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Molecular tectonics: from a binuclear metallamacrocycle to a 1D isostructural coordination network based on tetracyanomethyl[1.1.1.1]metacyclophane and a silver cation

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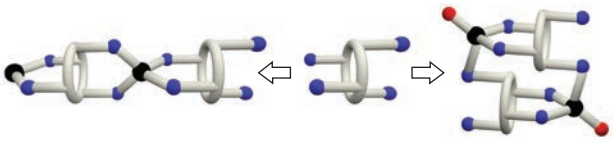
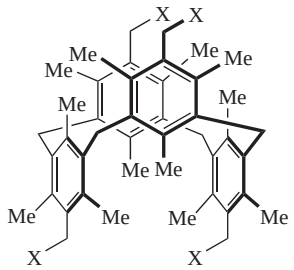
Depending on the anion (NO_3^- or BF_4^-) and stoichiometry, the combinations of [1.1.1.1]metacyclophane adopting a blocked *1,3-alternate* conformation and bearing four cyanomethylene groups with silver cations under self-assembly conditions lead to the formation of either a 1D coordination network or a discrete binuclear metallomacrocycle.



Coordination polymers (CPs)[1,2] or coordination networks[3] are extended periodic architectures generated by self-assembly processes. This class of crystalline materials has been extensively studied,[1] in particular, for their applications.[4]

According to principles established in molecular tectonics,[2,5] coordination networks may be regarded as infinite assemblies displaying translational symmetry. Thus, they might be designed by combining coordinating tectons and metal centres or metal complexes. The reliability of the design of coordination networks depends on the flexibility of the coordination tecton, the coordination requirement of the metal centre and the nature of the anion when neutral coordinating tectons and metal cations are used.[6]

For the design of coordination networks, the macrocyclic [1.1.1.1]metacyclophane backbone is of particular interest. Indeed, owing to the presence of methyl groups, this rigid macrocyclic platform adopts a stable *1,3-alternate* conformation both in a solid state and in solutions in a temperature range from –60 to 150 °C.[7] The *1,3-alternate* conformation allows up to four coordinating sites to be positioned in a divergent manner thus leading to a variety of coordinating tectons. Many tetrasubstituted [1.1.1.1]metacyclophanes bearing hydroxyl,[7(c)] cyano,[8] mercapto,[9] pyridyl,[10] bipyridyl, quinolinyl[11] and imidazolyl[12] groups have been reported. Based on the above tectons, several coordination networks have been obtained upon their combinations with Hg^{II} or Ag^{I} cations.[8,12,13]



1 X = Cl
2 X = CN

Figure 1 *1,3-Alternate* conformation of [1.1.1.1]metacyclophanes **1** and **2**.

Here, we report on the synthesis of tecton **2** (Figure 1) and the formation of silver coordination compounds generated upon its combinations with two different silver salts $AgNO_3$ and $AgBF_4$.

Compound **2** is based on [1.1.1.1]metacyclophane adopting a *1,3-alternate* conformation and bearing four nitrile units. The spacer connecting the coordinating sites with the backbone is a methylene group. Owing to the conformation adopted by **2**, the four nitrile units are located below and above the main plane of the macrocycle in an alternate fashion; thus, they occupy the apexes of a pseudo-tetrahedron. The analogue of compound **2**, in which the nitrile units are directly connected to the backbone, has been reported.[8]

The synthesis of **2** was accomplished in 81% yield upon the replacement of all four chlorine atoms in **1**[7(c)] with CN groups by refluxing in a DMF–acetone mixture in the presence of a 10-fold excess of KCN.[†]

[†] Synthesis of 4,11,18,25-tetrakis(chloromethyl)-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane **1** was performed by modifying a previously reported procedure[7(c)] using $CHCl_3$ instead of CS_2.

