Exploring the reversible host-guest chemistry of a crystalline octanuclear Ag(I) metallosupramolecular macrocycle formed from a simple pyrazinylpyridine ligand

Hannah L. Dalton,* Amy D. Lynes, Brendan Twamley, Kevin Byrne, Wolfgang Schmitt, Chris S. Hawes* and Thorfinnur Gunnlaugsson*

Electronic Supporting Information (ESI)

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Methods

X-ray Powder diffraction

X-ray powder diffraction patterns were measured on a Bruker D2 Phaser instrument operating using Cu K α (λ = 1.54178 Å) radiation and a Lynxeye detector at room temperature, with samples mounted on a zero-background silicon single crystal sample stage. The patterns collected at room temperature were compared with the patterns simulated from the single crystal data (collected at 100 K) to establish phase purity of each crystalline material.

X-ray Crystallography

Structural and refinement parameters are presented in Tables S1-S3. Diffraction data were collected using a Bruker APEX-II Duo dual-source instrument and using graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) or microfocus Cu K α ($\lambda = 1.54178$ Å) radiation as specified. In case of **acetone** \subset (1, 4-dioxane \subset 4) the X-ray diffraction data were measured on a Bruker D8 Quest ECO instrument. Datasets were collected using ω and φ scans with the samples immersed in oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The data were reduced and processed using the Bruker APEX suite of programs.^{S1} Multi-scan absorption corrections were applied using SADABS.^{S2} The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI.^{S3} The functions minimized were $\Sigma w(F_0^2 - F_0^2)$, with $w = [\sigma^2(F_0^2) + aP^2 + bP]^{-1}$, where $P = [max(F_0)^2 + 2F_0^2]/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. In cases where U_{ij} or position restraints were necessary, these were employed as sparingly as possible and only for the purpose of maintaining chemically sensible geometries and ADPs. Specific refinement strategies are briefly outlined below and detailed in full in the combined crystallographic information file. In order to compare the cell parameters associated with each solvent exchange the cells of complexes, 1. 4-dioxane⊂4 and benzene⊂4 were reoriented to match the cell setting of the remaining complexes; although this is not the standard cell setting for these two structures we consider this more instructive to the structural comparisons. CCDC 1872462-1872474

Complex **4** and each of the solvent-exchanged derivatives exhibited significant crystallographic disorder on the guest solvent molecules and triflate anions. Most of the atoms involved could be located from the Fourier residuals and their positions and ADPs refined either freely or with the restraint strategies outlined below. However, in the case of CCl₄⊂4, toluene⊂4, THF⊂ and hexane⊂4 several triflate counter ions were inserted as rigid groups using FRAG and modelled as split across three positions. Occupancies of the lattice solvent molecules and triflate anions (when split over multiple orientations) were initially ascertained with free variable refinement; in most cases, however, this led to difficulties in achieving convergence for the refinement, and so these parameters were generally fixed to the nearest sensible fractional occupancy to avoid over-parameterizing.

Restraints:

1: DFIX and DANG were used to model the hydrogen atom of the coordinating methanol.

2: DFIX and DANG were used to model the hydrogen atom of the coordinating methanol. RIGU and ISOR were also used to model a coordinating lattice methanol.

4: DFIX, SADI and RIGU were used to model the disorder present in some of the triflate anions and acetone molecules within the lattice and DFIX and RIGU was used for the disorder of acetone molecules.

1, 4-dioxane \subset 4: DFIX, RIGU, SADI and ISOR was used to model the disorder in several triflate anions. DFIX, RIGU and ISOR was used to model the disorder present in the 1, 4-dioxane molecules. RIGU was used to restrain a carbon atom in the scaffold of L1.

PhMe⊂4: DFIX, SIMU and ISOR restraints and FRAG constraints were used to model the disorder of triflate anions where required. DANG, FLAT and ISOR restraints were used to model the overlapping toluene molecules within the lattice, and EADP constraints were used for co-incident atoms.

THF⊂4: RIGU, SIMU and ISOR restraints and FRAG constraints were used to model several of the disordered triflate anions with EADP constraints for co-incident atoms. SIMU, RIGU and ISOR were used for the THF solvent molecules in the lattice and SADI and SIMU were used to model the disorder in the nitrophenyl group of the L1 scaffold.

