



# **Discrete Di- and Tetranuclear Silver Complexes Based on ortho -Imino- or ortho -Amino-methylpyridyl-Appended p-tert -Butylcalix[4]arene or p-tert -Butylthiacalix[4]arene in 1,3-Alternate Conformation**

M. H. Noamane, Sylvie Ferlay, Rym Abidi, Nathalie Kyritsakas, Mir Wais Hosseini

## **► To cite this version:**

M. H. Noamane, Sylvie Ferlay, Rym Abidi, Nathalie Kyritsakas, Mir Wais Hosseini. Discrete Di- and Tetranuclear Silver Complexes Based on ortho -Imino- or ortho -Amino-methylpyridyl-Appended p-tert -Butylcalix[4]arene or p-tert -Butylthiacalix[4]arene in 1,3-Alternate Conformation. European Journal of Inorganic Chemistry, 2017, 2017 (27), pp.3327-3336. <10.1002/ejic.201700459>. <hal-02300946>

**HAL Id: hal-02300946**

**<https://hal.science/hal-02300946v1>**

Submitted on 10 Dec 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# Discrete binuclear and tetranuclear silver complexes based on *ortho*-imino- or *ortho*-amino-methylpyridyl appended *p*-*tert*-butyl-calix[4]arene or *p*-*tert*-butyl-thiacalix[4]arene in 1,3-alternate conformation

M. H. Noamane,<sup>[a],[b]</sup> S. Ferlay,<sup>[a],\*</sup> R. Abidi,<sup>[b]</sup> N. Kyritsakas,<sup>[a]</sup> M. W. Hosseini,<sup>[a],\*</sup>

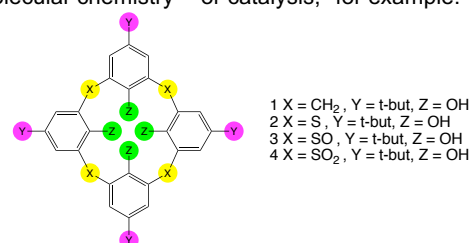
**Abstract:** The four new multivalent ligands **5–8** derived from calix[4]arene and thiacalix[4]arene backbones in 1,3-Alternate conformation bearing *ortho*-imino- and *ortho*-amino-methylpyridine chelating sites have been designed, prepared and characterized. Owing to the imposed 1,3-Alternate conformation of the backbone, ligands **5–8** offer two coordinating pockets composed of two sets of chelates located above and below the mean plane of the macrocyclic framework. Ligands **6–8**, independent of the nature of the anion associated with Ag<sup>+</sup> cation, form binuclear silver complexes (AgX, X = BF<sub>4</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup>, SbF<sub>6</sub><sup>−</sup>, AsF<sub>6</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup>) in solution and in the solid state. Ligand **7**, in the presence of an excess of Ag<sup>+</sup>, also forms tetranuclear silver complexes **7**-(AgBF<sub>4</sub>)<sub>4</sub>, and **7**-(AgNO<sub>3</sub>)<sub>4</sub> in presence of two different auxiliary ligands (H<sub>2</sub>O or NO<sub>3</sub><sup>−</sup>) that have been characterized in the solid state. Due to a rather short Ag–Ag distance of ca 2.89 Å, the tetranuclear complex **7**-(AgBF<sub>4</sub>)<sub>4</sub> is emissive in the solid state, at 298 K ( $\lambda_{\text{exc}}$  = 295 nm,  $\lambda_{\text{em}}$  = 425 nm) resulting from argentophilic interactions between the closely positioned silver cations.

## Introduction

Multivalent ligands are of interest for the formation of multinuclear metal complexes. For the design of such complexing agents, calix[4]arene (CA, **1**, X = CH<sub>2</sub>, Z = OH),<sup>1</sup> thiacalix[4]arene (TCA, **2**, X = S, Z = OH),<sup>2</sup> and its sulfonyl (Z = OH, X = SO, **3**)<sup>3</sup> or sulfinyl (Z = OH, X = SO<sub>2</sub>, **4**)<sup>4</sup> derivatives are backbones of interest (Scheme 1). Indeed, for steric reasons this class of molecule can not be planar and adopts four limit conformations (cone, partial cone, 1,2-Alternate and 1,3-Alternate). For all conformers, the nature of the substituent Y in the *para* position of the phenolic rings (Scheme 1) may be varied.

Finally, using the reactivity of the phenolic OH group under basic conditions towards electrophiles, the backbone may be functionalized with a variety of groups.

Over the past three decades, calix[4]arene and thiacalix[4]arene derivatives have been widely exploited in several areas of supramolecular chemistry<sup>5,6</sup> or catalysis,<sup>7</sup> for example.



**Scheme 1:** Generic representation of calix[4]arene derivatives **1–4** showing all possible modification sites (Y (upper rim), Z (lower rim) and X (bridge)).

Examples of nanometric multinuclear metal complexes based on calix[4]arene or thiacalix[4]arene derivatives in different conformations, have been well documented.<sup>8,9,10</sup>

Among the four possible conformations adopted by calix[4]arene backbone, the 1,3-Alternate conformer is particularly well suited for the design of multivalent ligands. Indeed, the latter allows to position in an alternate fashion up to four interaction sites forming two distinct coordinating pockets above and below the mean plane of the macrocyclic unit.

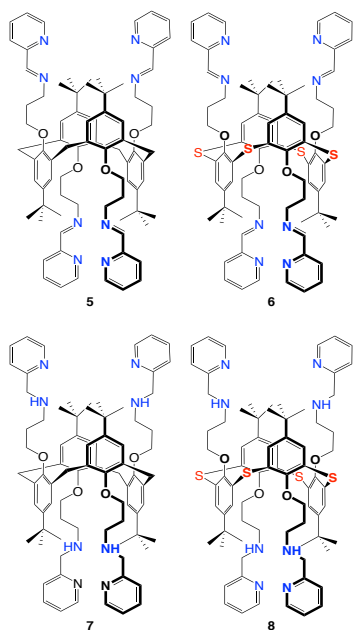
Multinuclear silver complexes with short Ag<sup>+</sup>–Ag<sup>+</sup> distances are of particular interest since, owing to argentophilic interactions, they emit light upon excitation, in the solid state and also in solution.<sup>11</sup>

Here we report on a series of four new ligands **5–8** based on either *p*-*tert*-butylcalix[4]arene **1** or *p*-*tert*-butylthiacalix[4]arene **2** in 1,3-Alternate conformation (Scheme 1) bearing four *ortho*-imino (ligands **5** and **6**) or *ortho*-amino (ligands **7** and **8**) chelating units and their propensity to form binuclear or tetranuclear silver complexes (Figures 1 and 2).

