Molecular tectonics: on the formation of 1-D silver coordination networks by thiacalixarenes bearing nitrile groups

Marina N. Kozlova,[a,b] Sylvie Ferlay,[a,*] Svetlana E. Solovieva,[b] Igor S. Antipin,[b,c]† Alexander I. Konovalov,[b] Nathalie Kyritsis,[a] Mir Wais Hosseini[a]*

Introduction

The design, formation and characterisation of coordination networks, infinite periodic architectures formed upon mutual interconnection between organic units and metal centres or metal complexes are areas of current interest.1 Molecular tectonics is an efficient and operational approach in this area.2-7 It is based on two main principles which are specific coordination events taking place between organic and metallic construction units called tectons8 leading to an assembling pattern and the iteration of the process transforming the latter into the nodes of the network. Thus, for coordination networks, the organic tecton must offer coordinating sites (often donor hetero elements) and the metal centre or metal complex must possess free coordination sites. The formation of coordination networks occurs under self-assembly processes (for crystalline materials during the crystallisation event) and one of the driving forces is the establishment of coordination bonds between the donor sites located on the organic tecton and available coordination sites on the metal centre. Since almost two decades, considerable effort has been invested in obtaining coordination networks and a large variety of examples have been reported.8-16 Molecular networks are defined by their dimensionality (1-, 2- or 3-D) which results from the number of translations in different directions of space operating on the assembling pattern. Within each dimensional category, these networks are defined by their geometry. For example, within 1-D networks, several types of arrangements (linear, stair type, zigzag type, helical, tubular etc.) may be formed. The geometry of the final assembly is obviously governed by both the structural and coordination features of the organic tecton and the metal centre. Dealing with linear and tubular coordination networks (Fig. 1), one may design an organic tecton offering four coordinating sites located in an alternate fashion above and below a cyclic unit (S4 symmetry). Using a metal connector adopting linear coordination geometry, one may envisage the formation of a tubular network (Fig. 1 top) in which the tecton behaves as tetakis monodentate unit towards metal centres. We have previously demonstrated this possibility by combining [1,1,1,1]-metacyclophane derivatives in 1,3-altinate conformation bearing either four nitrile groups17 or four pyridyl units,18 with silver cation. In the case of tectons offering the proper orientation and an appropriate distance between the coordinating sites on the same face allowing the two sites to bind to the same metal centre infinite 1-D non-tubular architectures may be generated in the presence of metal centres adopting the tetrahedral coordination geometry (Fig. 1 bottom). We have also reported such a case using a calix[4]arene derivative in 1,3-altinate blocked coordination bearing four nitrile groups at the upper rim.19

Fig. 1 Schematic representation of the formation of a tubular (top) or non-tubular (bottom) 1-D networks based on the self-assembly of a tecton bearing four coordinating sites occupying the apices of a tetrahedron and metal centres offering either linear or tetrahedral coordination geometries.

In this contribution, we report on the formation of three homometallic 1-D coordination networks based on combinations of AgX salts (X = BF$_4$, PF$_6$ and SbF$_6$) and the p-tertbutylthiacalix[4]arene derivative 3 in 1,3-altinate conformation bearing four butynonitrile groups at the lower

[a] Laboratoire de Chimie de Coordination Organique, UMR CNRS 7140, Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France, hosseini@chimie.u-strasbg.fr
[b] A.E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Science, Arbuzov str. 8, Kazan 420088, Russian Federation
[c] Kazan State University, Kremlevskaya str. 18, Kazan 420008, Russian Federation
† Electronic Supplementary Information (ESI) available: [Crystallographic data in cif format]. See http://dx.doi.org/10.1039/b000000x/
For the design principle of 1-D networks discussed above, the calix[4]arene derivatives and thiacalix[4]arene derivatives are interesting backbones. However, when unsubstituted at the lower rim, these tetr phenolic macrocycles are flexible entities and exist in solution as a mixture of four conformers (cone (C), partial cone (CP), 1,2-alternate (1,2-A) and 1,3-alternate (1,3-A)). In the solid state, both p-tertbutylcalix[4]arene and p-tertbutylthiacalix[4]arene adopt the cone conformation. Among the four conformers, only the 1,3-A one fulfills the orientation requirement discussed above. Based on the calix[4]arene backbone, using the functionalisation of both the lower rim to impose the 1,3-A conformation and the upper rim to introduce coordination sites, we have demonstrated the viability of the approach by generating 1-D silver coordination networks. One may also envisage another strategy which consists of imposing the 1,3-A conformation by functionalising only the lower rim with a fragment bearing at its extremity a monodentate coordination site. This was applied using the p-tertbutylthiacalix[4]arene for which only few examples of infinite coordination have been reported.