EtOAc⊂4: SADI, RIGU and ISOR were used to model the disorder of the triflate counter ions and SIMU and ISOR restraints were used to model disorder of an ethyl acetate solvent molecule within the lattice.

C₆H₆ \subset 4: DFIX, SADI, SIMU, RIGU and ISOR restraints and an EADP constraint were used to model the disordered triflate counterions. SIMU, RIGU and EADP was necessary to model the benzene solvent molecules, and ISOR and EADP were used to model the disorder in some of the acetone solvent molecules within the lattice.

n-Hexane \subset 4: DFIX, SADI, RIGU and ISOR restraints and EADP and FRAG constraints were used to model the disorder present for several triflate anions. RIGU was used in the modelling of the disordered acetone solvent molecules.

CCl₄C4: DFIX, SADI, RIGU and ISOR restraints and EADP and FRAG constraints were used to model the disorder of several triflate anions. SADI and ISOR restraints and EADP constraints were used to model the disorder of the acetone solvent molecules, and EADP was used for near-overlapping chlorine atoms in the disordered CCl₄ molecule.

Acetone \subset (1,4-dioxane \subset 4): DFIX, SADI, SIMU, RIGU and ISOR restraints, and EADP constraints were used in modelling several disordered triflate anions. DFIX restraints and EADP constraints were used to model the disorder of several lattice acetone molecules. DFIX was used to restrain the distance between the hydrogen atoms of the partial-occupancy aqua ligand and a nearby acetone molecule.

Synthesis of 2-pyrazinacyl pyridinium iodide: 2-acetyl pyrazine (1 g, 16.3 mmol) was added to a mixture of iodine (2.5 g,



16.6 mmol) and pyridine (30 mL) and the mixture was heated under reflux for 1 hr. The reaction mixture was cooled in ice to yield a light brown crystalline solid which was filtered and air-dried; (2.2 g, 82%); m.p. 207-210 °C; m/z (HR-ESI⁺) 200.0812 [M+H]⁺, calcd. for C₁₁H₁₀N₃O 200.0818; $\delta_{\rm H}$ (600 MHz, DMSO-d₆) 9.25 (H₇, d, J = 1.5 Hz, 1H), 9.08 (H₅, d, J = 2.5 Hz, 1H), 9.00 – 8.97 (H₃₊₈₊₉, m, 3H), 8.75 (H₁, tt, J = 7.9, 1.3 Hz, 1H), 8.29 (H₂₊₄, ddd, J = 9.9, 5.0, 2.4 Hz, 2H), 6.48

 $(H_{6+6'}, s, 2H); \ \delta_C \ (150 \ MHz, d_6\text{-DMSO}) \ 191.1, \ 146.5, \ 146.4, \ 145.2, \ 144.4, \ 143.0, \ 127.8, \ 66.4, \ 63.5; \ \nu_{max} \ (cm^{-1}) \ 2051 w \ br, \ 1701 m \ sh, \ 1524 m \ sh, \ 1437 w, \ 1404 s, \ 1358 m, \ 1337 m, \ 1245 m, \ 1157 m, \ 1053 m, \ 1017 w, \ 991 s \ sh, \ 866 m \ , \ 837 w, \ 779 s \ sh, \ 712 s \ sh, \ 667 s \ sh, \ 585 m, \ 561 s \ sh; \ Found C, \ 40.09; \ H, \ 3.00; \ N, \ 12.56\%. \ C_{11}H_{10}N_3OI \ requires: \ C, \ 40.38; \ H, \ 3.08; \ N, \ 12.84\%.$

Synthesis of 4-/3-nitrophenyl-(pyridyn-2yl) pyrazine - PyPz (L1 and L2 respectively) The appropriate chalcone (1.35/1.3 g L1/L2), 2-pyrazinacyl pyridinium iodide (1.17/1.20 g L1/L2) and ammonium acetate (3.8/3.6 g L1/L2) were added to H₂O (80 mL) and heated under reflux for 5 hrs. Upon cooling to room temperature, the resulting precipitate of the ammonium salt was isolated by filtration and washed with H₂O and acetone (2 x 20 mL), and air-dried. The ammonium salt then underwent thermal decarboxylation with heat (>200 °C) under vacuum until the evolution of CO₂ ceased. The black residue was dissolved in EtOAc and activated charcoal was added. The mixture was heated under reflux for 30 minutes before being filtered hot through Celite and washed with CH₂Cl₂ (2 x 15 mL). The combined filtrate was concentrated *in vacuo* giving the product, L1/L2 as a beige solid.

