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On rhenium(I)–silver(I) cyanide porous macrocyclic clusters†

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The first cyanide rhenium(I)–silver(I) clusters were synthesized in the course of simple one-pot high-yielding reactions. This new class of obtained self-assembled, cyclic octanuclear complexes is composed of pseudo-square-shaped $\{Re_4Ag_4(\mu\text{-}CN)_8\}$ units, which, along with PPh_3 ligands, adopt an approximately block-like overall geometry. We discovered that the studied cavity-shaped clusters feature a channeling crystal network capable of hosting smaller molecules and exhibit the ability to undergo reversible guest solvent sorption. Depending on the reaction conditions, the tetranuclear complex $[Re_2Ag_2(\mu\text{-}CN)_4(CO)_4(PPh_3)_6]$ and the species of the formal motif $\{ReAg_{1.5}(CN)_{2.5}(CO)_2(PPh_3)_2\}$ can be formed.

Introduction

Dynamic progress towards design of new gas/solvent storage and delivery materials as well as solvent sorption systems has been observed in the past decade.[1] Self-assembly of cage clusters has attracted extensive interest due to the application of such systems as host-complexes for smaller molecules.[2] Supramolecular macrocyclic systems based on rhenium are a promising group of porous materials due to their cavity shapes or self-assembly in the solid state, among which various metallacycles with topologies such as pseudo-square, gondola-shaped, tetragonal prismatic structures and other cavity modes can be distinguished.[3] Coordination chemistry provides a diversity of ligands to design complexes including large cavities, among which cyanide ligands are widely used to create porous materials.[4] Considering different kinds of cyanide polynuclear complexes, a variety of cyclic systems in both discrete clusters and polymeric coordination networks is observed.

However, we have discovered that new kinds of geometries among cyanide mixed-metal silver–rhenium complexes can be created in simple, one-pot self-assembly reactions. In this work, species composed of eight-membered Re–Ag metallacycles are considered. To date, clusters containing cyclic units built up from eight metal centres combined by cyanide bridges are rather scarce.[5] The majority of such species can be analyzed as adopting approximately planar tetrameric entities that joined together to form discrete octanuclear clusters or complex polymeric networks.[6] Among macrocyclic poly- and heteronuclear cyanide complexes based on rhenium, including $\{Re_nM_m\}$ units, where $n \geq 4$, two kinds of geometries, cube-like units $\{Re_4M_4(\mu\text{-}CN)_{12}\}$ (M = Mn, Fe, Co, Ni, Zn) and clusters composed of rhenium octahedra $\{Re_6M_8(\mu_6\text{-}M)(\mu\text{-}CN)_8\}$ (M = Mn, Fe), can be highlighted.[7,8] Herein, we report the first cyanide macrocyclic octanuclear clusters containing pseudo-cylindrical cavities capable of hosting smaller molecules. The rhenium(I)–silver(I) complex of the formula $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$ (**1**) establishes a new class of octanuclear mixed-metal rhenium clusters adopting the pseudo-square geometry of the $\{Re_4Ag_4(\mu\text{-}CN)_8\}$ core and an approximately block-like overall geometry, which makes it a discrete hollow species, potentially suitable for host–guest applications. The majority of multinuclear cyclic discrete rhenium–silver species contain a $\{Re_xAg_y\}$ ($x = 1, 2, 3$; $y = 1, 2$) core, where metal atoms are bridged by different ligands.[9,10] However, rhenium–silver complexes of higher nuclearity are unusual to date.[11]

Results and discussion

We discovered that in the course of simple one-pot reactions of $[Re(CO)_2(OAc)(PPh_3)_2]$ and $K[Ag(CN)_2]$, depending on the temperature and stoichiometry, Re(I)–Ag(I) cyanide compounds, which are discrete host–guest complexes, including the octanuclear framework $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$ (**1**) [octacarbonyl-octa-μ-cyanido-octa(triphenylphosphino)

