

Template Synthesis of Tetrakis–triazolylthiacalix[4]arene in the Cone Conformation and Supramolecular Structure of Its Hexanuclear Complex with Ag(I)

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Dedicated to the Corresponding Member of Russian Academy of Sciences Prof. Oscar I. Koifman on the occasion of his 70th Birthday

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A stereoselective synthesis of the cone stereoisomer of thiacalix[4]arene bearing four triazolyl coordinating sites at the lower rim, 2, has been achieved by the 1,3-dipolar cycloaddition of p-nitrophenylazide to tetrakis-(propargyloxy) thiacalix[4]arene, 1, in presence of copper(I) iodide. A combination of 2 with AgNO₃ leads to the formation of hexanuclear silver(I) complex with M:L ratio of 6:2. The latter forms a 3D π-bonded molecular network in the crystalline phase.

Keywords: Template synthesis, thiacalix[4]arenes, 1,3-dipolar cycloaddition reaction, 1,2,3-triazole.

Темплатный синтез тетракис–триазолилтиакаликс[4]арена в конформации конус и супрамолекулярная структура его гексаядерного комплекса с Ag(I)

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Осуществлен стереоселективный синтез 1,2,3-триазолилтиакаликс[4]арена в конфигурации конус реакцией 1,3-дипольного циклоприсоединения п-нитрофенилазида к тетракис-(пропаргилокси)тиакаликс[4]арену в присутствии иодида меди. Получен гексаядерный комплекс 1,2,3-триазолил-тиакаликс[4]арена с нитратом серебра состава L:M=2:6, представляющий собой трёхмерную π-связанную молекулярную сетку.

Ключевые слова: Темплатный синтез, тиакаликс[4]арены, реакция 1,3-дипольного циклоприсоединения, 1,2,3-триазол.

Introduction

Calix[4]arene derivatives^[1,2] are among the most investigated platform in supramolecular chemistry. Due to their unique structural features and synthetic availability, this class of molecules is widely used as building blocks for the formation of complex supramolecular architectures.^[3-5] The selective functionalization of the calix[4]arene platform by different substituents at the lower and/or upper rim as well as its existence as four conformers: *cone*, *partial cone*, *1,2-alternate* and *1,3-alternate* leads to almost endless possibilities for the design and generation of molecular and supramolecular systems displaying specific properties and functions.

Using coordination bonds, combinations of thiacalix[4]-arene derivatives^[6] with metallic cations, lead to the formation of complexes of various nuclearity,^[7] up to 32 metallic atoms for example.^[8]

Heterocycles such as 1,2,3-triazoles are suitable units for the formation of either H- or coordination-bonds.^[9] These species may be synthesized with high yields by the 1,3-dipolar cycloaddition^[10] catalyzed reaction. The combination of such heterocycles with the calix[4]arene backbone is of particular interest since it leads to a variety of multidentate coordinating ligands.^[11]

Here we report on the synthesis of the *cone* conformer of a *tetrakis*-triazolylthiacalix[4]arene **2** and its combination with silver(I) nitrate leading to the formation of a hexanuclear complex in the solid state.

Experimental

The solvents and reagents, when necessary, were purified according to the commonly described methods.^[12] Commercially available reagents from Acros, Alfa Aesar and Lancaster were used without any purification. All reactions were carried out under argon atmosphere. **1** was obtained according to the already reported procedure.^[13]

The NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ solvents on Bruker spectrometer Avance 600. Bruker Vector 22 Fourier spectrometer was used to record IR spectra in the wavenumber range of 400-4000 cm⁻¹ in KBr pellets or nujol. MALDI TOF mass spectra were recorded from the solutions of substances on a Bruker Ultraflex III mass-spectrometer in the concentration range of 10⁻³-10⁻⁵ M (*p*-nitroaniline matrix). Elemental analysis was performed on a CHN-analyzer *via* combustion of sample; melting point was measured on a Boetius compact heating table.

X-Ray data were collected at 173(2) K using a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation. The diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).^[14]

The atomic coordinates for **2** and 2₂-(AgNO₃)₆ structures have been deposited at the Cambridge Crystallographic Data Centre as CCDC 936529-936530. This material is available free of charge *via* Internet on <http://www.ccdc.cam.ac.uk>.