 $\textbf{L1:} (0.9 \text{ g}, 53\%); \textbf{m.p.} \ 152-155 \ ^\circ\text{C}; \textit{m/z} \ (\text{HR-ESI}^+) \ 279.0874 \ [\text{M}+\text{H}]^+, \textbf{calcd. for } C_{15}H_{11}N_4O_2 \ 279.0877; \ \delta_{\text{H}} \ (600 \ \text{MHz}, \text{DMSO-1}) \ (\delta_{11} + \delta_{12} + \delta_{12}$



 d_6) 9.60 (H₄, d, J = 1.2 Hz, 1H), 8.91 (H₅, dd, J = 5.6, 2.9 Hz, 1H), 8.82 (H₆, dd, J = 2.3, 1.6 Hz, 1H), 8.708 (H₂, d, J = 2.4 Hz, 1H), 8.69 (H₃, d, J = 1.2 Hz, 1H), 8.40 (H₇₊₉, dd, J = 9.1, 2.3 Hz), 8.19 (H₈₊₁₀, dd, J = 7.9, 3.3 Hz, 2H), 7.97 (H₁, dd, J = 5.1, 1.8 Hz, 1H); δ_C (150 MHz, DMSO-d₆) 155.0, 151.1, 150.4, 148.5, 146.9, 145.9, 144.7, 143.8, 143.0, 129.0, 124.8, 123.2, 119.12; v_{max} (cm⁻¹) 3449w br, 3064w, 1940w, 1763m, 1724m, 1575s sh, 1545w, 1534m sh, 1508s sh, 1456m sh, 1406w, 1345s sh, 1322w, 1243m, 1157m, 1088m sh, 1109m, 1034m sh, 1016m sh, 919w,

857m, 837s sh, 823s, 781w, 749s sh, 698s sh, 684m, 660m, 622w, 578w.

L2: (0.75 g, 46%); m.p. 168-170 °C; m/z (HR-ESI⁺) 279.0878 [M+H]⁺, calcd. for C₁₅H₁₁N₄O₂ 279.0877; $\delta_{\rm H}$ (400 MHz, DMSO-d₆) 9.61 (H₃, d, J = 1.5 Hz, 1H), 8.89 (H₆, dd, J = 5.1, 0.7 Hz, 1H), 8.82 (H₂, dd, J = 2.5, 1.5 Hz, 1H), 8.79 (H₂, d, J = 2.5 Hz, 1H), 8.70 (H₅, dd, J = 1.9, 0.7 Hz, 1H), 8.65 (H₁₀, t, J = 2.0 Hz, 1H), 8.39 – 8.34 (H₇₊₈, m, 2H), 8.01 (H₄, dd, J = 5.1, 1.9 Hz, 1H), 7.87 (H₉, t, J = 8.0 Hz, 1H); $\delta_{\rm C}$ (100 MHz, DMSO-d₆) 154.4, 150.6, 150.0, 148.6, 146.4, 145.3, 144.2, 142.5, 138.7, 133.6, 131.0, 124.1, 122.6, 121.7, 118.5; v_{max} (cm⁻¹) 1973w, 1766m, 1727m, 1599m sh, 1524m br, 1479w, 1458m sh, 1422w, 1343s sh, 1284w, 1240w, 1194w, 1156m sh, 1113m sh, 1086m sh, 1039m sh, 1017m sh,

1002w, 920w, 889m sh, 865w sh, 839m sh, 823m sh, 800m sh, 759w, 745m, 735s sh, 689s sh, 678s sh, 639w, 616s sh, 574w br.

