

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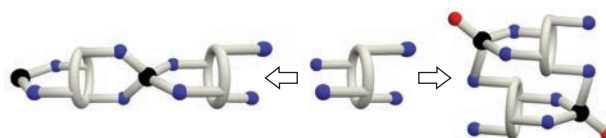
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Depending on the anion (NO_3^- or BF_4^-) and stoichiometry, the combinations of [1.1.1.1]metacyclophane adopting a blocked 1,3-alternate conformation and bearing four cyanomethylene groups with silver cations under self-assembly conditions lead to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



Coordination polymers (CPs)^{1,2} or coordination networks³ 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, quinolonyl¹¹ and imidazolyl¹² 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}

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**^(c) with CN groups by refluxing in a DMF–acetone mixture in the presence of a 10-fold excess of KCN.[†]

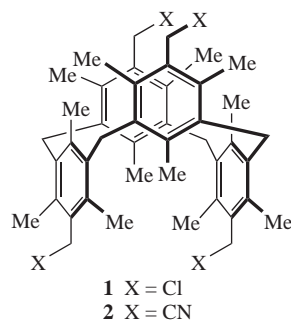


Figure 1 1,3-Alternate conformation of [1.1.1.1]metacyclophanes **1** and **2**.

[†] 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 . $^1\text{H NMR}$ (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- CH_2 -Ar). $^{13}\text{C NMR}$ (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 ($\text{C}\equiv\text{N}$). 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 $\text{C}_{48}\text{H}_{52}\text{N}_4$ (%): C, 84.17; H, 7.65; N, 8.18.