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† Electronic supplementary information (ESI) available: Additional information as noted in the text including X-ray crystallographic data in CIF format for **1a**–**3**, selected crystal data and structure refinement parameters, tables of hydrogen bonds, UV-vis, IR, FIR, ESI-MS mass spectra, TGA diagrams and descriptions of crystal structures. CCDC 1531338–1531343 and 1531345. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ce00646b

tetrarhenium(ɪ)tetrasilver(ɪ)] and the tetranuclear complex of the formula [Re$_2$Ag$_2$(μ-CN)$_4$(CO)$_4$(PPh$_3$)$_6$] (**2**) [tetracarbonyl-tetra-μ-cyanido-hexa(triphenylphosphino)dirhenium(ɪ)disilver-(ɪ)] as well as the complex of the formal unit {ReAg$_{1.5}$(CN)$_{2.5}$(CO)$_2$(PPh$_3$)$_2$} (**3**), are formed (Scheme 1). Cluster **1** was synthesized by using an equimolar ratio of the reagents ([Re(CO)$_2$(OAc)(PPh$_3$)$_2$] and K[Ag(CN)$_2$]). When a threefold increase in the silver–rhenium ratio is applied, the mixture of **1** and some amount of **3** are formed. In the case of **2**, the reaction is carried out using **1** as a starting material in the presence of PPh$_3$ at the boiling point of the reaction mixture or in the course of an alternative refluxing procedure employing an equimolar mixture of the reagents [Re(CO)$_2$(OAc)(PPh$_3$)$_2$], K[Ag(CN)$_2$] and PPh$_3$.

Both complexes **1** and **2** comprise a core of Re and Ag atoms bridged by cyanide ligands resulting in the formation of a cyclic structure adopting pseudo-square- (**1**) or pseudo-rhombic-shaped (**2**) geometries, which along with coordinated triphenylphosphine create block-like compositions forming cavities. In the cyclic core of **1**, Re atoms are located in the vertices of the pseudo-square, while four Ag atoms with coordinated CN$^-$ ligands form its sides (Fig. 1). By comparison with **1**, the pseudo-rhombus in **2** is built up from both Re and Ag atoms alternately occupying its vertices and linking cyanide ligands (Fig. 2). Moreover, in both clusters **1** and **2**, the Re atoms are coordinated by terminal carbonyl and triphenylphosphine groups; additionally, in **2**, the PPh$_3$ ligands are also bound to the Ag atoms. In the crystals of **1** (*viz.* **1a**–**e** crystals, Table 1), cavity-shaped molecules are linked to each other by weak C–H⋯π hydrogen bonds forming 1D channels stretching along the [100] direction. Along two other crystallographic axes, these molecules interact *via* C–H⋯O and/or C–H⋯π hydrogen bonds appearing between peripheral carbonyl groups and phosphine ligands. The created crystal compositions feature porous networks (Fig. 3). Contrary to the structures of **1**, in the crystal of tetranuclear cluster **2**, a layered architecture is observed. Mole-
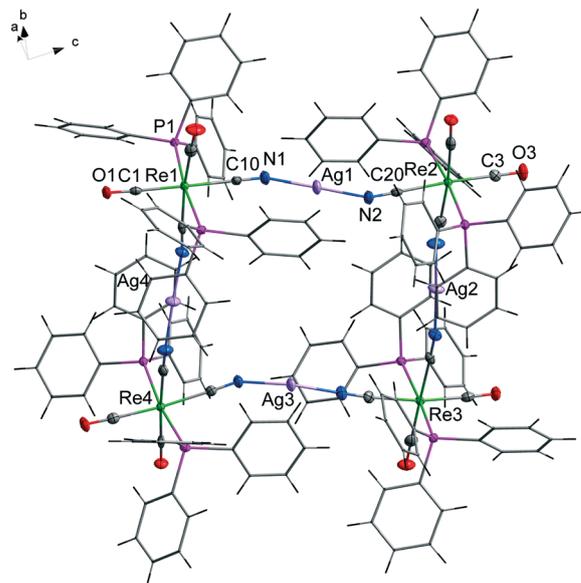

Fig. 1 Overall geometry of the octanuclear complex [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$]·5EtOH (**1a**). Displacement ellipsoids of Re, Ag, P, O and N atoms are shown at the 50% probability level. For clarity, phenyl rings with attached H atoms are shown in the wireframe representation and the molecules of ethanol included in the cavity are omitted.