Solvent exchange general procedure for 4: The supernatant of **4** was decanted off and the crystals of **4** were rinsed with a small quantity of the exchanged guest to remove any trace amounts of acetone. Guest solvent (4 mL) was then added to the glass vial containing crystalline material of **4**. The vessel was sealed with light excluded for 36 hrs.

1, 4-Dioxane4: v_{max} (cm⁻¹) 3080w br, 2963w, 2855w, 1598m, 1553m, 1518m sh, 1485w, 1479m, 1410w, 1348m, 1246sh, 1223sh, 1081sh, 1055sh, 1045w, 1025sh, 890w, 871sh, 859m sh, 841sh, 829sh, 764sh, 694m sh

EtOAc⊂4: v_{max} (cm⁻¹) 3150w br, 1725 m, 1600m, 1552 w sh, 1518m sh, 1495 w, 1420w, 1347m sh, 1238s br, 1154 sh, 1051w, 1023s sh, 995w, 842m sh, 830m sh, 720m sh, 694m, 631s sh, 568m

THFC4: v_{max} (cm⁻¹) 3472br, 3260w br, 3150w, 1600m, 1556s, 1515sh, 1450s, 1351sh, 1225sh, 1242sh, 1156sh, 1120s, 1025sh, 920s, 875w, 841m sh, 755m sh, 6933m sh, 640m

C₆**H**₆**⊂4**: v_{max} (cm⁻¹) 3088w br, 1702m, 1600m, 1552w, 1518m sh, 1478w sh, 1411m, 1348sh, 1242s sh, 1200w, 1155s sh, 1024s sh, 851w, 840s, 753sh, 684sh, 631s sh, 571m sh

PhMeC4: v_{max} (cm⁻¹) 3084br, 1703w, 1599m sh, 1553m, 1518sh, 1478w, 1412w, 1348s sh, 1241s br, 1355w, 1155s sh, 1050w, 1035w, 1025s sh, 850w, 841sh, 753sh, 736m, 695m sh, 632s sh, 572m sh.

n-Hexane⊂4: v_{max} (cm⁻¹) 3076w br, 2400w, 2200w br, 1703m, 1599m, 1550m, 1518m sh, 1499w, 1413m, 1348s sh, 1241s, sh, 1213w, 1154s sh, 1080w, 1024s sh, 841m sh, 753m sh, 695m sh, 632s sh, 571m sh

CCl₄⊂4: v_{max} (cm⁻¹) 3095w br, 1703m, 1600m, 1552m, 1517m sh, 1480w, 1411m, 1348m sh, 1241s sh, 1195w, 1154s sh, 1110w, 1024s sh, 860w br, 842m sh, 801w, 752m sh, 695m sh, 632s sh, 572m sh.

Acetone⊂(1,4-dioxane⊂4): v_{max} (cm⁻¹) 3108w br, 2981w sh, 1702m, 1597m, 1552m sh, 1518m sh, 1485w, 1413w, 1348s sh, 1242s sh, 1195w, 1154s br, 1119w, 1024s sh, 842m sh, 830m sh, 754m sh, 696m sh, 633s sh, 571m sh.



Figure S1 Asymmetric unit (left) and complete structure, including disorder, (right) of 2-pyrazinacyl pyridinium iodide with ADPs rendered at 50% probability level. Hydrogen atoms are omitted for clarity. Atom colour code: Blue = Nitrogen, Red = Oxygen, grey = Carbon, Purple = Iodine.