[a] M. H. Noamane, S. Ferlay,<sup>\*</sup> N. Kyritsakas and M. W. Hosseini<sup>\*</sup>  
Molecular Tectonics Laboratory, Université de Strasbourg, CNRS,  
CMC UMR 7140, F-67000 Strasbourg, France  
E-mail: [ferlay@unistra.fr](mailto:ferlay@unistra.fr), [hosseini@unistra.fr](mailto:hosseini@unistra.fr)

[b] M. H. Noamane, R. Abidi  
Université de Carthage, Laboratoire d'Application de la Chimie aux  
Ressources et Substances Naturelles et à l'Environnement  
(LACReSNE), unité des interactions moléculaires spécifiques,  
Faculté des Sciences de Bizerte, 7021 Bizerte, Tunisia

Supporting information for this article is given via a link at the end of the document: <sup>1</sup>H-NMR spectra for **5–8** and Crystallographic tables for **6**, **7**, **6**-(AgX)<sub>2</sub> (X = SbF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>, AsF<sub>6</sub><sup>−</sup> and NO<sub>3</sub><sup>−</sup>), **8**-(AgX)<sub>2</sub> (X = AsF<sub>6</sub><sup>−</sup> and PF<sub>6</sub><sup>−</sup>) **7**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>−</sup> and PF<sub>6</sub><sup>−</sup>), **7**-(AgBF<sub>4</sub>)<sub>4</sub> and **7**-(AgNO<sub>3</sub>)<sub>4</sub>.

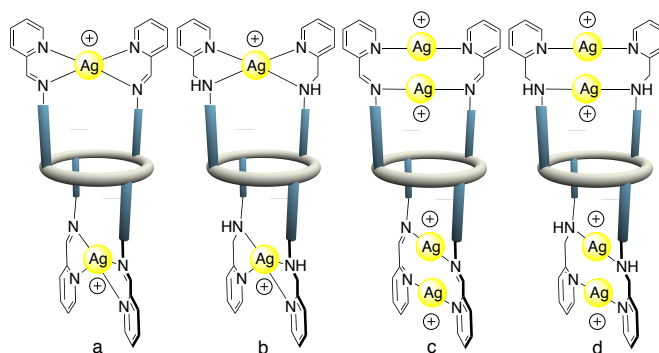


**Figure 1:** *ortho*-imino- and *ortho*-amino ligands **5–8** based on either *p*-*tert*-butylcalix[4]arene **1** or *p*-*tert*-butylthiacalix[4]arene **2** in 1,3-Alternate conformation.

## Results and Discussion

### Design of ligands 5–8

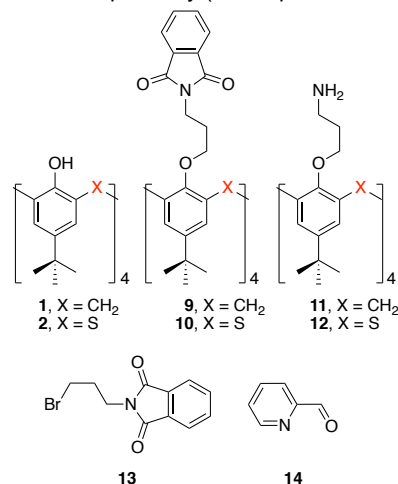
With aim of preparing binuclear (Figure 2a and 2b) and tetranuclear silver complexes (Figure 2c and 2d) with short  $\text{Ag}^+ \cdots \text{Ag}^+$  distance, ligands **5–8** based on calix[4]arene CA (compounds **5** and **6**) and thiacalix[4]arene TCA (compounds **7** and **8**) macrocyclic backbones in 1,3-Alternate conformation were designed (Figure 1). The backbone is equipped with four *ortho*-imino-methylpyridyl (ligands **5** and **6**) or *ortho*-amino-methylpyridyl (ligands **7** and **8**) chelating units. Ligands based on *ortho*-iminomethylpyridyl coordinating group and their transition metal complexes have been scarcely documented in the literature.<sup>12</sup> Calixarene derivatives involved in complexes with silver cations have been widely described in the literature.<sup>8,13</sup> In the present work, the coordinating moieties are connected to the backbone through a propyl fragments using ether junctions. The choice of the pyridyl unit is based on its ability to bind metal cations such as  $\text{Ag}^+$  or  $\text{Hg}^{2+}$ .<sup>14</sup> The design principle discussed above should, on one hand, lead to the formation of binuclear species (Figure 2a and 2b) through independent binding of the cation by the two chelates located on each face of the ligand and, on the other hand, to the formation of tetranuclear complexes resulting from binding of two silver cations by each coordinating pockets located above and below the macrocyclic backbone (Figure 2c and 2d). Although the coordination mode for the binuclear complexes is rather classical and previously described, to the best of our knowledge, the coordination of two silver cations with argentophilic interactions within each coordinating pocket is unusual and has not been reported



**Figure 2:** Schematic representations of possible binuclear (a and b) and tetranuclear (c and d) silver complexes by ligands **5–8**.

### Synthesis of ligands 5–8

The synthesis of the ligands **5–8** (Figure 1) was achieved using a stepwise strategy. Starting with either calix[4]arene derivative **1** or thiacalix[4]arene derivative **2**, their condensation with *N*-(3-bromopropyl)phthalimide **13** (Scheme 2) in the presence of  $\text{Cs}_2\text{CO}_3$  afforded the amino-protected compounds **9** and **10** in 1,3-A conformation respectively (see experimental section).