Synthesis of 4,11,18,25-tetracyanomethyl-3,5,7,10,12,14,17,19,21,24,26,28-dodecamethyl[1.1.1.1]metacyclophane **2**. Compound **1** (1 g, 1.38 mmol) was suspended in DMF–acetone (3 : 1, 40 ml) and KCN (0.72 g, 11.06 mmol) was added. The reaction mixture was stirred for 30 h at reflux. After cooling to room temperature, the solvent was evaporated at a reduced temperature and the residue was treated with 50 ml of CH_2Cl_2. After filtration, the organic solvent was evaporated to dryness. After the addition of MeOH (50 ml) to the residue and filtration, pure compound **2** was obtained as a white powder, yield 0.77 g (81%), mp 246 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ: 1.07 (s, 12H, *p*-Me), 2.43 (s, 24H, *o*-Me), 3.73 (s, 8H, CH_2CN), 4.02 (s, 8H, Ar–C*H*$_2$–Ar). ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C) δ: 17.8, 18.9, 20.1, 33.3, 118.3, 126.1, 132.4, 135.8, 138.2. IR (ν/cm^{-1}): 2246 (C≡N). MS (MALDI-TOF), *m*/*z*: 684.24 [M$^+$] (calc., *m*/*z*: 684.96). Found (%): C, 84.02; H, 7.62; N, 8.15. Calc. for $C_{48}H_{52}N_4$ (%): C, 84.17; H, 7.65; N, 8.18.

The silver cation was used as a connecting metallic node since, on the one hand, it forms kinetically labile complexes and, on the other hand, it requires a rather loose coordination demand in terms of coordination number, geometry and bond distance.

Under self-assembly conditions, combinations of tecton **2** with two silver salts ($AgNO_3$ and $AgBF_4$) using different metal : tecton stoichiometries allowed us to obtain crystalline materials which were studied by X-ray diffraction (XRD) analysis on single crystals.‡

When a 2 : 1 metal : tecton stoichiometry is used in the synthesis, the combinations of tecton **2** with $AgBF_4$ or $AgNO_3$ lead to the formation of isostructural 1D coordination polymers **2**-AgX (X = NO_3 or BF_4) [Figure 2(*a*)].

Note that the same architecture was obtained regardless of the anion (trigonal NO_3^- or tetrahedral BF_4^-). In both cases, the crystal (**2**-$AgNO_3$ and **2**-$AgBF_4$) is composed of neutral tecton **2**, an Ag^+ cation and anions (BF_4^- or NO_3^-). Within the 1D network, a metal : tecton ratio of 1 : 1 is observed. The crystal (space group *Ia*3*d*) is composed of 1D cationic silver coordination networks separated by BF_4^- or NO_3^- anions [Figure 3(*a*)]. No specific and strong interactions between the anions and the cationic architectures are spotted. The cationic part of the crystal is generated by mutual interconnection between organic tectons **2** and silver cations through C≡N–Ag^+ interactions with Ag–N distances of 2.257(5) and 2.265(5) Å for **2**-$AgBF_4$ and **2**-$AgNO_3$, respectively (Table 1). The silver cation in a deformed tetrahedral coordination geometry is surrounded by four N atoms belonging to two consecutive tectons **2** with the N–Ag–N angle of 96.9(3)–132.7(3)°.

The cubic packing of the 1D networks is unusual.[15] Three identical 1D networks are aligned along the *a*, *b* and *c* axes [Figures 3(*b*),(*c*)]. The packing is compact thus preventing the presence of solvent molecules.

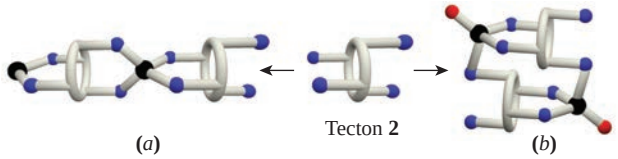


Figure 2 Schematic representations of (*a*) an extended 1D silver (in black) coordination network and (*b*) a discrete metallamacrocycle formed upon combining tecton **2** with the silver cation.

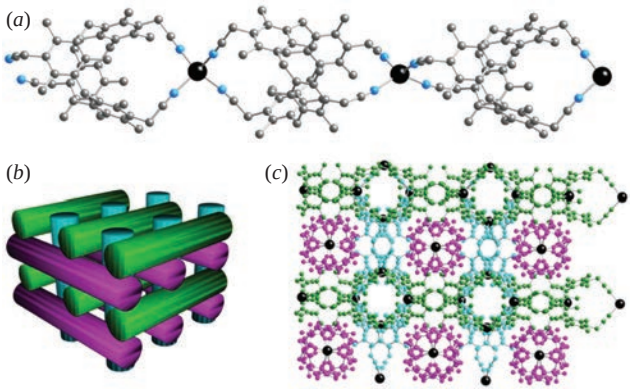


Figure 3 A portion of (*a*) isostructural 1D networks formed upon the combinations of tecton **2** with either $AgBF_4$ or $AgNO_3$, (*c*) their packing in a cubic arrangement and (*b*) schematic representation of the latter packing mode. Hydrogen atoms are not presented for clarity. For bond distances and angles, see the text and Table 1.