Table S1 Crystal data and structure refinement					
Identification code	1	2	3	4	2-Pyrazinacyl- pyridinium-iodide
Empirical formula	C32H28Cu2N8	C34H37.34Cu2N	C ₁₆ H ₁₀ AgF ₃ N ₄ O	C79H71.5Ag4F12N16O	C ₁₁ H ₁₀ N ₃ OI
	$O_{14}S_2$	8O16.67S2	5 S	25.75 S 4	
Formula weight	939.82	1015.98	535.21	2444.74	327.12
Temperature/K	99.99	99.94	99.95	99.99	100
Crystal system	triclinic	triclnic	monoclinic	triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	Сс	<i>P</i> -1	$P2_1/m$
a/Å	9.5753(5)	7.5980(4)	20.4459(7)	12.5643(4)	7.6519(7)
b/Å	9.5924(5)	10.5330(5)	22.1125(7)	15.0925(5)	7.1833(7)
c/Å	10.1968(5)	13.8045(7)	28.6080(11)	25.2576(8)	10.9347(11)
α/°	112.189(3)	69.674(4)	90	103.2190(10)	90
β/°	95.042(4)	87.047(4)	104.973(2)	93.3530(10)	100.319(2)
γ/°	102.088(3)	74.857(4)	90	92.5540(10)	90
Volume/Å ³	833.44(8)	999.07(9)	12494.8(8)	4646.3(3)	591.31(10)
Z	1	1	28	2	2
$\rho_{calc}g/cm^3$	1.872	1.689	1.992	1.747	1.837
µ/mm ⁻¹	3.529	3.044	10.828	1.028	2.69
F(000)	478	521	7392	2447	316
Crystal size/mm ³	0.09 imes 0.06 imes	0.07 imes 0.06 imes	0.08 imes 0.03 imes	0.36 imes 0.28 imes 0.09	0.11 imes 0.07 imes 0.01
	0.05	0.03	0.02		
Radiation	$CuK\alpha (\lambda =$	$CuK\alpha (\lambda =$	$CuK\alpha (\lambda =$	MoK α (λ =	MoKa ($\lambda = 0.71073$)
	1.54178)	1.54178)	1.54178)	0.71073)	
20 range for data	9.53 to	6.834 to	6 to 136.774	2.776 to 61.2	3.786 to 56.632
collection/°	136.958	137.962			
Index ranges	$-11 \le h \le 11, -$	$-8 \le h \le 9, -12$	$-24 \le h \le 24, -$	$-17 \le h \le 17, -21 \le$	$-10 \le h \le 9, -9 \le k \le 9, -$
	$10 \le k \le 11, -$	$\leq k \leq 12, -15$	$26 \le k \le 26, -34$	$k \le 21, -36 \le l \le 33$	$12 \le l \le 14$
	$12 \le l \le 12$	$\leq l \leq 16$	$\leq l \leq 34$		
Reflections collected	8144	8955	81266	117829	6664
Independent	3028 [R _{int} =	3634 [Rint =	22170 [R _{int} =	28499 [R _{int} =	1581 [$\mathbf{R}_{int} = 0.0480$,
reflections	0.0471,	0.0511,	$0.0866, R_{sigma} =$	$0.0375, R_{sigma} =$	$R_{sigma} = 0.0459$]
	$R_{sigma} =$	Rsigma =	0.1143]	0.0359]	
	0.0541]	0.0628]			
Data/restraints/param	3028/3/266	3634/12/318	22170/2/1891	28499/231/1448	1581/38/111
eters	1.040	1.0.4	1.026	1.054	1.040
Goodness-of-fit on F ²	1.048	1.04	1.026	1.054	1.048
Final R indexes	$R_1 = 0.0619,$	$R_1 = 0.0636$,	$R_1 = 0.0522,$	$R_1 = 0.0436, wR_2 =$	$R_1 = 0.0277, wR_2 =$
$[I \ge 2\sigma(I)]$	$wR_2 = 0.1515$	$wR_2 = 0.1681$	$wR_2 = 0.1202$	0.1016	0.0503
Final R indexes [all	$R_1 = 0.0665,$	$R_1 = 0.0799,$	$R_1 = 0.0660,$	$R_1 = 0.0710, wR_2 =$	$R_1 = 0.0412, wR_2 =$
data]	$wR_2 = 0.1586$	$wR_2 = 0.1826$	$wR_2 = 0.1287$	0.1177	0.0534
Largest diff.	1.20/-0.76	1.01/-0.61	2.33/-1.08	1.96/-1.03	0.65/-0.69
peak/hole / e Å ⁻³					
Flack parameter	-	-	-0.011(6)	-	-
CCDC no.	1872471	1872472	1872473	1872466	1872474