Synthesis

25,26,27,28-O-[(1-(*p*-Nitro)-phenyltriazolyl-4)-methoxy]-2,8,14,20-tetrathiacalix[4]arene [C₆₀H₄₀O₁₂S₄N₁₆] (**2**). **1** (0.1 g,

0.154 mmol), 1-azido-4-nitrobenzene (0.12 g, 0.694 mmol) and triethylamine (2 ml) were dissolved in dry toluene (5 ml) and stirred under argon at room temperature for 1 hour. A catalytic amount of CuI was added and the reaction mixture was stirred for 17 hours at 80 °C. After cooling, the red precipitate was filtrated and washed with toluene (10 ml) and diethylether (10 ml). The solid residue, corresponding to the compound **2**, in *cone* conformation (0.18 g, 0.138 mmol, yield: 90%). *R*_f = 0.80 (CH₃OH: CH₂Cl₂ = 0.1:10). M.p: 157-159 °C. ¹H NMR ([D₆]DMSO, 295 K) δ ppm: 5.41 (8H, s, -OCH₂). 6.86 (4H, t, *J*^β = 8 Hz, ArH), 6.99 (8H, d, *J*^β = 8 Hz, ArH), 8.08 (8H, d, *J*^β = 8 Hz, ArH), 8.32 (8H, d, *J*^β = 8 Hz, ArH), 9.02 (4H, s, CH). Anal. Calcd. for C₆₀H₄₀O₁₂S₄N₁₆: C, 55.21; H, 3.07; S, 9.82; N, 17.18 %. Found: C, 54.97; H, 3.15; S, 9.91; N, 17.25 %. *m/z* (MALDI-TOF): 1327 [M+Na]⁺, 1343 [M+K]⁺.

Crystallisation Conditions

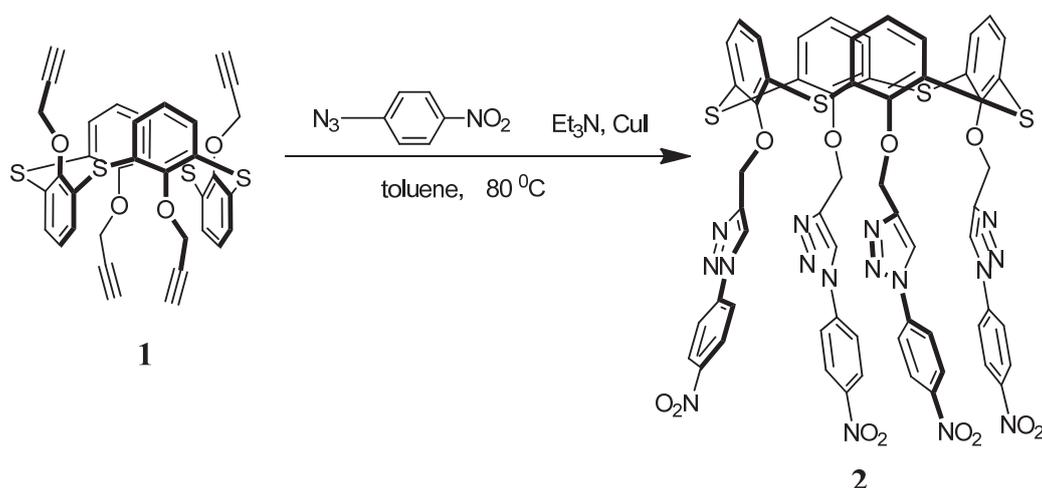
2: In a crystallization tube (20×4 mm), **2** (3 mg, 0.0023 mmol) was dissolved in 1.0 ml of a 1/1 DMF/CH₂Cl₂ mixture and layered with a 1/1 CH₂Cl₂/*iso*-PrOH mixture (0.1 ml). Then 1.0 ml of methanol was carefully added. The slow diffusion of the non-solvent at room temperature produced colourless single crystals of **2** which were analysed by X-ray diffraction on a single crystals. The crystallographic data are presented in the Table 3 (see Annex).