The design of compounds 2 and 3 (Scheme) is based on p-tertbutylthiacalix[4]arene 1 in 1,3-A conformation as a backbone, four nitrile groups as coordinating sites and alkyl spacer connecting the two parts. The junction between the calix and the spacer occurs at the lower rim and is ensured by an ether link. The two ligands 2 and 3 differ by the length of the spacer (CH₂ for 2 and (CH₃)₃ for 3) connecting the nitrile group to the calix moiety. The length of the spacer was varied in order to explore its role on the conformational mobility of the calix backbone. Indeed, as previously reported for calix[4]arene derivatives, whereas for 2 one would expect interconvertible conformers, for 3 blocked conformers should be obtained. Furthermore, for the 1,3-A conformer, the length of the spacer would allow to control the positioning and distance of the nitrile groups with respect to the p-tertbutyl groups on the same face of the backbone.

**Results and discussion**

The synthesis of 2 and 3 was rather straightforward (see experimental part). The starting material for the preparation of 2 and 3 was p-tertbutylthiacalix[4]arene 1. Both compounds 2 and 3 were obtained upon condensation of 1 with α-halonitriles under basic conditions (K₂CO₃) in refluxing dry acetone. Whereas for the synthesis of 2 the condensation was performed between 1 and bromoacetonitrile, for the preparation of compound 3, 4-chlorobutyronitrile was reacted with 1. For the compound 2, although overall yield was 76%, in solution (CDCl₃) ¹H-NMR investigations revealed the simultaneous presence of the partial cone (PC) and 1,3-alternate (1,3-A) conformers in 1/1.5 ratio at room temperature. The equilibrium between the two conformers could be shifted to 1/2 by heating the solution to 50 °C for 30 minutes. Based on the nature of the spacer connecting the nitrile group to the calix oxygen atom (CH₂), this conformational mobility is expected. In marked contrast, compound 3 was isolated in 67% yield under experimental conditions used, as a pure 1,3-A conformer. No interconversion between conformers was observed by NMR in CDCl₃.

The solid state structure of both ligands 2 and 3 were investigated using X-ray diffraction on single crystal (see experimental part). Although in CDCl₃ solution, the compound 2 presents conformational mobility with the PC and 1,3-A conformers as dominant species, upon crystallisation, only the 1,3-A conformer was obtained under the conditions used (see experimental part) (Figure 2). Compound 2 crystallises in the trigonal system (Space group P321). No solvent molecule is present in the lattice. The observed C-S distance, in the range of 1.76-1.80 Å, is in agreement with the one observed for the parent compound 1 (1.79 Å).²³ For the ether junction between the calix and the pendant arms, the carbon to oxygen distances are in the range of 1.38 - 1.39 Å for O-C(Ph)) and 1.42 - 1.43 Å for C-O. The four nitrile groups (C≡N distance of 1.10 Å and 1.14 Å) are located in an alternate fashion below and above the main plane of the thiacalixarene. The CH₂CN fragments are almost linear with NCC angle of 173.3 and 178.5°. The pendant arms bearing the nitrile groups are oriented almost parallel to the calix long axis (CCO angle in the range of 106.4° and 109.0°, COC angle in the range of 110.2° and 111.7°). The aromatic moieties on the same face of the molecule are almost parallel. It is worth noting that because of the short nature of the spacer connecting the nitrile group to the calix, the CN groups are in close proximity with the t-butyl moieties located on the same face (distance in the range of ca. 3.6 – 4.6 Å).
The packing of calix units 2 is rather peculiar as shown on figure 3. Indeed, among the three thiacalixarene moieties in the unit cell, two present short N-N distances of 3.88 Å between nitrile groups belonging to two different calix 2, (see below for comparison with the packing of free ligands 3).