Table S2 Crystal data and				
Identification code	4⊂1, 4-dioxane	4⊂THF	4⊂EtOAc	4⊂1, 4-dioxane⊂acetone
Empirical Formula	$C_{77.75}H_{63.83}Ag_4F_{12}N_{16}O_{27}\\.16S_4$	$\begin{array}{c} C_{77}H_{64}Ag_{4}F_{12}N_{16}\\ O_{23.25}S_{4} \end{array}$	$\begin{array}{c} C_{77.34}H_{65.67}Ag_{4}F_{12}N_{1}\\ {}_{6}O_{26.33}S_{4}\end{array}$	$C_{77.01}H_{67.02}Ag_4F_{12}N_{16}O_{25}S_4$
Formula weight	2382.93	2373.16	2428.22	2404.32
Temperature/K	99.99	100(2)	99.99	100(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a/Å	12.532(3)	12.6763(9)	12.5618(11)	12.499(2)
b/Å	15.486(4)	15.3591(11)	15.2290(13)	12.145(3)
c/Å	25.142(6)	25.2633(18)	24.842(2)	25.237(5)
α/°	107.193(2)	104.2650(10)	102.9490(10)	103.550(4)
β/°	83.606(3)	94.1030(10)	92.2200(10)	93.043(6)
γ/°	92.800(2)	90.1400(10)	94.3740(10)	92.900(7)
Volume/Å ³	4631.5(18)	4753.8(6)	4610.5(7)	4610.5(7)
Z	2	2	2	2
$\rho_{calc}g/cm^3$	1.709	1.658	1.749	1.725
μ/mm ⁻¹	1.025	1	1.036	1.03
F(000)	2377	2368	2425	2402
Crystal size/mm ³	$0.46 \times 0.33 \times 0.17$	$0.37 \times 0.31 \times 0.07$	$0.3\times0.19\times0.1$	$0.47 \times 0.47 \times 0.09$
Radiation	MoKa ($\lambda = 0.71073$)	MoKα (λ = 0.71073)	MoK α ($\lambda = 0.71073$)	$MoK\alpha (\lambda = 0.71073)$
2⊖ range for data collection/°	3.27 to 53.478	2.83 to 56.792	2.882 to 56.616	4.812 to 50.962
Index ranges	$-15 \le h \le 15, -19 \le k \le 19, -31 \le 1 \le 31$	$\begin{array}{c} -16 \leq h \leq 11, \ -20 \leq \\ k \leq 19, \ -33 \leq l \leq \\ 33 \end{array}$	$ \begin{array}{c} -15 \leq h \leq 16, -20 \leq k \\ \leq 20, -33 \leq l \leq 33 \end{array} $	$ \begin{array}{c} -15 \leq h \leq 15, -18 \leq k \leq 18, -30 \\ \leq 1 \leq 30 \end{array} $
Reflections collected	67205	61346	69623	96627
Independent	19517 [$R_{int} = 0.0505$,	23747 [R _{int} =	22892 [R _{int} =	17077 [$R_{int} = 0.1595$, $R_{sigma} =$
reflections	$R_{sigma} = 0.0570$]	0.0294, R _{sigma} = 0.0415]	$0.0754, R_{sigma} = 0.0928]$	0.0824]
Data/restraints/paramet ers	19517/115/1392	23747/504/1492	22892/63/1430	17077/204/1340
Goodness-of-fit on F ²	1.108	1.041	1.005	1.031
Final R indexes [I>=2σ (I)]	$R_1 = 0.0959, wR_2 = 0.1992$	$\begin{array}{l} R_1 = 0.0759, \\ wR_2 = 0.2091 \end{array}$	$R_1 = 0.0583, wR_2 = 0.1465$	$R_1 = 0.0746, wR_2 = 0.1969$
Final R indexes [all data]	$R_1 = 0.1504, wR_2 = 0.2318$	$\begin{array}{l} R_1 = 0.1121, \\ wR_2 = 0.2421 \end{array}$	$R_1 = 0.1377, wR_2 = 0.1934$	$R_1 = 0.1364, wR_2 = 0.2478$
Largest diff. peak/hole / e Å ⁻³	2.27/-2.03	2.54/-2.05	1.49/-1.32	2.96/-1.08
CCDC no.	1872467	1872468	1872469	1872470