cules linked to each other by weak C–H⋯O, C–H⋯N and C–H⋯π hydrogen bonds are arranged in layers parallel to the (010) crystallographic plane. Different kinds of metallacycles of the pseudo-rectangular topology can be distinguished in the structure of **3**, compared to discrete ones in the structures of **1** and **2**. The structure of **3** constitutes decanuclear macrocyclic frameworks, each created from four rhenium atoms acting as core vertices and six silver atoms with bridging cyanide ligands as sides of the polygon (Fig. S1 in the ESI†). The cross-sections of the cavities can approximately be described as a square (**1**) or a rhombus (**2**) with an average
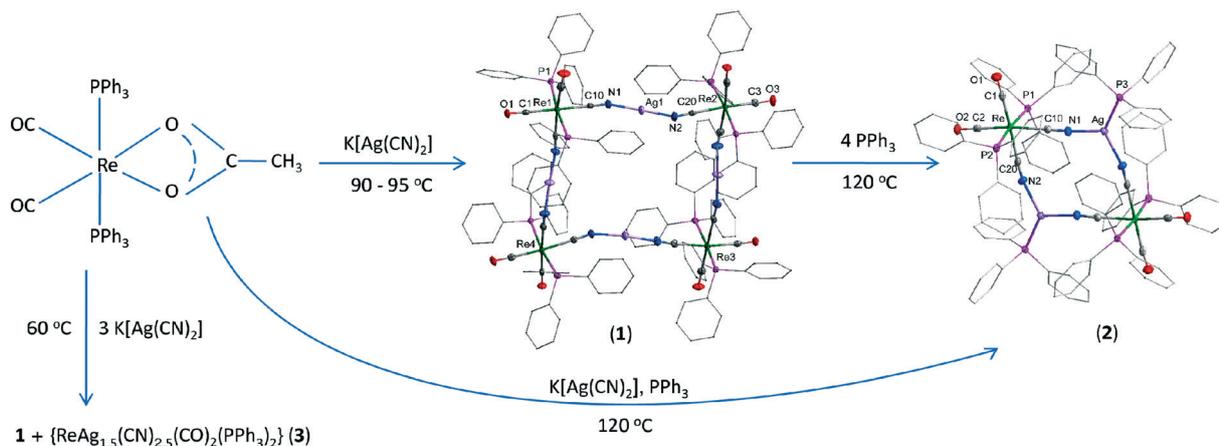
Scheme 1 Reaction pathways showing the syntheses of compounds **1**–**3**. The hydrogen atoms are omitted for clarity. 4[Re(OAc)(CO)$_2$(PPh$_3$)$_2$] + 4K[Ag(CN)$_2$] → [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$] (**1**) + 4AcOK. [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$] (**1**) + 4PPh$_3$ → 2[Re$_2$Ag$_2$(μ-CN)$_4$(CO)$_4$(PPh$_3$)$_6$] (**2**).
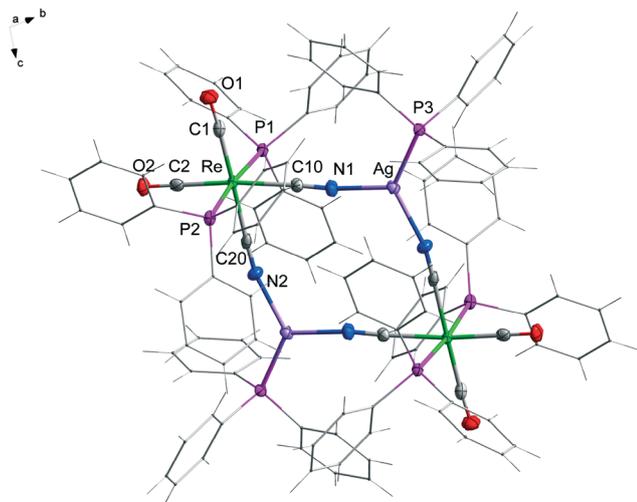
Fig. 2 Structure of the tetranuclear centrosymmetric complex [Re₂Ag₂(μ-CN)₄(CO)₄(PPh₃)₆] molecule (**2**). Displacement ellipsoids of Re, Ag, P, O and N atoms are shown at the 50% probability level. Phenyl rings with attached H atoms are shown in the wireframe representation.