**Scheme 2:** Starting compounds **1** and **2** and precursors **9–14** used for the synthesis of ligands **5–8**.

The synthesis of **9** has been previously investigated.<sup>15</sup> It was reported that the formation of the cone conformer in high yield (83%) was favoured by the stepwise use of (i)  $\text{K}_2\text{CO}_3$ /acetonitrile for disubstitution and  $\text{NaH}/\text{DMF}$  for tetrasubstitution<sup>15c</sup> or (ii)  $\text{NaH}/\text{DMF}$  (yield 55 %).<sup>15b, 16</sup> In our hand, the combination  $\text{Cs}_2\text{CO}_3$  and DMF afforded the intermediate **9** in 1,3-A conformation in a relatively good yield (55%). The phthalimido derivative **10** in cone and 1,3-A conformation<sup>17 18</sup> was also reported with 68% yield for the latter. The deprotection of phthalimido derivatives **9** and **10** was achieved by treatment with hydrazine.<sup>19</sup> The amino compounds **11** and **12** were obtained in 98% and 97% yields respectively.

The imino compounds **5** and **6** were obtained in 63% and 78% yields respectively upon condensation of 2-Pyridinecarboxaldehyde **14** with the amino derivatives **11** and **12** in DMF/EtOH (scheme 2). Compounds **5** and **6** are unstable under acidic conditions. Finally, the *ortho*-aminomethylpyridine ligands **7** and **8** were obtained in 84% and 85% yields respectively upon reduction of compounds **5** and **6** using NaBH<sub>4</sub> in MeOH (or EtOH).

All four ligands (**5-8**), in addition to usual characterisation methods, were studied in solution by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. As expected, the <sup>1</sup>H-NMR study revealed that the imino N=CH group signals were downfield shifted (8.23 and 8.24 ppm for **5** and **6** respectively) with respect to signals corresponding to the amino HN-CH<sub>2</sub> unit (3.83 and 3.78 ppm for **7** and **8** respectively) (see figure S1 in Supporting Information). The imino ligands **6** based on the TCA backbone and the amino ligand **7** based on the CA platform have been also characterized in the solid state by X-ray diffraction on single crystals.

### Solid-state description of ligands **6** and **7**

After many attempts, we were only able to grow single crystals for compounds **6** and **7**. Crystals of compounds **6** were obtained upon CH<sub>3</sub>CN vapours diffusion into CHCl<sub>3</sub> solutions of **6**, whereas crystals of **7** were obtained upon Hexane vapours diffusion into a CHCl<sub>3</sub> solution of **7**. The structural investigations of ligands **6** and **7** were carried out by X-ray diffraction methods on single crystals (Crystallographic table S1 (Supporting Information) and Figure 3).

In agreement with solution NMR studies, both compounds **6** and **7** adopt the expected 1,3-A conformation in the crystalline phase. Compound **6** and **7** crystallise in the *P*2<sub>1</sub>/*n* and *P*2/*n* space groups respectively. Whereas crystals of compounds **6** contain CHCl<sub>3</sub> molecules with no specific interactions with the ligand, for ligand **7**, no solvent molecule is found in the crystal.

For both compounds **6** and **7**, metrics for the macrocyclic part are close to those observed for the parent CA and TCA and will not be detailed here. Relevant distances and angles are gathered in table 1. For compounds **6**, one of the four *tert*-butyl groups was found to be disordered, the same holds for one of the four imino-pyridyl appended group.

For the imino derivative **6**, the C=N distances are in the 1.203(7) - 1.340(10) Å range (see table 1) with the CNC angles ranging from 108.0(7)° to 119.2(5)°. For the amino derivative **7**, the HC-NH distances are in the 1.409(5)Å -1.435(6)Å range with CNC angles ranging from 111.8(6)° to 113.3(4)°. These bond distances and angles confirm the presence of sp<sup>3</sup> nitrogen atoms.

Table 1: Useful angles and distances in **6** and **7**.

	<b>6</b>	<b>7</b>
d-(C <sub>A</sub> -S) (Å)	1.760(5)-1.776(4)	-
d-(C <sub>A</sub> -C) (Å)	-	1.511(5)-1.516(5)
d-(O - C) (Å)	1.360(5)	1.388(4)-

C <sub>A</sub> (Å)	-	1.452(5)
	1.439(5)	
C=N (imino)	1.203(7) 1.233(7) 1.256(11) 1.340(10)	-
C-N (amino)	-	1.409(5) 1.435(6)
CNC (imino or amino)	108.0(7) 109.5(7) 118.5(10) 119.2(5)	111.8(6) 113.3(4)

Owing to the presence of propyl linker connecting the imino- or amino-pyridyl units to the macrocyclic calix[4]arene backbone, no rational trend could be spotted for the position and orientation of pyridyl groups (see Figure 3).

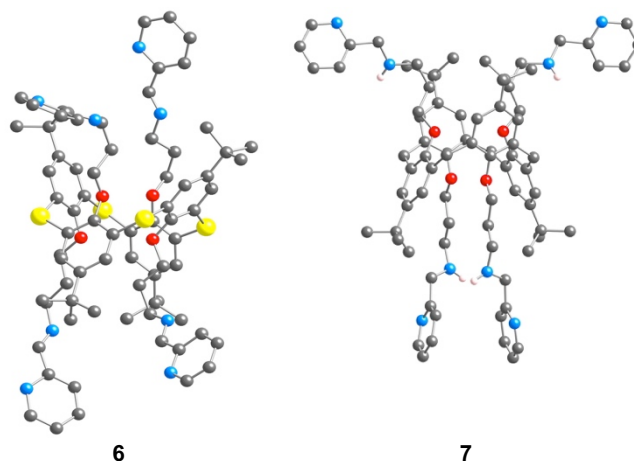


Figure 3: The solid-state structures of **6** (left) and **7** (right) showing the 1,3-A conformation of both ligands. H atoms and solvent molecules in the case of compound **6**, are not presented for clarity. For **6**, disordered *tert*-butyl groups and imino-pyridine group are not presented. For bond distances and angles see text.