2₂-(AgNO₃)₆: In a crystallization tube (20×4 mm), **2** (3 mg, 0.0023 mmol) was dissolved in 1.0 ml of a 1/1 DMF/CH₂Cl₂ mixture, and layered with a 1/1 CH₂Cl₂/*iso*-PrOH mixture (0.1 ml). Then 1.0 ml of methanol solution containing AgNO₃ (0.0039 g, 0.023 mmol) was carefully added. The slow diffusion at room temperature produced colourless single crystals of 2₂-(AgNO₃)₆. The crystallographic data are presented in the Table 4 (see Annex). Anal. Calcd. for C₁₂₇H₁₀₆Ag₆Cl₆N₃₈O₄₆S₈: C, 37.97; 2, 66 ; N, 13.25 %; Found: C, 37.65; 2.75; N, 13.36 %.

Results and Discussion

Recently, we have reported the synthesis of *tetrakis*(propargyloxy)thiacalix[4]arene^[13] (**1**), in *1,3-alternate* conformation. The latter was obtained by alkylation of the lower rim by propargyl bromide in acetone in presence of Cs₂CO₃. With the aim of preparing the 1,2,3-triazolyl derivative **2** using click chemistry, the reactivity of the precursor **1** towards azide derivatives was investigated under mild conditions and in presence of triethylamine and a catalytic amount of CuI. Generally, this 1,3-dipolar cycloaddition proceeds with high regioselectivity as well as high yields.^[15] Indeed, the reaction of **1** with *p*-nitrophenylazide afforded the desired *tetrakis*-1,2,3-triazolylthiacalix[4]arene **2** in 90 % yield (Scheme 1, see Experimental part). Surprisingly, for **2**, instead of the expected *1,3-alternate* conformation, only the *cone* conformer, for which all four substituents are located on the same side of the thiacalix[4]arene backbone, was obtained.

For the passage from the *1,3-alternate* conformation adopted by **1** to the *cone* conformation for **2**, two explanations may be given. First of all, the replacement of the methylene groups connecting the aryl units in the classical calix[4]-arene by S atoms in **1** causes an increase in the size of the macrocycle, leading thus to decrease in the interconversion energy barrier between the different conformers of **1**. Secondly, copper(I) cation, catalysing the click reaction, might act as template promoting the formation of the *cone* conformer through its coordination by the triazolyl moieties located on the same side of the calix[4]arene **2** derivative.



Scheme 1. Cu⁺ catalyzed synthesis of **2**.

Compound **2** was characterized by NMR spectroscopy in solution and by mass MALDI TOF spectrometry. Furthermore, its structure in the solid state was investigated by X-ray diffraction on single crystal. Data gathered in solution and in the crystalline phase are in agreement with the *cone* conformation of **2**. It is worth noting that the cycloaddition of azides to the thiacalix[4]arene derivative proceeds in high yield and produces only the 1,4-regioisomer. Furthermore, the reaction proceeds in an analogue fashion as the one reported for the calix[4]arene derivative.^[16] Thus, the presence of sulphur atoms in thiacalix[4]arene exerts no influence on the reaction pathway and on the regioselectivity.

The slow diffusion, through a 1/1 CH₂Cl₂/*iso*-PrOH mixture, of a methanolic solution into a 1/1 DMF/CH₂Cl₂ mixture of **2** leads to the formation of colourless single crystals (see Experimental part). Compound **2** (2(C₆₀H₄₀N₁₆O₁₂S₄)·3(CH₂Cl₂)) crystallises in the presence of CH₂Cl₂ solvent molecules. Metrics observed for the thiacalix[4]arene backbone are close to those reported for the parent compound.^[17] In the crystal lattice, the tetrasubstituted thiacalix[4]arene derivative adopts a *pinched cone*

conformation (Figure 1) with two dihedral angles between distal aryl moieties of -65.40° and 138.50°.

The peculiar disposition of the aryl rings results from the establishment of multiple π - π interactions between the bulky triazolyl substituents at the lower rim and the aryl moieties of the adjacent calix unit. The main structural characteristics of the π - π interactions are presented in Table 1.

Table 1. Main characteristics of π - π interacting aromatic systems in the crystal structure of **2**.