diagonal length (the Re–Re distance) of about 14.7 Å in **1** and about 8 Å in **2**. In the case of structure **3** of the formula {ReAg₁.₅(CN)₂.₅(CO)₂(PPh₃)₂} (the asymmetric part of the unit cell), a pseudo-rectangular-shaped framework with the longest diagonal length of about 18.5 Å compared to those in **1** and **2** can be distinguished. However, in **3**, mutual spatial arrangement of adjacent macrocyclic species leads to the location of the PPh₃ groups within the neighboring cavities. Therefore, close crystal packing that prevents smaller molecules from entering is observed. Instead of the hollow species that was expected in **3**, a layered architecture (Fig. S2 and S3 in the ESI†) is featured. The presence of the cavity in **1** provides the possibilities of hosting molecules of solvents. The formation of **1** from solvents such as EtOH, MeCN and MeOH resulted in obtaining isomorphous **1a–c** solvates, respectively, and revealed that the guest molecules incorporated into the channels can be exchanged (Fig. 4). Furthermore, the crystal structure of **1** is robust and maintained despite the loss of guest solvents. This showed that the release of solvent from the crystals of **1** marginally influenced the stability of the crystal structure, although the crystals after being exposed to air underwent partial fracture. A diffraction pattern with weaker signals for selected monocrystals and lattice constants similar to those recorded for the former **1a–c** crystals were obtained. Powder X-ray diffraction experiments performed for **1** after solvent removal also proved that the basic crystal structure was maintained (Fig. 5, see also TGA diagrams in Fig. S19 and S20 in the ESI†). Such a robust structure capable of inclusion of solvent molecules within the cavity seemed to be a promising candidate for the exchange of guest solvents acting as a porous material. Successful soaking of crystals of **1**, accomplished after their desolvation, showed that framework **1** exhibits the storage ca-

pacity for smaller molecules that are able to play the role of a molecular sponge, hosting molecules such as acetone, butan-1-ol and ethanol. Through soaking, the following crystals were obtained: [Re₄Ag₄(μ-CN)₈(CO)₈(PPh₃)₈]·3Me₂CO (**1d**), [Re₄Ag₄(μ-CN)₈(CO)₈(PPh₃)₈]·2BuOH (**1e**) (Table 1) and [Re₄Ag₄(μ-CN)₈(CO)₈(PPh₃)₈]·4EtOH (**1f**) (Table S1 in the ESI†).

Inclusion of acetone molecules resulted in acquisition of the isomorphous **1d** crystals with a preserved metallacyclic framework, however absorption of molecules of butan-1-ol led to crystal-to-crystal transformation (unit cell parameters changed), where a new **1e** host–guest complex was created (Table 1). From a chemical point of view, the host framework in **1e** is similar to those in the **1a–d** crystals and the geometrical parameters Re–C₍CO₎, Re–C₍CN₎, Re–P and Ag–N bond lengths as well as C₍CN₎–Re–C₍CN₎ and N–Ag–N angles are also comparable to those of **1a–d** (Table 2). In all crystal structures **1a–e**, the guest molecules incorporated into the channels weakly interact with the host cluster molecules via hydrogen bonds such as C–H⋯O, C–H⋯π and C–H⋯N and/or van der Waals contacts. Moreover, they are linked to each other by O–H⋯O and C–H⋯O hydrogen bonds, which was depicted in the IR spectra (see Tables S2–S14 and Fig. S17 and S18 in the ESI†). It is worthwhile noting that **1** exhibit reversible guest solvent sorption and the ability to undergo reversible crystal-to-crystal transformations. As mentioned before, sorption of butan-1-ol performed for **1a** crystals dried beforehand resulted in a transition to a new crystalline phase **1e**, which after being desolvated and subsequently soaked in ethanol, was reversibly converted into the original crystalline phase. The obtained crystals [Re₄Ag₄(μ-CN)₈(CO)₈(PPh₃)₈]·4EtOH denoted as **1f** (Experimental section; Table S1 in the ESI†) adopt the same crystal lattice featuring the same porous architecture as the former crystalline phase **1a**, but with a decreased number of EtOH molecules per cluster compared to **1a**. Although numerous sorption–desorption processes influence the quality of the crystals (as mentioned above) that was observed as weaker diffraction intensity and partially occupied positions of ethanol molecules in cavities, the host channeling structure remains rigid. The achieved results are promising for future sorption experiments we will carry out.