The binding propensity of all four multivalent ligands **5-8** towards silver cation, in particular the formation of tetranuclear species, was investigated both in the solid state and in solution.

### Silver complexes in the solid state

After many attempts to prepare crystalline species upon combining ligands **5-8**, with different silver salts (AgX, X = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>), only for ligands **6**, **7** and **8** crystalline complexes have been obtained (see experimental section). All three ligands **6**, **7** and **8**, when combined with Ag<sup>+</sup> cation with Metal/Ligand (M/L) ratio of 2 or 3, form, independent of the nature of the anion, binuclear complexes (M<sub>2</sub>L, L = **6**, **7** or **8**) in the solid state.

Interestingly, in the case of ligand **7**, for M/L ratio greater than 4, tetranuclear species have been observed in the solid-state with two different counter-anions (BF<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>).

For all ligands **5-8**, owing to the remote position of S atoms, the latter do not participate in the binding of silver cation.

Since metrics associated with the calix backbones for the binuclear and tetranuclear complexes was found to be close to those observed for the parent compounds **6** and **7**, they will not be discussed in detail here.

### Binuclear silver complexes

As stated above, the role played by the anion on the formation of binuclear complexes was studied by using different Ag<sup>+</sup> salts with weakly (BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>) to strongly (NO<sub>3</sub><sup>-</sup>) coordinating anions. Furthermore, the role of the M/L ratio (2:1 or 3:1) on the stoichiometry of the complex was also investigated.

*Ortho*-iminopyridine TCA based binuclear complexes **6**-(AgSbF<sub>6</sub>)<sub>2</sub>, **6**-(AgAsF<sub>6</sub>)<sub>2</sub>, **6**-(AgBF<sub>4</sub>)<sub>2</sub> and **6**-(AgNO<sub>3</sub>)<sub>2</sub> were obtained at room temperature as single crystals (see table 4) upon slow diffusion of a MeOH solution containing the silver salt into a CHCl<sub>3</sub> solution of **6**, through a *iso*-PrOH/CHCl<sub>3</sub> layer with a 3:1 or 2:1 M/L ratio (see experimental part). Using *Ortho*-aminomethylpyridine CA based ligand **7** or TCA based compound **8**, single crystals of **7**-(AgBF<sub>4</sub>)<sub>2</sub> and **7**-(AgPF<sub>6</sub>)<sub>2</sub> and **8**-(AgAsF<sub>6</sub>)<sub>2</sub>, **8**-(AgPF<sub>6</sub>)<sub>2</sub>, (table S2, Supporting Information) were obtained upon ether vapour diffusion into a MeOH/CH<sub>2</sub>Cl<sub>2</sub> mixture containing **7** (or **8**) and the silver salt with a 3:1 or 2:1 M/L ratio (see experimental part).

The unit cell of all binuclear compounds **6**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) are isometric and crystallises in the orthorhombic system (space group *Pccn* for X = BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> and *Pna*2<sub>1</sub> for SbF<sub>6</sub><sup>-</sup>) (table S2, Supporting Information).

**7**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) are isometric and crystallise in the monoclinic system in the space group *P2<sub>1</sub>c*, *P2/c* or *C2/c*. (see crystallographic table 4). **8**-(AgPF<sub>6</sub>)<sub>2</sub> is also isometric to the above mentioned series and crystallise in the *Pccn* space group. Binuclear complexes **8**-(AgAsF<sub>6</sub>)<sub>2</sub> and **6**-(AgSbF<sub>6</sub>)<sub>2</sub> crystallise with CHCl<sub>3</sub> solvent molecules, **6**-(AgAsF<sub>6</sub>)<sub>2</sub> with H<sub>2</sub>O molecules, **7**-(AgPF<sub>6</sub>)<sub>2</sub> with MeOH molecules, **6**-(AgNO<sub>3</sub>)<sub>2</sub> with MeOH and H<sub>2</sub>O molecules and **7**-(AgBF<sub>4</sub>)<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub> solvent molecules. Owing to the presence of disorder, structures of **6**-(AgBF<sub>4</sub>)<sub>2</sub>, **6**-(AgNO<sub>3</sub>)<sub>2</sub>, **8**-(AgAsF<sub>6</sub>)<sub>2</sub> and **8**-(AgPF<sub>6</sub>)<sub>2</sub> were refined using the SQUEEZE command.<sup>20</sup>

For the imino binuclear compounds **6**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>), the C=N distances are in the 1.241(16) - 1.334(10) Å range with the CNC angles varying between 114.9(6)° and 120.1(13)° (table 2).

For the amino binuclear compounds **8**-(AgX)<sub>2</sub> (X = AsF<sub>6</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>), **7**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>), C-N distances are in the 1.443(13) - 1.537(19) Å range with CNC angles varying between 107.8(4)° and 115.8(9)° (table 3).

Table 2: useful angles and distances for the imino binuclear compounds **6**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>). im and py indicate the localization of the N atom on either imino or pyridyl units.