Type of π - π interacting aromatic system	Centroid-centroid distance, Å	Dihedral angle, °
triazolyl (D)-nitrophenyl (B)	3.66	16.0
triazolyl (B)-triazolyl (C)	3.98	14.9
nitrophenyl (A)-nitrophenyl (B)	4.00	18.3

While relatively strong π - π interactions are observed between the triazolyl (D) and nitrophenyl (B) with a distance of 3.66 Å, for both triazolyl units (B) and (C) interacting

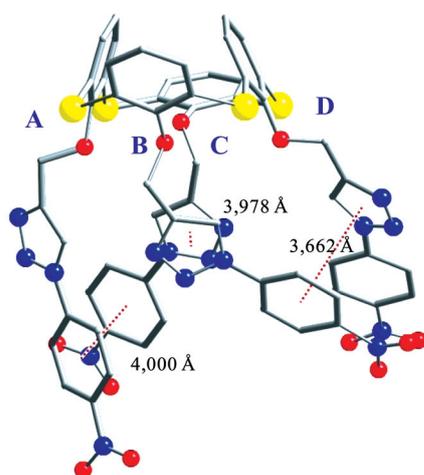


Figure 1. The solid state structure of **2**.

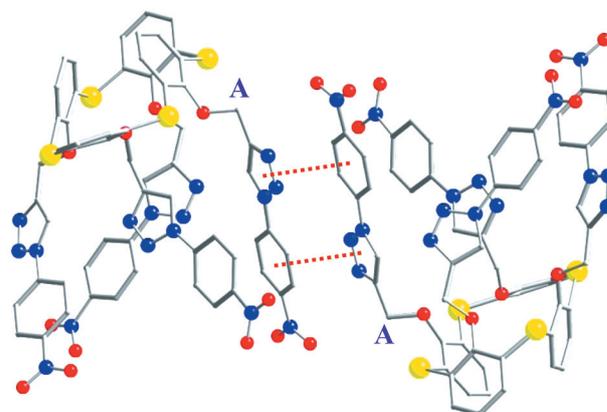


Figure 2. Crystal structure of centrosymmetric π -bonded dimer formed by two consecutive molecules **2** orientated in an alternate fashion.

with nitrophenyl units (A) and (B), the π - π interactions are considerably weaker with distance of 3.98 Å and 4.00 Å respectively. It is interesting to note that the triazolyl and nitrophenyl moieties belonging to the same pendent arm are not coplanar but tilted (\angle triazolyl (A) – nitrophenyl (A) = 2.3°, \angle triazolyl (B) – nitrophenyl (B) = 18.1°, \angle triazolyl (C) – nitrophenyl (C) = 26.9°, \angle triazolyl (D) – nitrophenyl (D) = 22.9°, for definition of A, B, C and D, see Figure 1).

In **2**, three types of intermolecular π - π interactions are observed in the solid state. The strongest one concerns interactions between triazolyl (A) and nitrophenyl (A) of neighbouring thiacalix[4]arene moieties (centroid-centroid distance of 3.61 Å, dihedral angle of 2.3°). This type of interaction leads to the formation of a centrosymmetric dimer (Figure 2). Along the (0,0,1) crystallographic plane, a second weaker π - π interaction takes place between aryl moieties of adjacent thiacalix[4]arenes (centroid-centroid distance of 4.10 Å, dihedral angle of 0°, distance between consecutive planes of 3.53 Å) (Figure 3a,b).

A third type of π - π intermolecular interaction, the weakest in nature, appears between aryl aromatic system (B) of thiacalix[4]arene backbone and nitrophenyl aromatic system (C) belonging to two consecutive thiacalix[4]arenes (centroid-centroid distance of 4.27 Å, dihedral angle of 28.9°) (Figure 4).

Thiacalix[4]arene derivatives bearing peripheral coordinating sites have been shown to form extended coordination networks, in particular with silver cation.^[18,19] It appeared of interest to investigate the propensity of compound **2** to form either discrete complexes or infinite networks in the presence of Ag(I) cation.

The slow diffusion, in the dark, of a methanolic solution of AgNO₃ through a 1/1 CH₂Cl₂/*iso*-PrOH mixture as buffer into a 1/1 DMF/CH₂Cl₂ mixture containing compound **2**, afforded colourless single crystals (see Experimental part). The crystal ([C₁₂₂H₈₈N₃₆O₃₆S₈·Ag₆(NO₃)₆·3(CH₂Cl₂)·2(CH₃OH)·2(H₂O)]·(2₂-(AgNO₃)₆)), is composed of hexanuclear discrete neutral silver complexes containing two ligands **2**, six Ag(I) cations and six nitrate anions as well as solvent molecules (Figure 5). Among H₂O, CH₂Cl₂, MeOH solvent molecules presenting in unit cell, only MeOH molecules are coordinated to silver cations. The neutral complex is centrosymmetric displaying two identical [2-Ag₃] cationic complexes orientated in a head-to-head fashion. The two units are interconnected by two S-Ag⁺-S coordination bonds.