Table 1 Bond distances and angles for **2**-$AgBF_4$, **2**-$AgNO_3$ and [(**2**)$_2$-$(AgNO_3)_2$].

Compound	Ag–N/Å	Ag–O/Å	O–Ag–N/°	N–Ag–N/°	C≡N/Å
2-$AgBF_4$	2.257(5)	–	–	96.9(3) 102.9(3) 131.1(3)	1.190(8)
2-$AgNO_3$	2.265(5)	–	–	98.2(2) 100.3(3) 132.7(3)	1.169(7)
[(**2**)$_2$-$(AgNO_3)_2$]	2.238(5) 2.272(5)	2.371(4) 2.382(4)	95.80(17) 111.07(16) 123.88(18)	87.45(17) 110.24(16) 122.3(2)	1.134(7)

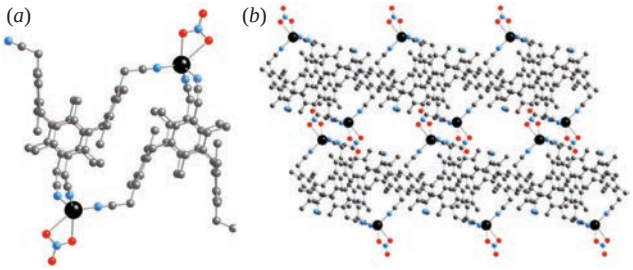


Figure 4 (*a*) Solid state structure of the metallamacrocyle [(**2**)$_2$-$(AgNO_3)_2$] and (*b*) the packing of molecular units in the crystal. $CHCl_3$ solvent molecules and hydrogen atoms are omitted for clarity. For bond angles and distances, see the text and Table 1.

Synthesis of [$Ag_3(C_{48}H_{52}N_4)_3(BF_4)_3$] **2**-$AgBF_4$. In a crystallization tube (diameter, 4 mm), a solution of **2** (5 mg, 7.3 μmol) in $CHCl_3$ (1 ml) was layered with a $CHCl_3$–MeOH (1 : 1) mixture (0.5 ml). A solution of $AgBF_4$ (3.39 mg, 14.6 μmol) in MeOH (1 ml) was then carefully added. At room temperature, slow diffusion in the dark afforded colourless crystals suitable for XRD after several days. Found (%): C, 65.76; H, 5.81; N, 6.25. Calc. for $C_{144}H_{156}Ag_3B_3F_{12}N_{12}$ (%): C, 65.54; H, 5.96; N, 6.37.

Synthesis of [$Ag_3(C_{48}H_{52}N_4)_3(NO_3)_3$] **2**-$AgNO_3$. In a crystallization tube (diameter, 4 mm), a solution of **2** (5 mg, 7.3 μmol) in $CHCl_3$ (1 ml) was layered with a $CHCl_3$–MeOH (1 : 1) mixture (0.5 ml). A solution of $AgNO_3$ (2.48 mg, 14.6 μmol) in MeOH (1 ml) was then carefully added. Slow diffusion in the dark and at room temperature afforded colourless crystals suitable for XRD after several days. Found (%): C, 67.68; H, 6.05; N, 8.12. Calc. for $C_{144}H_{156}Ag_3N_{15}O_9$ (%): C, 67.44; H, 6.13; N, 8.19.

Synthesis of [$Ag_2(C_{48}H_{52}N_4)_2(NO_3)_2$, $6CHCl_3$] (**2**)$_2$-$(AgNO_3)_2$. In a crystallization tube (diameter, 4 mm), a solution of **2** (5 mg, 7.3 μmol) in $CHCl_3$ (1 ml) was layered with a $CHCl_3$–MeOH (1 : 1) mixture (0.5 ml). A solution of $AgNO_3$ (4.96 mg, 29.2 μmol) in MeOH (1 ml) was then carefully added. At room temperature, slow diffusion in the dark produced colourless crystals suitable for XRD after several days. Found (%): C, 50.86; H, 4.42; N, 5.56. Calc. for $C_{102}H_{110}Ag_2Cl_{18}N_{10}O_6$ (%): C, 50.50; H, 4.57; N, 5.77.

‡ *Crystal data for* **2**-$AgBF_4$: $3(C_{48}H_{52}AgN_4)\cdot 3(BF_4)$, M_r = 2638.84, cubic, space group *Ia*3*d*, *a* = 29.4672(11) Å, *Z* = 8, d_{calc} = 1.370 g cm^{-3}, μ = 0.529 mm^{-1}, *F*(000) = 10944, the final *R* = 0.1043, *wR* = 0.3306. 24812 collected and 3125 independent reflections (R_{int} = 0.0567) were used in further refinement.