	<b>6</b> -(AgSbF <sub>6</sub> ) <sub>2</sub>	<b>6</b> -(AgAsF <sub>6</sub> ) <sub>2</sub>	<b>6</b> -(AgBF <sub>4</sub> ) <sub>2</sub>	<b>6</b> -(AgNO <sub>3</sub> ) <sub>2</sub>
C=N	1.241(16)	1.255(7)	1.249(7)	1.260(8)
(imino)	1.256(12)	1.275(9)	1.259(8)	1.334(10)
	1.294(13)			

	1.315(15)			
CNC	117.7(9)			
(imino)	118.2(10)	117.7(5)	117.4(5)	114.9(6)
	119.1(10)	117.9(7)	117.6(6)	118.7(7)
	120.2(9)			
Ag-N	2.216(8)) (im)			
	2.238(9) (im)			
	2.240(8)	2.216(6)	2.197(6)	2.188(8)
	(im)	(im)	(im)	(im)
	2.254(9)	2.244(5)	2.240(4)	2.255(5)
	(im)	(im)	(im)	(im)
	2.372(10)	2.424(5)	2.413(6)	2.417(8)
	(py)	(py)	(py)	(py)
	2.410(8)	2.381(7)	2.427(5)	2.435(6)
	(py)	(py)	(py)	(py)
	2.421(7)			
	(py)			
	2.441(9)			
	(py)			
NAgN	72.2(3)	- 72.37(18)-	71.71(17)-	72.38(15)-
	155.9(3)	160.7(2)	162.7(3)	160.0(2)

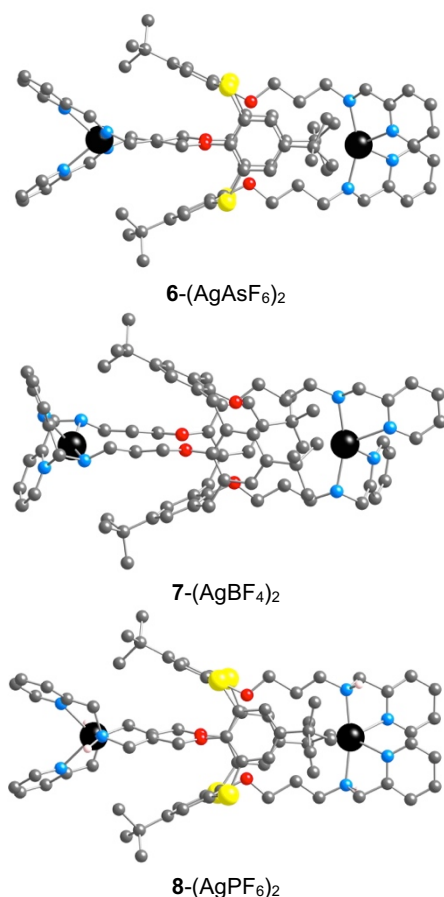
Table 3: useful angles and distances for the amino binuclear compounds **7**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) and **8**-(AgX)<sub>2</sub> (X = AsF<sub>6</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>). am and py indicate the localization of the N atom on either amino or pyridyl units.

	<b>7</b> -(AgBF <sub>4</sub> ) <sub>2</sub>	<b>7</b> -(AgPF <sub>6</sub> ) <sub>2</sub>	<b>8</b> -(AgAsF <sub>6</sub> ) <sub>2</sub>	<b>8</b> -(AgPF <sub>6</sub> ) <sub>2</sub>
C-N	1.465(7)			
(amino)	1.481(7)	1.456(10)	1.443(13)	1.435(8)
	1.488(6)	1.482(7)	1.537(19)	1.443(13)
	1.490(7)			
CNC	107.8(4)			
(amino)	110.8(4)	111.0(5)	115.2(12)	109.5(10)
	110.9(4)	111.4(6)	115.8(9)	110.9(5)
	111.0(4)			
Ag-N	2.273(4) (am)			
	2.273(5) (am)			2.331(6) (am)
	2.281(4)	2.307(6) (py)	2.299(8)	2.284(11)
	(am)	2.350(6) (py)	(am)	(am)
	2.320(5)	2.355(6)	2.359(12)	2.403(5)
	(am)	(am)	(am)	(py)
	2.366(4) (py)	2.358(5)	2.402(7) (py)	2.449(16)
	2.449(4) (py)	(am)	2.468(6) (py)	(py)
	2.466(5) (py)			
	2.499(4) (py)			
NAgN	73.52(15)- 161.32(14)	74.45(19)- 144.32(18)	73.9(3)- 169.6(4)	68.5(8)- 168.2(2)

For all the binuclear compounds **6**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>), **7**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) and **8**-(AgX)<sub>2</sub> (X = AsF<sub>6</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>), the metal centre is tetra-coordinated and the environment around the silver cations is similar and composed of 4 nitrogen atoms, two of them belonging to the amino (or imino) coordinating groups and two of the pyridyl type (Figure 3), for relevant distances see tables 2 and 3. The d<sub>Ag-N</sub> varies between 2.197(6) and 2.499(4) Å and the NAgN angles are in the 68.5(8) - 169.6(4)° range showing a strong deformed

tetrahedral environment around the silver cations (Figures 4). In all cases (except for **7**-(AgPF<sub>6</sub>)<sub>2</sub>), the Ag-N<sub>py</sub> distances are always longer than Ag-N<sub>im</sub> or Ag-N<sub>am</sub> (see tables 2 and 3). It is worth noting that for all binuclear complexes, owing to the tetrahedral coordination geometry around the silver cation, for each metallic centre one expects either a *R* or a *S* configuration. For the binuclear species, one thus expects (*RR*), (*SS*) and (*RS*) = (*SR*) (*meso* form due to the symmetry of the ligand). For **7** out of the 8 binuclear complexes, the crystal contains both (*RR*) and (*SS*) enantiomers thus forming an internal racemate. Interestingly, only for the **8**-(AgAsF<sub>6</sub>)<sub>2</sub>, within the complex both *R* and *S* configuration for the two silver cation leading thus to an achiral *meso* form.

In all cases, no specific interactions between anions and the binuclear complexes could be spotted. Only short van der Waals contacts with C-F distance of *ca* 3.1 Å for **6**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> and SbF<sub>6</sub><sup>-</sup>), **7**-(AgX)<sub>2</sub> (X = BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) and **8**-(AgX)<sub>2</sub> (X = AsF<sub>6</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) are observed.



**Figure 4:** Solid state structures of binuclear complexes **6**-(AgAsF<sub>6</sub>)<sub>2</sub>, **7**-(AgBF<sub>4</sub>)<sub>2</sub> and **8**-(AgPF<sub>6</sub>)<sub>2</sub> formed by combination of the organic tectons **6**, **7** and **8** with AgX salts. H atoms, anions and, solvent molecules, when present, are not presented for clarity. For bond angles and distances see text and tables.