As for **2**, in the hexanuclear complex 2₂-(AgNO₃)₆, the thiacalix[4]arene moiety adopts a *pinched cone* conformation with dihedral angles between the distal aryl rings of the macrocyclic backbone of 109.16° and -38.22°. For 2₂-(AgNO₃)₆, the metrics observed for the thiacalix[4]arene

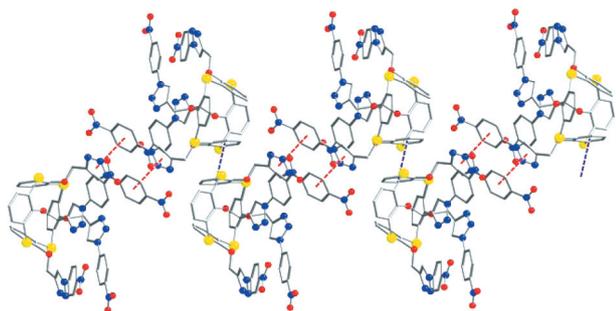


Figure 3a. A portion of the crystal structure of **2**: π - π interaction between the dimmers leading to the formation of a 1D π -bonded chain.

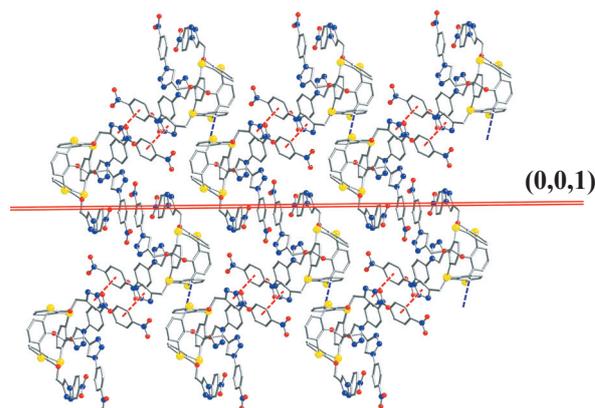


Figure 3b. Crystal packing of **2**. View along the (0,0,1) crystallographic plane.

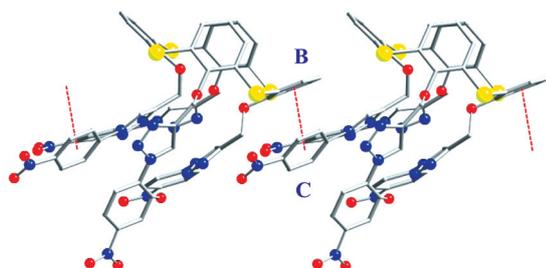


Figure 4a. A portion of the crystal structure of **2**: π - π interactions between the nitrophenyl aromatic system (C) and aryl aromatic system of thiacalix[4]arene backbone (B) belonging to two consecutive macrocycles.

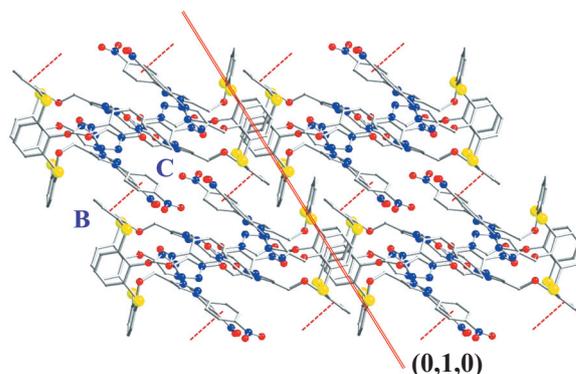


Figure 4b. Crystal packing of **2**. View along the (0,1,0) crystallographic plane.