Conclusions

In summary, we synthesized porous macrocyclic octanuclear rhenium(I)–silver(I) host–guest cyanide complexes, which are capable of storage and exchange of guest solvents. The structure of the [Re₄Ag₄(μ-CN)₈(CO)₈(PPh₃)₈] host framework undergoes reversible cyclic sorption/desorption processes during which such framework is preserved. We showed that, depending on the stoichiometry and reaction temperature, the tetranuclear complex [Re₂Ag₂(μ-CN)₄(CO)₄(PPh₃)₆] as well as species of the formula {ReAg₁.₅(CN)₂.₅(CO)₂(PPh₃)₂} can be obtained.

Table 1 Selected crystallographic data and structure refinement parameters

	1a	1b	1c	1d	1e	2	3
Empirical formula	$[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$·5EtOH	$[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$·2MeCN·$H_2O$	$[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$·5MeOH·0.75$H_2O$	$[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$·3$Me_2CO$	$[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$·2BuOH	$[Re_2Ag_2(\mu\text{-}CN)_4(CO)_4(PPh_3)_6]$	$\{ReAg_{1.5}(CN)_{2.5}(CO)_2(PPh_3)_2\}$
Formula weight (g mol⁻¹)	3937.01	3806.80	3880.39	3880.91	3852.95	2377.87	993.61
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	12.282(2)	12.224(2)	12.252(3)	12.275(2)	12.157(3)	12.864(4)	10.252(3)
b (Å)	18.475(4)	18.438(5)	18.571(5)	18.433(5)	18.455(5)	14.241(4)	10.457(3)
c (Å)	35.979(8)	35.881(9)	35.873(10)	36.135(9)	18.440(5)	15.442(5)	19.169(5)
α (°)	83.56(3)	83.40(3)	83.68(3)	82.79(3)	78.16(3)	93.85(3)	77.39(5)
β (°)	89.19(3)	89.05(3)	88.96(3)	88.71(3)	75.56(3)	107.03(3)	75.51(4)
γ (°)	72.42(3)	71.89(3)	72.12(3)	72.06(3)	73.82(3)	110.46(3)	65.29(5)
V (Å³)	7732(3)	7634(3)	7720(4)	7716(3)	3806.6(19)	2488.5(14)	1792.3(12)
Z	2	2	2	2	1	1	2
μ (mm⁻¹)	3.76	3.80	3.76	3.77	3.81	2.96	4.31
F(000)	3876	3724	3811	3808	1890	1180	962
Crystal size (mm)	0.34 × 0.22 × 0.13	0.28 × 0.15 × 0.10	0.26 × 0.20 × 0.10	0.09 × 0.06 × 0.06	0.11 × 0.09 × 0.08	0.20 × 0.09 × 0.07	0.11 × 0.06 × 0.05
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal form	Block	Block	Block	Block	Block	Block	Plate
Diffractometer	Kuma KM-4-CCD	Kuma KM-4-CCD	Kuma KM-4-CCD	Xcalibur with CCD Ruby detector	Kuma KM-4-CCD	Xcalibur with CCD Ruby detector	Xcalibur with CCD Ruby detector
Radiation type, wavelength, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
T (K)	100(2)	100(2)	100(2)	80(2)	100(2)	100(2)	80(2)
Θ range (°)	2.9–28.8	2.8–26.5	2.8–25.5	2.7–25.5	2.9–25.5	2.7–30.8	2.8–25.5
h, k, l range	−14 ≤ h ≤ 14, −19 ≤ k ≤ 22, −43 ≤ l ≤ 43	−15 ≤ h ≤ 15, −23 ≤ k ≤ 23, −45 ≤ l ≤ 40	−14 ≤ h ≤ 14, −19 ≤ k ≤ 22, −43 ≤ l ≤ 43	−12 ≤ h ≤ 14, −22 ≤ k ≤ 15, −43 ≤ l ≤ 41	−14 ≤ h ≤ 14, −22 ≤ k ≤ 22, −22 ≤ l ≤ 20	−17 ≤ h ≤ 18, −19 ≤ k ≤ 18, −22 ≤ l ≤ 11	−12 ≤ h ≤ 12, −12 ≤ k ≤ 10, −23 ≤ l ≤ 15
Measured reflections	58 775	73 485	61 817	43 104	26 469	25 067	14 859
Independent reflections	28 576	31 443	28 614	27 573	14 034	13 932	6682
Observed refl. ($I > 2\delta(I)$)	24 328	23 503	25 160	12 447	6862	10 545	4460
Transmission max/min	0.362/0.666	0.481/0.707	0.377/0.735	0.804/0.850	0.752/0.799	0.709/0.863	0.711/0.835
R_{int}	0.030	0.042	0.039	0.121	0.141	0.046	0.079
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	28 576/31/1869	31 443/4/1778	28 614/21/1841	27 573/871/1672	14 034/441/868	13 932/0/604	6682/72/445
$R[F^2 > 2\sigma(F^2)]$	0.035	0.048	0.040	0.092	0.086	0.053	0.062
$wR(F^2)$	0.094	0.126	0.105	0.137	0.177	0.079	0.100
GoF = S	0.91	1.07	0.97	0.92	0.093	1.02	1.01
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å⁻³)	1.97/−1.22	3.12/−1.81	2.01/−1.04	1.47/−1.31	2.25/−1.93	1.40/−0.95	1.24/−1.14
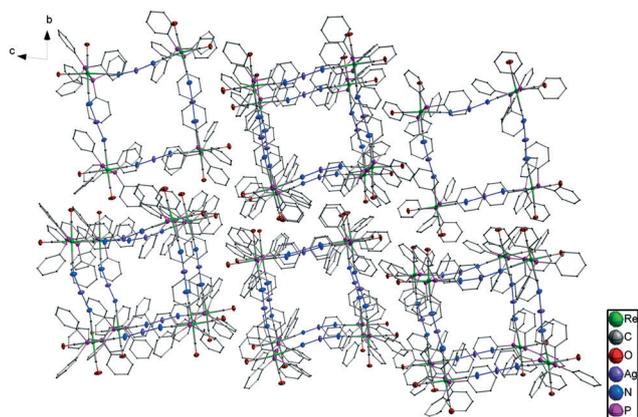
Fig. 3 Packing diagram showing a porous architecture of the [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$]·5MeOH·0.75H$_2$O (**1c**) framework. The molecules of methanol were omitted. Displacement ellipsoids of Re, Ag, P, O and N atoms are shown at the 50% probability level. For clarity, phenyl rings are shown in the wireframe representation and H atoms are omitted.

