₂₇ Ag ₅
M/g mol ⁻¹	3625.85	1971.54	2322.95	3667.16
Space group	P-1	P-1	P2 ₁ /n	P-1
a/Å	18.1183(3)	14.4639(3)	14.9657(3)	17.7963(6)
b/Å	19.5986(4)	17.1573(5)	31.1456(7)	20.7997(6)
c/Å	24.7135(5)	19.8936(8)	22.3769(6)	24.3087(5)
α/°	75.3850(7)	67.754(3)	90	92.255(2)
β/°	83.6250(6)	71.544(3)	94.729(2)	98.785(2)
γ/°	74.0640(11)	88.853(2)	90	106.258(3)
V/Å ³	8157.1(3)	4306.2(3)	10394.8(4)	8504.8(4)
Z	2	2	4	2
T/K	173.0	120.0	120.0	123.0
λ/Å	0.71073	1.54184	1.54184	1.54184
D _c /g cm ⁻³	1.476	1.521	1.484	1.432
μ/mm ⁻¹	0.807	7.495	8.537	6.162
Refl. meas.	40597	26379	77724	52066
Data	22433	16614	20645	32678
Restraints	208	280	419	337
Parameters	1910	1098	1290	1997
R _{int}	0.0393	0.0366	0.0952	0.0780
R ₁ [I > 2σ(I)]	0.0952	0.0856	0.0918	0.0739
wR ₂ [I > 2σ(I)]	0.2465	0.0996	0.2610	0.1970
Goof	1.071	1.035	1.040	0.991

^a Mask option in Olex2 was used to remove diffuse electron density.

and 0.7 Å grid spacing using contact surface. The crystallographic parameters are shown in Table 1. CCDC 1449683–1449686 contains the supplementary crystallographic data for this paper.

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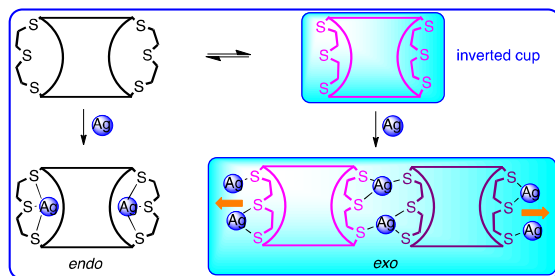
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Graphical abstract:



Exo-cavity binding into resorcinarene based inverted molecular cups creates 1-D and 2-D silver coordination polymers with argentophilic interactions.