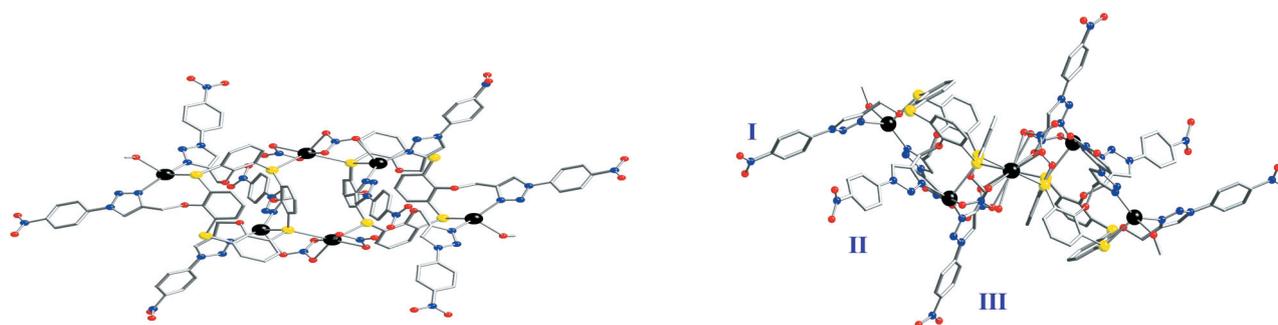


Figure 5. Two views of the X-ray structure of the hexanuclear $2_2-(\text{AgNO}_3)_6$ complex.

backbone is close to the one reported for the crystal structure of the free ligand **2**.

The coordination sphere of the silver cations is composed of nitrogen atoms belonging to the appended triazolyl moieties, oxygen atoms of the coordinating nitrate anions or methanol molecules, as well as sulphur atoms belonging to the thiacalix[4]arene backbone. Three non equivalent silver cations are present in $[2-\text{Ag}_3]$. Two of them, adopting both a distorted tetrahedral coordination geometry (Ag1 and Ag2), slightly differ by their coordination environ-

ments. Ag3, adopts a distorted octahedral environment. Ag1 cations are bound to two N-atoms belonging to proximal triazolyl moieties of the same thiacalix[4]arene, one S-atom and one methanol O-atom (Figure 6a) with Ag-N, Ag-S and Ag-O distances of 2.249(5) and 2.253(5), 2.7266(18) and 2.432(11) respectively and NAgN, NAgS, NAgO and OAgS angles of 138.1(2), 100.69(15) and 113.13(14), 107.7(4) and 91.2(4), and 99.0(6) respectively (see Table 2). The coordination sphere of Ag2 resembles the one of Ag1, however, the O-atoms belonging to coordinating methanol in Ag1 are

Table 2. Main characteristics (distances and angles) of coordination bonds in $2_2-(\text{AgNO}_3)_6$.