### Tetranuclear silver complexes

The tetranuclear complexes **7**-(AgNO<sub>3</sub>)<sub>4</sub> and **7**-(AgBF<sub>4</sub>)<sub>4</sub> were also obtained by ether vapour diffusion into a CH<sub>3</sub>CN solution (or H<sub>2</sub>O/CH<sub>3</sub>CN mixture) of **7** and the silver salt AgX (X = BF<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>) with the M/L ratio of 4:1 (see experimental part). **7**-(AgBF<sub>4</sub>)<sub>4</sub> crystallizes in the tetragonal system (*I*<sub>4</sub>/a space group), whereas **7**-(AgNO<sub>3</sub>)<sub>4</sub> crystallizes in the monoclinic system (*C*2 space group) (see crystallographic table S3, Supporting Information). Whereas crystals of **7**-(AgBF<sub>4</sub>)<sub>4</sub> contain H<sub>2</sub>O molecules in the unit cell, those of **7**-(AgNO<sub>3</sub>)<sub>4</sub> contain both H<sub>2</sub>O and CHCl<sub>3</sub> molecules.

C-N distances of 1.484(7) and 1.489(8) Å and 1.484(6) Å are observed for **7**-(AgNO<sub>3</sub>)<sub>4</sub> and **7**-(AgBF<sub>4</sub>)<sub>4</sub> respectively. The CNC angles vary between 110.5(5) and 112.1(5)° (table 4).

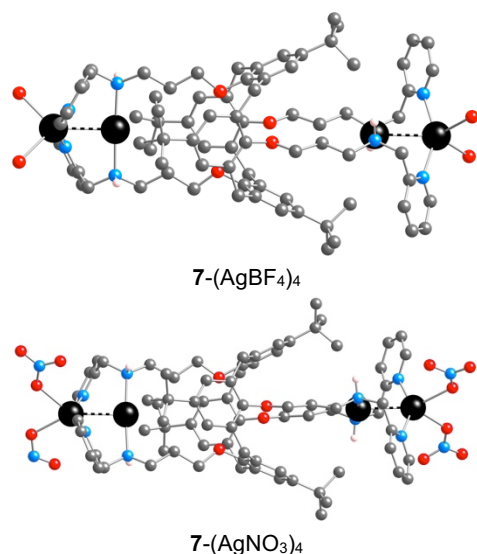
Table 4: useful angles and distances for the tetranuclear compounds **7**-(AgX)<sub>4</sub> (X = BF<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>). am and py indicate the localization of the N atom on either amino or pyridyl units.

	<b>7</b> -(AgNO <sub>3</sub> ) <sub>4</sub>	<b>7</b> -(AgBF <sub>4</sub> ) <sub>4</sub>
C-N (amino)	1.484(7) 1.489(8)	1.484(6)
CNC (amino)	110.5(5) 112.1(5)	111.9(3)
Ag-N	2.161(5) (Triangular)	(am)
	2.164(5) (Triangular)	(am)
	2.245(6) (Tetrahedral)	2.173(3) (am) (Triangular) 2.228(4) (py) (Tetrahedral)
	2.269(6) (Tetrahedral)	(py)
		(py)
Ag-O	2.423(5) (Tetrahedral) 2.438(6) (Tetrahedral)	2.458 (Tetrahedral)
Ag-Ag	2.8775(5)	2.8928(7)
NAgN	144.48(18) (Tetrahedral) 175.4(17) (Linear)	147.7(2) (Tetrahedral) 177.80(19) (Linear)
NAgO	101.5(4) 101.6(2) 108.4(4) 108.9(4)	95.9(2) 105.2(2)
OAgO	73.9(2)	98.4(5)

Owing to the distance between the two binding pockets composed of a N4 set of coordinating sites located above and below the mean plane of the ligand and the absence of electronic communication between them, they behave independently and each binds two silver cations leading thus to the tetranuclear silver complex **7**-(AgBF<sub>4</sub>)<sub>4</sub> and **7**-(AgNO<sub>3</sub>)<sub>4</sub> differing by the nature of the anion (BF<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>) (Figure 5). For the tetranuclear species, the set of two Ag<sup>+</sup> cations, located on the same side of the backbone, may be described as internal



and external metal centres (Figures 1 and 5). Interestingly, due to the proper positioning of the two chelating *ortho*-aminomethylpyridine units on each side of the macrocyclic backbone, a rather short Ag-Ag distance of 2.8928(7) Å and 2.8775(5) Å (table 4) are obtained for **7**-(AgBF<sub>4</sub>)<sub>4</sub> and **7**-(AgNO<sub>3</sub>)<sub>4</sub> respectively. Dealing with the surrounding of silver cations, for **7**-(AgBF<sub>4</sub>)<sub>4</sub> among the water molecules present in the crystal, two of them are located within the coordination sphere of the external silver cation, whereas for **7**-(AgNO<sub>3</sub>)<sub>4</sub>, then external metal centre interacts with two nitrate anions through Ag-O bonds.



**Figure 5:** Solid state structure of tetranuclear complexes **7**-(AgBF<sub>4</sub>)<sub>4</sub> and **7**-(AgNO<sub>3</sub>)<sub>4</sub> formed by combination of the organic ligand **7** with AgBF<sub>4</sub> and AgNO<sub>3</sub> respectively. H atoms, solvent molecules and anions in the case of **7**-(AgBF<sub>4</sub>)<sub>4</sub> are not presented for clarity. For bond angles and distances see text.