The solid state structure of the ligand 3 was also investigated by X-ray diffraction on single crystal (see experimental part). As in solution (CDCl₃), compound 3 adopts the 1,3-A conformation (Figure 4). Compound 3 crystallises in the orthorhombic system (Space group P222) with one CHCl₃ solvent molecule. The latter occupies the empty space with no specific interactions with calix unit. The C-S distance, in the range of 1.76 - 1.79 Å, is again in agreement with the one observed for 2 and for the parent compound 1 (1.79 Å).²³ For the ether junction between the calix and fragments bearing the nitrile groups, the carbon to oxygen distances are in the range of 1.38 - 1.39 Å for O-C(Ph)) and 1.43 – 1.47 Å for C-O. The four nitrile groups (C≡N distance in the range of 1.10 - 1.14 Å, NCC Angle in the range of 175.9 - 179.0°) are also located in an alternate fashion below and above the main plane of the thiacalixarene. However, in marked contrast with 2, among the four (CH₃)₂CN groups (CCO angle in the range of 106.5° and 110.0°, COC angle in the range of 111.0° and 114.0°), three of them are oriented towards the exterior whereas one is pointing towards the interior. Again in contrast with 2, the aromatic rings on the same face of the molecule are not almost parallel but tilted leading to a flattened 1,3-A conformation.

Fig. 3 Packing of three consecutive units 2 in the solid state (projection of the (001) plane). H atoms and solvent molecules are not presented for sake of clarity. For bond distances and angles see text.

The propensity of both ligands 2 and 3 to behave as a tecton by forming infinite coordination networks was tested in the presence of silver cation. In order to study the possible role played by the anion, BF₄⁻ and XF₆⁻ (X = P or Sb) anions possessing tetrahedral and octahedral coordination geometries respectively were used.

Fig. 4 The solid state structure of 3 showing the adopted 1,3-alternate conformation. Among the four arms bearing the nitrile groups, one is oriented outwardly. H atoms and solvent molecules are not presented for sake of clarity. For bond distances and angles see text.

For the compound 2, although we have made several attempts based on many combinations of solvent and crystallisation conditions, unfortunately, we were unable to produce crystalline material for structural investigations by X-ray diffraction methods. Based on the solid structure of 2 mentioned above (Fig. 2), this could have been anticipated for steric reasons. Indeed, because of the short nature of the spacer (CH₃) connecting the calix backbone to the nitrile group, the formation of a 1-D network upon connection of consecutive units by silver cation must generate severe steric interactions, in particular between t-butyl groups belonging to consecutive calix units.

On the other hand, the inspection of the packing of compound 3 in the crystalline phase (Fig. 5) clearly shows the proper predisposition of the units and thus the possibility of behaving as a coordinating tecton by bridging consecutive metal centres. This was indeed achieved by combining the tecton 3 with AgX (X = BF₄⁻, SbF₆⁻ and PF₆⁻). In all three cases, suitable crystals for X-ray diffraction on single crystal have been obtained upon slow liquid-liquid diffusion at room temperature using either CH₂Cl₂ or CHCl₃ to solubilize the tecton 3 and a iPrOH or EtOH solution of the silver salt (see experimental section). Since, independent of the nature of the anion used, almost identical polycationic silver 1-D networks were obtained, here, we shall only discuss in detail the combination of 3 with AgBF₄. In all three cases, the crystal is composed of neutral tecton 3, Ag⁺ cation, anion (BF₄⁻, PF₆⁻ or SbF₆⁻) and solvent molecules (CHCl₃ and iPrOH for AgBF₄, CHCl₃ for AgSbF₆ and CH₂Cl₂ for AgPF₆). In none of the...
three studied structures specific interactions between the Ag⁺
cation and anions could be observed. The solvent molecules
present in the lattice occupy the empty space again with no
specific interactions with 3 or Ag⁺ cation. For all three
crystals, the 3/Ag⁺ stoichiometry is 1/1. When considering
the interactions between organic tectons 3 and silver cations, the
crystal may be described as 1-D cationic silver coordination
networks separated by anions and solvent molecules. The
cationic part of the crystal is generated by mutual
interconnection of organic moieties and metallic centres
through nitrile silver interactions (Fig. 6). The other
heteroatoms (O and S) are not involved in bonding
interactions with the cation.