Experimental section

Procedures

[Re(CO)$_2$(OAc)(PPh$_3$)$_2$] used for syntheses was prepared and purified according to the procedure published beforehand.[12] K[Ag(CN)$_2$] was purchased from Alfa Aesar and was not further purified.

Synthesis of [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$]·5EtOH (1a)

For the synthesis of **1a**, [Re(CO)$_2$(OAc)(PPh$_3$)$_2$] (0.155 g, 0.188 mmol) and K[Ag(CN)$_2$] (0.0377 g, 0.188 mmol) were mixed in a 1:1 molar ratio and about 12 ml of ethyl alcohol was added. The mixture was refluxed by stirring for about 4 h at about 90–95 °C in an oil bath. Afterwards, the colourless fine crystalline product that was formed was filtered off and washed with ethyl alcohol. Further investigations reported below were performed after removing ethanol from the crystals (*Caution! Although we have not experienced any problem with the reported compound in this work, cyanide compounds are potentially dangerous and should be handled with care*). Yield: 0.164 g, 0.0442 mmol, 95%. IR (nujol): v = 2139 (m), 2126 (m) cm^{-1} (C≡N); v = 1949 (s), 1939 (s), 1894 (s), 1878 (s) cm^{-1} (C≡O). ESI-MS (CH$_3$CN): m/z = 3706.17 [M]$^+$ (calcd for [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$]$^+$ 3706.16). Anal calcd (%) for C$_{160}$H$_{120}$Ag$_4$N$_8$O$_8$P$_8$Re$_4$ (3706.80 g mol^{-1}): C, 51.84; H, 3.26; N, 3.02. Found: C, 51.82; H, 3.06; N, 2.70.