	Ag1	Ag2	Ag3
$d(\text{Ag}_x-\text{N}_y), \text{Å}$	2.249(5) (Ag_1-N_3) 2.253(5) ($\text{Ag}_1-\text{N}_{15}$)	2.175(5) (Ag_2-N_7) 2.180(5) ($\text{Ag}_2-\text{N}_{11}$)	-
$d(\text{Ag}_x-\text{S}_y), \text{Å}$	2.7266(18) (Ag_1-S_1)	2.9237(16) (Ag_2-S_3)	2.6377(15) (Ag_3-S_3) 2.5951(16) (Ag_3-S_4)
$d(\text{Ag}_x-\text{O}_y), \text{Å}$	2.432(11) ($\text{Ag}_1-\text{O}_{22}$)	2.567(6) ($\text{Ag}_2-\text{O}_{13}$)	2.726(7) ($\text{Ag}_3-\text{O}_{14}$) 2.447(8) ($\text{Ag}_3-\text{O}_{15}$) 2.486(6) ($\text{Ag}_3-\text{O}_{16}$) 2.628(8) ($\text{Ag}_3-\text{O}_{17}$)
$\angle (\text{N}_y-\text{Ag}_x-\text{N}_z), ^\circ$	138.1(2) ($\text{N}_3-\text{Ag}_1-\text{N}_{15}$)	145.5(2) ($\text{N}_7-\text{Ag}_2-\text{N}_{11}$)	-
$\angle (\text{N}_y-\text{Ag}_x-\text{S}_z), ^\circ$	100.69(15) ($\text{N}_{15}-\text{Ag}_1-\text{S}_1$) 113.13(14) ($\text{N}_3-\text{Ag}_1-\text{S}_1$)	94.96(15) ($\text{N}_7-\text{Ag}_2-\text{S}_3$) 110.41(15) ($\text{N}_{11}-\text{Ag}_2-\text{S}_3$)	
$\angle (\text{N}_y-\text{Ag}_x-\text{O}_z), ^\circ$	91.2(4) ($\text{N}_3-\text{Ag}_1-\text{O}_{22}$) 107.7(4) ($\text{N}_{15}-\text{Ag}_1-\text{O}_{22}$)	89.9(2) ($\text{N}_7-\text{Ag}_2-\text{O}_{13}$) 117.2(2) ($\text{N}_{11}-\text{Ag}_2-\text{O}_{13}$)	
$\angle (\text{O}_y-\text{Ag}_x-\text{S}_z), ^\circ$	99.0(6) ($\text{O}_{22}-\text{Ag}_1-\text{S}_1$)	78.54(17) ($\text{O}_{13}-\text{Ag}_2-\text{S}_3$)	73.2(2) ($\text{O}_{14}-\text{Ag}_3-\text{S}_3$) 82.3(2) ($\text{O}_{15}-\text{Ag}_3-\text{S}_3$) 140.0(2) ($\text{O}_{16}-\text{Ag}_3-\text{S}_3$) 91.4(2) ($\text{O}_{17}-\text{Ag}_3-\text{S}_3$) 89.8 ($\text{O}_{14}-\text{Ag}_3-\text{S}_4$) 128.3(2) ($\text{O}_{15}-\text{Ag}_3-\text{S}_4$) 77.1(2) ($\text{O}_{16}-\text{Ag}_3-\text{S}_4$) 94.5(2) ($\text{O}_{17}-\text{Ag}_3-\text{S}_4$)
$\angle (\text{O}_y-\text{Ag}_x-\text{O}_z), ^\circ$	-	-	115.8(2) ($\text{O}_{15}-\text{Ag}_3-\text{O}_{16}$) 50.7(2) ($\text{O}_{15}-\text{Ag}_3-\text{O}_{14}$) 133.2(2) ($\text{O}_{15}-\text{Ag}_3-\text{O}_{17}$) 146.3(2) ($\text{O}_{14}-\text{Ag}_3-\text{O}_{16}$) 163.9(2) ($\text{O}_{14}-\text{Ag}_3-\text{O}_{17}$) 49.6(2) ($\text{O}_{16}-\text{Ag}_3-\text{O}_{17}$)
$\angle (\text{S}_y-\text{Ag}_x-\text{S}_z), ^\circ$	-	-	121.11(5) ($\text{S}_3-\text{Ag}_3-\text{S}_4$)

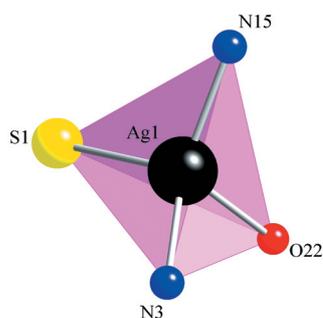


Figure 6a. Coordination environment of Ag1 cation.

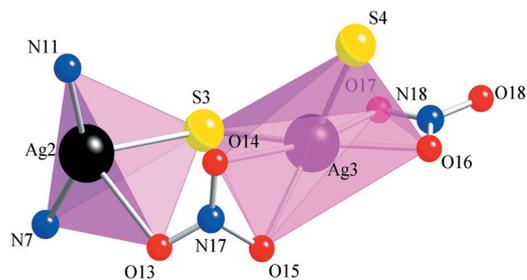


Figure 6b. Coordination environment of Ag2 and Ag3 cations.

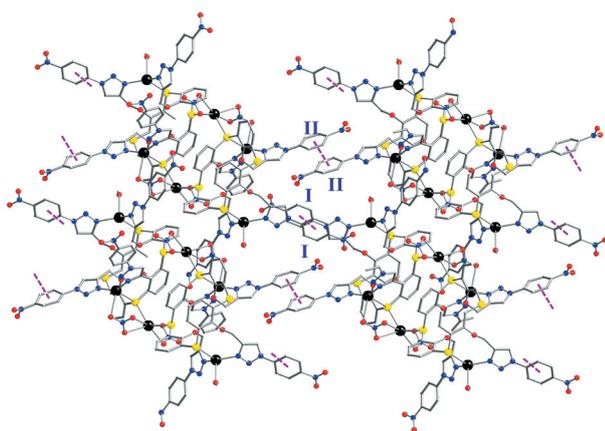


Figure 7a. A portion of the crystal structure of $2_2-(\text{AgNO}_3)_6$ showing the formation of a 2D network by π - π interactions between nitrophenyl moieties of the I-I and II-II types.