Fig. 6: A portion of the solid state structure obtained upon
combining compound 3 with AgBF₄ showing the mutual
bridging between the organic tecton 3 and Ag⁺ cations leading
to the formation of a cationic 1-D coordination network. H
atoms, anions and solvent molecules are not presented for sake of clarity. For bond distances and angles see text.

For the organic tecton 3, as for its free form, it adopts the 1,3-
A conformation with the four nitrile groups (C≡N distance in the
range of 1.03 - 1.15 Å, NCC Angle in the range of 171.0 -
177.2°) located in an alternate fashion below and above the
main plane of the thiacalixarene. The C-S distances, in the
range of 1.76 - 1.79 Å, are close to those observed for the free
tecton 3. For the ether junction, the carbon to oxygen
distances are in the range of 1.34 Å - 1.37 Å for O-C(Ph) and
1.41 Å - 1.46 Å for C-O. In marked contrast with the free
ligand 3, all four (CH₃)₂CN groups (CCO angle in the range of
100.9° and 107.5°, COC angle in the range of 113.0° and
115.4° and OCOC dihedral angle in the range of -179.2 -
179.9) are almost fully stretched. As for the free ligand 3, the
aromatic rings on the same face of the molecule are tilted
leading to a flattened 1,3-A conformation.
The Ag⁺ cation (two crystallographically non equivalent)
connecting consecutive tectons 3 is tetra coordinated. Its
coordination sphere is composed of four N atoms belonging to
two consecutive tectons 3 (Ag-N distance in the range of 2.19 -
2.33 Å). The coordination geometry around the cation is a
distorted tetrahedron (NAGN angle varying between 93° and
124°). Due to the length and flexible nature of the spacer
connecting the calix moiety to the nitrile group, tecton 3
behaves as a bischelating unit. Indeed, on each face of the
molecule, two nitriles bind to the same silver cation.
The distances between consecutive Ag⁺ cations within the 1-D
network are ca 16.20 and 16.46 Å. The shortest distances
between Ag⁺ cations belonging to two consecutive networks
along the a and b axis are 15.00 Å and 11.75 Å respectively.
In terms of packing (Fig. 7), the 1-D networks are arranged in
parallel (along the a axis) and antiparallel (along the b axis)
fashions.

Fig. 7: Packing of 1-D silver coordination networks generated
upon combining the tecton 3 with AgBF₄ showing the parallel
arrangement along the a axis(a) and the antiparallel
disposition along the b axis (b) of consecutive 1-D networks
in the crystal. H atoms, anions and solvent molecules are not
presented for sake of clarity. For bond distances and angles
see text.

Conclusions
Both ligands 2 and 3 in the 1,3-alternate conformation offer
four nitrile coordinating sites occupying the apices of a
pseudo tetrahedron. However, in the case of ligand 2 bearing
four CH₃CN groups, so far we have not been able to generate
silver coordination networks. This may be due to the length of
the spacer, a methylene group, connecting the thiacalix
backbone to the nitrile moiety which would generate steric
interactions between the ρ-butyl groups and the silver cation.
On the other hand, for the ligand 3, the propyl spacer,
connecting the nitrile to the oxygen atoms of the thiacalix,
is long enough to avoid such a steric interactions and thus,
allows the formation of linear 1-D silver coordination
networks in the presence of different silver salts. The ligand 3
behaves as a bischelating tecton, i.e. on each face of the unit
the two nitrile groups coordinate to the same metal cation.
Consequently, the formation of the network results from
bridging of consecutive silver cations adopting tetrahedral
coordination geometry. Interestingly, the generation of the
network is robust and independent of the nature of the anion.
The combination of ligands reported here and longer
alogues with other metal centres is currently under
investigation.

Experimental
General: All reagents were purchased from commercial
sources and used without further purification. p-tert-
Butylthiacalix[4]arene 1 was prepared according to
the literature.²² ¹H NMR spectra were recorded at room
temperature on a Bruker (300 MHz) NMR spectrometer. FT-
IR spectrum were recorded on a Perkin Elmer spectrometer.
Mass spectra (MS(ES⁺)) were obtained on a MALDI-TOF
Dynamo Finnigan mass spectrometer using 1,8,9-
Cristallisation of (3-AgPF$_6$)$_n$: In a crystallisation tube, a solution of 3 (3.0 mg) in CHCl$_3$ (1 mL) was carefully layered with THF (0.25 mL) and then a solution of AgPF$_6$ (7.7 mg) in EtOH (1 mL) was added. Upon slow diffusion at room temperature and in the dark, colourless crystals were obtained after several days.