Crystals of **1a** suitable for single crystal X-ray measurements were obtained as a result of the reaction of [Re(CO)$_2$(OAc)(PPh$_3$)$_2$] (0.0434 g, 0.0525 mmol) with K[Ag(CN)$_2$] (0.0105 g, 0.0525 mmol) (1:1 molar ratio) in a branched tube using a thermal gradient procedure. Reagents were placed in the main arm of the branched tube and ethyl alcohol was gently added, filling both arms to keep the solution undisturbed and let the reagents dissolve gradually. The main arm of the branched tube containing the reagents was placed in an oil bath at about 60 °C, while the other arm of
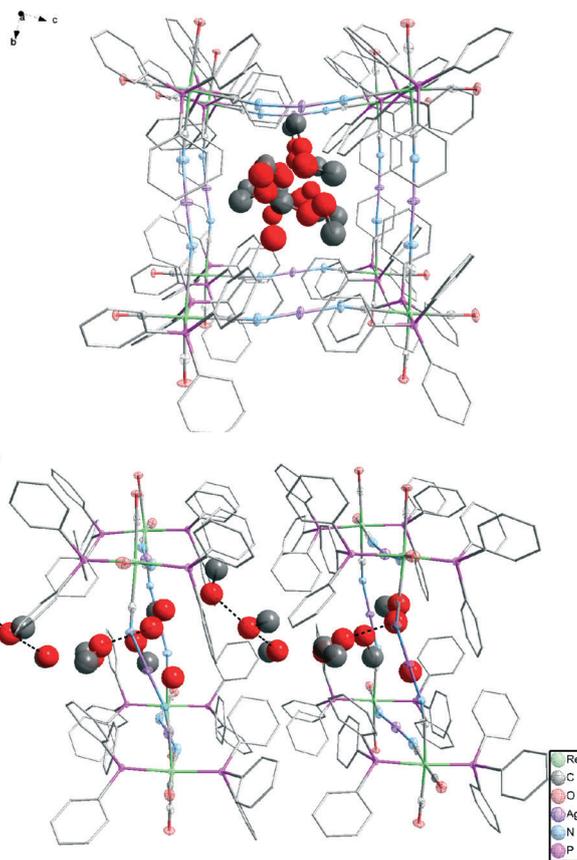
Fig. 4 Top: Channeling structure of [Re$_4$Ag$_4$(μ-CN)$_8$(CO)$_8$(PPh$_3$)$_8$] ·5MeOH·0.75H$_2$O (**1c**) viewed down the *a* axis; bottom: arrangement of methanol molecules within a channel linked to each other by hydrogen bonds (in the picture, O$_{donor}$···O$_{acceptor}$ distances were depicted) viewed down the *c* axis. H atoms were omitted for clarity.

the tube was left at ambient temperature. Colourless crystals of **1a** in the form of blocks were obtained over several days. An analogous procedure was followed in order to obtain

Fig. 5 Simulated diffractogram obtained for **1a** crystals and experimental diffractograms obtained for dried **1a** and **1c** crystals showing the robust structure of framework **1**.

Table 2 Ranges of selected geometrical parameters (Å, °) for compounds **1a**–**2**

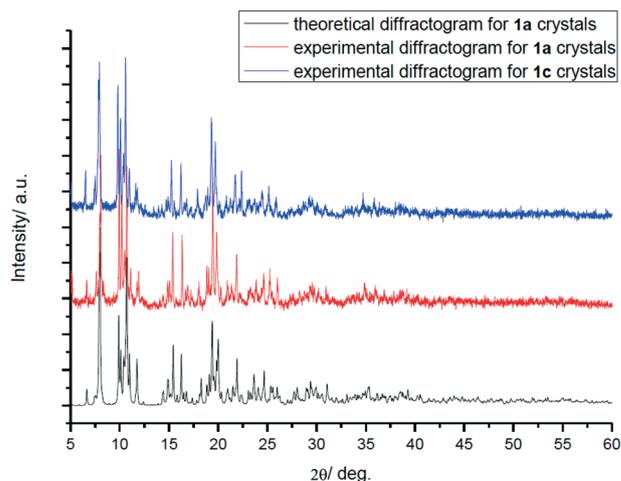|	$[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]$ (**1**)					**2**
	1a	**1b**	**1c**	**1d**	**1e**	
Re–C$_{(CO)}$	1.922(5)–1.946(5)	1.924(7)–1.960(7)	1.930(6)–1.951(6)	1.91(2)–1.948(16)	1.897(17)–1.977(17)	1.929(5)–1.935(5)
Re–C$_{(CN)}$	2.100(5)–2.112(5)	2.082(7)– 2.109(6)	2.097(5)–2.108(5)	2.07(2)–2.14(2)	2.028(17)–2.115(16)	2.107(5)–2.130(4)
Re–P	2.4058(12)–2.4224 (12)	2.4029(16)–2.4228 (18)	2.4043(14)–2.4245 (14)	2.415(4)–2.437 (4)	2.415(4)–2.425 (4)	2.4173(15)–2.4192 (14)
Ag–N	2.042(4)–2.056(4)	2.038(6)–2.051(6)	2.042(5)–2.057(5)	2.025(13)–2.076(15)	2.035(13)–2.092(13)	2.181(4)–2.200(4)
C$_{(CN)}$–Re–C$_{(CN)}$	84.94(18)–88.20(17)	84.0(3)–88.1(3)	84.9(2)–87.11(19)	91.8(9)–93.9(8)	91.3(6)–95.6(7)	84.42(16)
N–Ag–N	171.57(17)–177.67(17)	165.0(3)–176.3(3)	169.08(19)–177.66(19)	168.2(5)–177.0(7)	170.1(5)–175.3(6)	105.95(14)