Crystal data for **2**-$AgNO_3$: $2(C_{48}H_{52}AgN_4)\cdot 2NO_3\cdot 6CHCl_3$, M_r = 2564.44, cubic, space group *Ia*3*d*, *a* = 29.2699(9) Å, *Z* = 8, d_{calc} = 1.359 g cm^{-3}, μ = 0.530 mm^{-1}, *F*(000) = 10704, the final *R* = 0.0885, *wR* = 0.2272. 3064 collected and independent reflections (R_{int} = 0.0616) were used in further refinement.

Crystal data for [(**2**)$_2$-$(AgNO_3)_3$]: $3(C_{48}H_{52}AgN_4)\cdot 3NO_3$, M_r = 2425.83, triclinic, space group *P*1, *a* = 12.7017(9), *b* = 14.8810(9) and *c* = = 15.5594(10) Å, α = 73.798(3)°, β = 69.159(3)°, γ = 86.320(4)°, *Z* = 1, d_{calc} = 1.527 g cm^{-3}, μ = 0.886 mm^{-1}, *F*(000) = 1240, the final *R* = 0.0885, *wR* = 0.2272. 3064 collected and independent reflections (R_{int} = 0.0616) were used in further refinement.

All crystallographic data for X-ray analysis were collected at 173(2) K on a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated MoKα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97.[14] The hydrogen atoms were introduced at calculated positions and not refined (riding model).

CCDC 1504654–1504656 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

The formation of 1D coordination networks based on combinations of cyano[1.1.1.1]metacyclophane[8] or cyano appended calixarene derivatives[16] with silver cations, which present the same connectivity, has been previously documented.

Surprisingly, in contrast to the above case, upon using a 4 : 1 metal : tecton stoichiometry, the combination of **2** with $AgNO_3$ afforded a discrete binuclear metallamacrocycle[17] [(**2**)$_2$-($AgNO_3$)$_2$] [Figure 4(*a*)]. Figure 2(*b*) shows the metallamacrocycle of the [22] type composed of two ligands **2** and two Ag^+ cations. The metallamacrocycle crystallises in the $P\bar{1}$ space group, and the crystal contains NO_3^- anions and chloroform molecules in addition to Ag^+ cations and ligands **2**. Compound **2** behaves as a tridentate ligand with only three of the four coordinating C≡N groups participating in the binding of the Ag^+ cation. The two silver cations, equivalent by a centre of symmetry, are pentacoordinated, and their coordination sphere is composed of three N atoms belonging to three C≡N moieties of two different ligands [Ag–N distances of 2.238(5) and 2.272(5) Å] and two O atoms belonging to a chelating NO_3^- anion with Ag–O distances of 2.371(4) and 2.382(4) Å (Table 1). Within the rectangular shape of the metallamacrocycle, the Ag–Ag distance is 13.843(19) Å.

In the crystals, the packing of the metallamacrocycles leads to ribbons along the *b* axis and consecutive ribbons are packed in a parallel fashion along the *a* and *c* axes [Figure 4(*b*)]. No specific interactions with $CHCl_3$ solvent molecules present in the crystal were observed.

Using a variety of other ligands, we have previously reported several metallamacrocycles based on silver and other cations.[12,17]

In conclusion, we have studied the synthesis and the propensity of neutral [1,1,1,1]metacyclophane **2** adopting a *1,3-alternate* conformation and bearing four nitrile units connected to the macrocyclic backbone by methylene units to form coordination networks using a silver cation as a metallic connecting node. We have found that, regardless of the anion (trigonal NO_3^- or tetrahedral BF_4^-), the combinations of tetradentate tecton **2** with Ag^+ lead to the formation of isostructural 1D silver coordination networks. However, by varying the metal : tecton ratio, we have revealed that the above extended architectures are obtained for a 2 : 1 stoichiometry. In marked contrast, when the Ag^+ : **2** ratio is increased to 4 : 1 during the synthetic procedure, instead of the extended assembly, a discrete [22] type metallamacrocycle based on two Ag^+ cations and two ligands **2** is formed. The obtained results testify that in the design of coordination networks, the control of the rigidity of the coordinating organic tecton, the nature of the anion and the M : tecton ratio play important roles.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.05.014.

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