Table S3 Crystal data a				
Identification code	4⊂Benzene	4⊂PhMe	4⊂Hexane	4⊂CCl₄
Empirical formula	C79.5H60.75Ag4F11.75N16O 21.75S4	C78.25H60.17Ag4F12N16O 21.75S4	C79H71Ag4F12N16 O24S4	C77H60Ag4Cl4F12N16 O24S4
Formula weight	2371.16	2360.31	2416.23	2522.93
Temperature/K	100	100.02	99.98	99.93
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a/Å	12.1199(6)	12.1193(13)	12.5264(3)	12.5434(4)
b/Å	15.9796(7)	15.7806(17)	15.3015(4)	15.3059(5)
c/Å	24.4413(11)	24.659(3)	25.0246(7)	25.2934(8)
α/°	104.5980(10)	104.421(2)	103.4320(10)	103.3030(10)
β/°	88.806(2)	90.943(2)	93.0640(10)	93.6400(10)
γ/°	90.245(2)	91.173(2)	92.0220(10)	93.3890(10)
Volume/Å ³	4579.8(4)	4565.4(8)	4653.0(2)	4702.6(3)
Z	2	2	2	2
$\rho_{calc}g/cm^3$	1.719	1.717	1.725	1.782
µ/mm⁻¹	1.037	1.04	1.024	1.128
F(000)	2363	2351	2418	2508
Crystal size/mm ³	0.2 imes 0.15 imes 0.1	$0.55 \times 0.085 \times 0.07$	$0.46 \times 0.21 \times 0.16$	$0.23\times0.16\times0.04$
Radiation	MoKa ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)	MoKα (λ = 0.71073)	MoKa ($\lambda = 0.71073$)
2⊖ range for data collection/°	2.76 to 50.806	2.666 to 51.008	2.74 to 56.66	2.852 to 56.788
Index ranges	$\begin{array}{c} -13 \leq h \leq 14, -19 \leq k \leq \\ 18, -29 \leq l \leq 29 \end{array}$	$\begin{array}{c} -14 \leq h \leq 9, -19 \leq k \leq \\ 19, -29 \leq l \leq 29 \end{array}$	$\begin{array}{c} -16 \leq h \leq 16, -20 \\ \leq k \leq 20, -32 \leq l \leq \\ 33 \end{array}$	$\begin{array}{c} -16 \leq h \leq 16, -20 \leq k \\ \leq 20, -33 \leq l \leq 31 \end{array}$
Reflections collected	67105	69092	67838	66530
Independent reflections	$\frac{16628 \ [R_{int}=0.1388,}{R_{sigma}=0.1558]}$	$\frac{16601 \ [R_{int} = 0.0612,}{R_{sigma} = 0.0686]}$	$\begin{array}{l} 23053 \; [R_{int} = \\ 0.0340, \; R_{sigma} = \\ 0.0510] \end{array}$	$\begin{array}{l} 23507 \; [R_{int}=0.0322, \\ R_{sigma}=0.0459] \end{array}$
Data/restraints/para meters	16628/214/1297	16601/359/1379	23053/122/1398	23507/236/1431
Goodness-of-fit on F ²	1.011	1.039	1.025	1.07
Final R indexes [I>=2σ (I)]	$R_1 = 0.0820, wR_2 = 0.1789$	$R_1 = 0.0584, wR_2 = 0.1601$	$\begin{array}{l} R_1 = 0.0572, \\ wR_2 = 0.1308 \end{array}$	$\begin{array}{c} R_1 = 0.0654, wR_2 = \\ 0.1641 \end{array}$
Final R indexes [all data]	$R_1 = 0.1847, wR_2 = 0.2198$	$R_1 = 0.1139, wR_2 = 0.1944$	$\begin{array}{l} R_1 = 0.1034, \\ wR_2 = 0.1573 \end{array}$	$R_1 = 0.0988, wR_2 = 0.1849$
Largest diff. peak/hole / e Å ⁻³	1.83/-1.20	1.06/-1.05	4.42/-2.44	2.77/-2.41
CCDC no.	1872463	1872465	1872462	1872464





Figure S2 X-ray powder diffraction pattern for 1 measured at room temperature (red) compared to the pattern simulated from single crystal X-ray data obtained at 100K (blue).