crystals $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]\cdot2MeCN\cdot H_2O$ (**1b**) and $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]\cdot5MeOH\cdot0.75H_2O$ (**1c**), using acetonitrile or methanol as solvents in the syntheses, respectively.

An alternative synthesis of **1** can also be carried out using $[Re(CO)_2(OAc)(PPh_3)_2]$ and $K[Ag(CN)_2]$ in a molar ratio of 1 : 3 at 60 °C, which is accompanied by the formation of thin plate-shaped crystals of $\{ReAg_{1.5}(CN)_{2.5}(CO)(PPh_3)_2\}$ (**3**). Due to the low solubility of both complexes in most solvents, the crystals were separated under a microscope and determined independently of each other through X-ray studies.

Synthesis of $[Re_2Ag_2(\mu\text{-}CN)_4(CO)_4(PPh_3)_6]$ (2)

As a starting point for **2**, 0.0513 g (0.0138 mmol) of crystalline **1** was dried beforehand and used with PPh$_3$ (0.0146 g, 0.0557 mmol) in a molar ratio of 1 : 4 in the presence of 7 mL of ethyl alcohol. The mixture was refluxed for 4 h in an oil bath. As a result, a colourless fine precipitate of **2** was formed, which was then filtered off and washed with ethyl alcohol. Yield: 0.0610 g, 0.0256 mmol, 93%. IR (nujol): ν = 2140 (m), 2123 (m), 2111 (w), 2094 (w) cm^{-1} (C≡N); ν = 1929 (s), 1861 (s) cm^{-1} (C≡O). ESI-MS (CH$_3$CN): m/z = 2401.31 [M + Na]$^+$ (calcd for $\{[Re_2Ag_2(\mu\text{-}CN)_4(CO)_4(PPh_3)_6] + Na\}^+$ 2401.25). Anal calcd (%) for C$_{116}$H$_{90}$Ag$_2$N$_4$O$_4$P$_6$Re$_2$ (2377.97 g mol^{-1}): C, 58.59; H, 3.81; N, 2.36. Found: C, 58.34; H, 3.63; N, 2.34.

An alternative procedure for the preparation of **2** was as follows. An equimolar mixture of $[Re(CO)_2(OAc)(PPh_3)_2]$ (0.0507 g, 0.0614 mmol), $K[Ag(CN)_2]$ (0.0124 g, 0.0620 mmol) and PPh$_3$ (0.0169 g, 0.0644 mmol) was refluxed in ethanol (about 7 mL) by stirring for 4 h. However, this method is less effective than that described above because of the presence of trace impurities in **2**.

Crystal soaking procedures

Crystals of **1a** desolvated beforehand were placed in two vessels and small amounts of solvents, acetone or butan-1-ol, were added. The crystals were soaked in solutions of the target guest solvents in sealed vessels for several days, resulting in the formation of crystals including acetone, $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]\cdot3Me_2CO$ (**1d**), or butan-1-ol, $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]\cdot2BuOH$ (**1e**), in the cavities. Afterwards, good quality monocrystals **1d** and **1e** of a suitable size were collected and studied by single crystal X-ray diffraction. Crys-

tals of $[Re_4Ag_4(\mu\text{-}CN)_8(CO)_8(PPh_3)_8]\cdot4EtOH$ (**1f**) were obtained in the course of desorption of **1e** (after exposure to air) and further ethanol inclusion. The single-crystal X-ray diffraction studies revealed that the guest-absorbed monocrystals **1f** obtained are the same as the original crystalline phase **1a** (the atomic positions in both structures are equivalent), but with a lower ethanol occupancy of 80%.

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