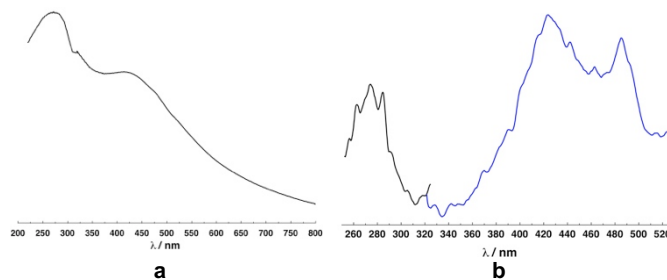
As stated above, for the tetranuclear silver complex, two types of silver cations are present on each side of the ligand. The internal cation is di-coordinated and its coordination sphere is composed of two N atoms belonging to two amino units located on the same side of the backbone. The Ag-N distances are 2.173(3) Å for **7**-(AgBF<sub>4</sub>)<sub>4</sub> and in the 2.161(5)-2.269(6) range for **7**-(AgNO<sub>3</sub>)<sub>4</sub>. The NAgN angles are 177.80(19)° and 175.4(17)° and NAgAg angles are 91.10(10)°, 90.90(13) and 93.64(12)° (table 4) showing a slightly distorted linear coordination geometry around the internal silver cation.

The external silver cation is tetracoordinated adopting a distorted tetrahedral coordination geometry and is surrounded by a N<sub>2</sub>O<sub>2</sub> set of coordinating atoms. The environment around the cation is composed of two nitrogen atoms belonging to two pyridyl units located on the same face of the ligand and two oxygen atoms either belonging to two H<sub>2</sub>O molecules in **7**-(AgBF<sub>4</sub>)<sub>4</sub> or to two nitrate anions in **7**-(AgNO<sub>3</sub>)<sub>4</sub> (Figure 5). For distances and angles see table 4.

#### Solid state emission

The rather short Ag-Ag distance of 2.8928(7) Å in **7**-(AgBF<sub>4</sub>)<sub>4</sub>, leads to strong d<sup>10</sup>-d<sup>10</sup> interactions<sup>11</sup> between vicinal silver atoms on each face of the complex. The emission due to argentophilic interaction was investigated using polycrystalline samples (Figure 6).

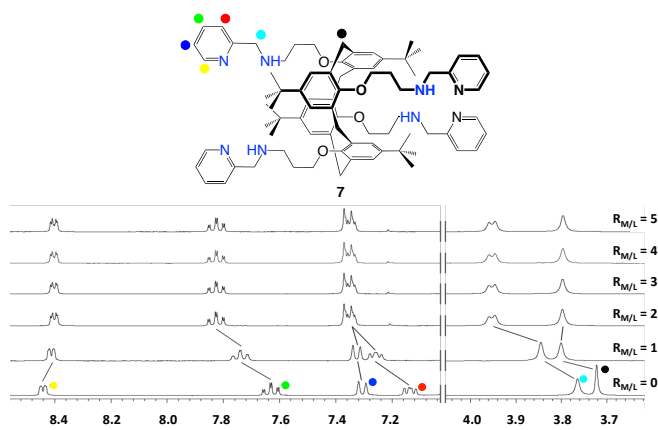
The solid-state reflectance spectra recorded at 298K displays two major bands at ca 295 nm and 450 nm (Figure 6 left). Upon excitation at  $\lambda_{\text{exc}} = 295$  nm, a dominant emission peak at  $\lambda_{\text{em}} = 425$  nm is observed (Figure 6 right). The latter is attributed to Ag-Ag argentophilic interactions. It is worth noting that no such an emission is observed for the binuclear complexes discussed above.



**Figure 6:** Solid state spectra recorded on a polycrystalline sample at 298K a) reflectance spectra and b) excitation (black,  $\lambda_{\text{em}} = 425$  nm) and emission (blue,  $\lambda_{\text{exc}} = 295$  nm) spectra for the tetranuclear complex **7**-(AgBF<sub>4</sub>)<sub>4</sub>.

#### Behaviour in solution

The binding of silver cation by the ligand **7** in solution was investigated. The complexation process was monitored by <sup>1</sup>H-NMR spectroscopy. Upon addition of AgBF<sub>4</sub>, in CD<sub>3</sub>CN, to a CD<sub>3</sub>CN solution of the ligand **7** at C = 8.05 · 10<sup>-3</sup> mol.L<sup>-1</sup> signals corresponding to the pyridyl moieties, CH<sub>2</sub>NH and the CH<sub>2</sub> bridging the aryl groups of the calix backbone were found to be shifted (Figure 7). The titration experiment in CD<sub>3</sub>CN consisting in addition of increasing amounts of the silver salt to a solution of **7** clearly showed the formation of the binuclear complex **7**-(AgBF<sub>4</sub>)<sub>2</sub>. Indeed, after reaching the 2:1 M/L ratio, further addition of the silver salt had no effect on the displacement of signals. In marked contrast with the solid state structural investigations discussed above, the solution study revealed that, even in the presence of 5 equivalents of silver cation, no trace of the tetranuclear silver complex could be detected.



**Figure 7:** Pyr-*H*, Ar-CH<sub>2</sub>-Ar and CH<sub>2</sub>-Pyr proton shift changes of the <sup>1</sup>H-NMR spectra (bottom) of **7** (top) with upon addition of increasing amount of AgBF<sub>4</sub>. (R<sub>M/L</sub> = Concentration of metal/concentration of ligand) C = 8.05 10<sup>-3</sup> mol.L<sup>-1</sup>

## Conclusions

four new multivalent ligands **5–8** derived from calix[4]arene and thiacalix[4]arene backbones in 1,3-Alternate bearing *ortho*-amino- and *ortho*-imino-pyridine chelating sites have been prepared and two of them (ligands **6** and **7**) have been structurally characterized in the solid state by X-ray diffraction methods. Owing to the imposed 1,3-Alternate conformation of the backbone, they offer two coordinating pockets composed of two sets of chelates located above and below the mean plane of the macrocyclic framework. Among the four unprecedented ligands, for compounds **6–8**, the two coordinating pockets behave independently and form binuclear silver complexes independent of the nature of the anion associated with Ag<sup>+</sup> cation. This propensity was established both in the solid state and in solution using <sup>1</sup>H-NMR spectroscopy. Interestingly, ligand **7**, based on four *ortho*-amino-pyridyl units, in addition to binuclear silver complexes, forms in the solid state tetranuclear silver complexes **7**-(AgBF<sub>4</sub>)<sub>4</sub>, and **7**-(AgNO<sub>3</sub>)<sub>4</sub> in presence of two different auxiliary ligands (H<sub>2</sub>O or NO<sub>3</sub><sup>-</sup>). In the solid state, the tetranuclear complex **7**-(AgBF<sub>4</sub>)<sub>4</sub>, due to a rather short Ag-Ag distance of ca 2.89 Å, displays argentophilic interactions leading, at 298 K, to an emission band at ca 425 nm (λ<sub>em</sub> = 295 nm). No such an emission was detected for the binuclear species. Finally, all attempts to generate the tetranuclear complexes in solution (CH<sub>3</sub>CN) failed. Combinations of the above mentioned ligands with other metal cations is currently under investigation.