Figure S3 X-ray powder diffraction pattern for 2 measured at room temperature (red) compared to the pattern simulated from single crystal X-ray data obtained at 100K (blue).



Figure S4 X-ray powder diffraction pattern for 3 measured at room temperature (red) compared to the pattern simulated from single crystal X-ray data measured at 100K (blue).



Figure S5 X-ray powder diffraction pattern for 4 (red) compared to the pattern simulated from the single crystal X-ray data (blue) both measured at 100K.



Figure S6 X-ray powder diffraction pattern for 1, 4-dioxane⊂4 (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.



Figure S7 X-ray powder diffraction pattern for THF⊂4 (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.





Figure S8 X-ray powder diffraction pattern for EtOAc⊂4 (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.

Figure S9 X-ray powder diffraction pattern for acetone⊂(1, 4-dioxane⊂4) (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.



Figure S10 X-ray powder diffraction pattern for $C_6H_6\subset 4$ (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.



Figure S11 X-ray powder diffraction pattern for Hexane⊂4 (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.



Figure S12 X-ray powder diffraction pattern for CCl₄⊂4 (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.



Figure S13 X-ray powder diffraction pattern for PhMe⊂4 (red) compared to the pattern simulated from single crystal X-ray data (blue), both obtained at 100K.



Figure S14 X-ray powder diffraction experimental pattern of 4 the pattern of 1,4-dioxane⊂4 and acetone⊂(1, 4-dioxane⊂4) demonstrating the initial change in crystalline material and reversion to the original pattern.



Figure S15 ¹H NMR spectrum of 4 digested into DMSO-d₆ (400 MHz)



Figure S16 ¹H NMR spectrum of 1,4-dioxane⊂4 digested into DMSO-*d*₆ (400 MHz)



Figure S17 ¹H NMR spectrum of THF⊂4 digested into DMSO-*d*₆(400 MHz)



Figure S18 ¹H NMR spectrum of EtOAc⊂4 digested into DMSO-d₆ (400 MHz)





Figure S19 ¹H NMR spectrum of C₆H₆⊂4 digested into DMSO-d₆ (400 MHz)





Figure S21 ¹H NMR spectrum of Hexane⊂4 digested into DMSO-d₆ (400 MHz)



Figure S22 ¹H NMR spectrum of acetone⊂(1, 4- dioxane⊂4) digested into DMSO-*d*₆ (400 MHz)



Figure S23 ¹H NMR spectrum of 1, 4-dioxane/THF (1:1)⊂4 digested into DMSO-d₆ (400 MHz)



Figure S24 ¹H NMR spectrum of 1, 4 –dioxane/EtOAc (1:1)⊂4 digested into DMSO-d₆



Figure S25 ¹H NMR spectrum of EtOAc/THF (1:1)⊂4 digested into DMSO-d₆ (400 MHz)

Thermogravimetric Analysis



Figure S26 Thermogravimetric analysis plot of 4 showing the loss of lattice solvent (acetone)



Figure S27 Overlay of the thermogravimetric analysis plots of the guest solvents that fully exchanged with 4 including acetone⊂(1, 4-dioxane⊂4).



Figure S28 Overlay of the thermogravimetric analysis plots of the guest solvents that partially exchanged with 4



Figure S29 Overlay of the thermogravimetric analysis of 4 upon guest exchange with the 50:50 mixtures of the fully exchanged guest solvents.



Figure S30 Thermogravimetric analysis plot of 1 showing the loss of the coordinated and lattice solvent.



Figure S31 Thermogravimetric analysis plot of the soft material of 2 indicating the gel-like nature



Figure S32 Thermogravimetric analysis plot of the crystalline material of 2 which shows the loss of lattice and coordinated solvent.

Gas Adsorption Data







CO₂ Physisorption Isotherm at 278K

Figure S34 CO_2 adsorption isotherms for 4 measured at 278K

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