Cristallisation of (3-AgSbF$_6$)$_n$: In a crystallisation tube, a solution of 3 (4.0 mg) in CHCl$_3$ (1 mL) was layered with a solution of AgSbF$_6$ (13.7 mg) in isopropanol (1 mL). The slow diffusion at room temperature and in the dark produced colourless crystals after several days.

Acknowledgements
Notes and references

1. S. R. Batten and R. Robson, Angew. Chem. Int. Ed., 1998, 37, 1460.
2. S. Mann, Nature, 1993, 365, 499.
3. J. D. Wuest, Chem. Comm., 2005, 5830.
4. M. W. Hosseini, Acc. Chem. Res., 2005, 38, 313.
5. M. W. Hosseini, Cryst. Eng. Comm., 2004, 6, 318.
6. M. Simard, D. Su and J. D. Wuest, J. Am. Chem. Soc., 1991, 113, 4696.
7. M. W. Hosseini, in NATO ASI Series, Eds. D. Braga, F. Grepiono, G. Orpen, Serie C, Kluwer, Dordrecht, Netherlands, 1999, 538, 181.
8. B. Moulton and M.J. Zaworotko, Chem. Rev., 2001, 101, 1629.
9. C. Janiak, Dalton Trans., 2003, 2781.
10. A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, Coord. Chem. Rev., 1999, 193, 117.
11. G. F. Swiegers and T. J. Malefetse, Chem. Rev., 2000, 100, 3483.
12. M. Eddaoui, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O’Keefe and O. M. Yaghi, Acc. Chem. Res., 2001, 34, 319.
13. L. Carlucci, G. Ciani and D. M. Proserpio, Coord. Chem. Rev., 2003, 246, 247.
14. S. Kitagawa, Angew. Chem. Int. Ed., 2004, 43, 2434.
15. G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, Acc. Chem. Res., 2005, 38, 218.
16. D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, Acc. Chem. Res., 2005, 38, 273.
17. C. Klein, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, Chem. Commun., 2000, 239.
18. G. Laugel, E. Graf, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, New J. Chem., 2006, 30, 1340.
19. G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas, J. Fischer, Chem Commun., 1998, 2545.
20. C.D. Gutsche in Calixarenes Revised: Monographs in Supramolecular Chemistry Vol. 6, The Royal Society of Chemistry, Cambridge, 1998.
21. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens in Calixarenes 2001, (Eds. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens) Kluwer Academic, Dordrecht, 2001.
22. H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, Tetrahedron Lett., 1997, 38, 3971.
23. H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. De Cian, J. Fischer, Tetrahedron Lett., 1998, 39, 2311.
24. M. W. Hosseini, ACS Series, Eds G. J. Lumetta, R. D. Rogers, A. S. Gopalan, 2000, 557, 296.
25. M.W. Hosseini in Calixarenes 2001, (Eds. Z. Asfari, V. Böhmer, J. Harrowfield and J. Vicens) Kluwer Academic, Dordrecht, 2001, pp.110.
26. P. Lhoták, Eur. J. Org. Chem., 2004, 1675.
27. N. Morohashi, F. Narumi, N. Iki, T. Hattori, S. Miyano, Chem. Rev., 2006, 106, 5291.
28. G. D. Andreetti, R. Ungaro, A. Pochini, Chem. Commun., 1979, 1005.
29. H. Akdas, E. Graf, M.W. Hosseini, A. De Cian, J.M. Harrowfield, Chem. Commun., 2000, 2219.
30. J. Sykora, M. Himl, I. Stobor, I. Cisarova, P. Lhotak, Tetrahedron, 2007, 63, 1675.
Graphical abstract

The combination of a thiacalix[4]arene in 1,3-alternate conformation bearing four nitrile groups at the lower rim with silver cation leads, independent of the nature of the anion used, to the formation of 1-D coordination networks in the crystalline phase.