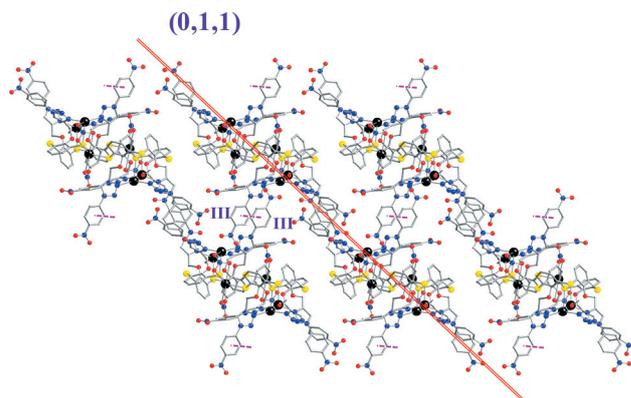


Figure 7b. Crystal packing of $2_2-(\text{AgNO}_3)_6$ (view along (0,1,1) plane) showing π - π interactions of the type III between nitrophenyl units.

replaced by O-atom of the bridging nitrate anion (Figure 6b), with Ag-N, Ag-S and Ag-O distances of 2.175(5) and 2.180(5), 2.9237(16) and 2.567(6) respectively and NAgN, NAgS, NAgO and OAgS angles of 145.5(2), 94.96(15) and 110.41(15), 89.9(2) and 117.2(2), and 78.54(17) respectively (see Table 2). Ag3, adopting an octahedral geometry, behaves as bridging atom holding together the two thiacalix[4]arene units through two Ag-S coordination bonds in *cis* position with the sulphur atoms belonging to two consecutive thiacalix[4]arene moieties. Thus, the octahedral environment of Ag3 is composed by two sulphur atoms and four oxygen atoms belonging to two different nitrate anions bridging Ag2 and Ag3 cations with Ag-S and Ag-O distances of 2.249(5) and 2.253(5), 2.7266(18) and 2.432(11) respectively and OAgS and OAgO angles in the 49.6(2) - 163.9(2)°, and 73.2(2) - 140.0(2)° range respectively (see Table 2).

In $2_2-(\text{AgNO}_3)_6$, the packing of the hexameric units results from π - π interactions and van der Waals contacts leading to a 3D π -bonded network. The π - π interactions take place between six out of the eight nitrophenyl moieties classified as I, II and III type (for definition see Figure 5). The nitrophenyl moieties I and II lead to π - π interactions of the I-I and II-II types forming thus a 2D π -bonded network in the (0,1,1) crystallographic plane (Figure 7a) with centroid-centroid distances for I-I and II-II of 4.04 Å and 3.65 Å, respectively and dihedral angle in both cases of 0° with

distances between planes of 3.28 Å (I-I) and 3.51 Å (II-II), respectively. The packing of the resulting parallel sheets leads to the formation of a 3D network through π -bonding of the III-III type (Figure 7b) with the centroid-centroid distance of 3.62 Å and dihedral angle of 0°. In the third dimension, the distance between planes is 3.48 Å.

No specific interaction between the cationic calixarene dimeric units with solvent molecules and non-bonded nitrate anions present in the crystal lattice has been found.

Conclusion

The 1,3-dipolar cycloaddition in presence of Cu(I) between *tetrakis*-(propargyloxy)thiacalix[4]arene (**1**) and *p*-nitrophenylazide leads to the regioselective synthesis of *tetrakis*-1,2,3-triazolylthiacalix[4]arene (**2**). X-Ray analysis of the latter revealed that whereas the parent compound **1** was in the *1,3-alternate* conformation, compound **2** adopts the *cone* conformation. The shift in conformation from *1,3-alternate* to *cone* could result from a template effect exerted by Cu(I) cation. The combination of the ligand **2** with AgNO_3 salt was found to lead to the formation of a hexanuclear silver complex. Within this complex, all silver cations are coordinated by four triazolyl appended moieties of **2** in *cone* conformation. When taking into account π - π interactions

between the *p*-nitrophenyl units, the overall structure may be described as a 3D π -bonded network.

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