## Experimental Section

### Materials and methods

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at room temperature on a Bruker (300, 400 or 500 MHz) NMR spectrometer.

Mass spectra (ESI) were obtained on a MicroTOF-Q (BRÜKER) equipped with an electrospray source.

Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

Melting points were measured in capillar on a Stuart Scientific Melting Point SMP-1 apparatus.

Reflectance spectra in the solid state were recorded on a Perkin-Elmer Lambda 650 spectrometer.

Luminescence spectra in the solid state were recorded on a Perkin-Elmer LS55 spectrophotometer.

### Single-Crystal Studies

Data were collected at 173(2) K on a Bruker Apex-II-CCD Diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all the structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F<sup>2</sup> using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>21</sup> They can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif). CCDC: 1538265-1538276.

### Synthetic procedures

General: All reagents were purchased from commercial sources and used without further purification. *p*-*tert*-butylcalix[4]arene **1** is commercial product and *p*-*tert*-butylthiacalix[4]arene **2**<sup>2</sup> was prepared according to the literature procedures. The synthesis of **10** has already been reported.<sup>17</sup>

All the reactions were performed under a N<sub>2</sub> atmosphere.

### Compound 9

A mixture of *p*-*tert*-butylcalix[4]arene **1** (1.50 g, 2.31 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (7.5 g, 23.11 mmol) in DMF (80 mL) was stirred at R.T. for 2 hours. *N*-(3-bromopropyl)phthalimide **13** (6.19 g, 23.11 mmol) was added to the mixture and stirring was further continued for 3 days at 50 °C during. After cooling to R.T., the reaction mixture was filtrated. The filtrate was washed three times with CHCl<sub>3</sub> (3x50 mL). Washes were combined and evaporated. The yellow oil thus obtained was dissolved in 50 mL of CHCl<sub>3</sub> and washed twice with HCl (1N, 2x50 mL). After evaporation, the residue was recrystallised twice from MeOH (50 mL) affording the pure product **9** in 1,3-*A* conformation as a white solid (1.77 g, 55%). mp = 256 °C. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.17 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 1.69 (8H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.47 (8H, t, -Phth-CH<sub>2</sub>-), 3.63 (8H, t, Ar-O-CH<sub>2</sub>-), 3.69 (8H, s, Ar-CH<sub>2</sub>-Ar), 6.95 (8H, s, Ar-H), 7.70 (8H, m, Ar-H), 7.82 (8H, m, Ar-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 29.4, 31.5, 33.7, 35.2, 38.8, 68.6, 123.1, 126.3, 132.1, 132.9, 133.8, 143.7, 154.4, 168.1. Anal. Calcd. for C<sub>88</sub>H<sub>92</sub>N<sub>4</sub>O<sub>12</sub>: C, 75.62%; H, 6.63%; N, 4.01%; Found: C, 75.86%; H, 6.56%; N, 4.01%.

### Compound 11

The synthesis was adapted from an already published procedure.<sup>19</sup>

A mixture of **9** (2.00 g, 1.43 mmol) and hydrazine (14.1 mL, 286 mmol) in 70 mL of EtOH was stirred and refluxed for 24h. After cooling to at RT, 150 mL of distilled H<sub>2</sub>O was added and the reaction mixture was filtrated. The white solid thus obtained was washed three times with Et<sub>2</sub>O (3x30 mL). The white solid was dried for 4h under vacuum at 100 °C, affording the pure product **11** in 1,3-*A* conformation (1.22 g, 98%). mp = 248 °C. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.27 (8H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.28 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 2.48 (8H, t, NH<sub>2</sub>-CH<sub>2</sub>-), 3.43 (8H, t, Ar-O-CH<sub>2</sub>-), 3.79 (8H, s, Ar-CH<sub>2</sub>-Ar), 6.97 (8H, s, Ar-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 31.6, 33.5, 33.9, 39.2, 39.6, 68.7, 125.9, 133, 143.6, 154.9. Anal. Calcd. for C<sub>56</sub>H<sub>64</sub>N<sub>4</sub>O<sub>4</sub>: C, 76.67%; H, 9.65%; N, 6.39%; Found: C, 76.32%; H, 9.66%; N, 6.38%.

### Compound 12

The synthesis was adapted from an already published procedure.<sup>19</sup>

A mixture of compound **10** (2.00 g, 1.36 mmol) and hydrazine (13.3 mL, 272 mmol) in 70 mL of a THF/EtOH (1/1) mixture was stirred and



refluxed for 24h. After cooling to room temperature, 150 mL of distilled H<sub>2</sub>O was added and the reaction mixture was filtrated. The white solid thus obtained was washed three times with Et<sub>2</sub>O (3x30 mL). The white solid was dried for 4h under vacuum at 100 °C, affording the pure product **12** in 1,3-A conformation (1.25 g, 97%). mp = 274 °C. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.23 (8H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.28 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 2.44 (8H, t, NH<sub>2</sub>-CH<sub>2</sub>-), 3.90 (8H, t, Ar-O-CH<sub>2</sub>-), 7.33 (8H, s, Ar-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 31.3, 33.3, 34.3, 39.4, 67.1, 127.8, 128.1, 145.5, 157.1. Anal. Calcd. for C<sub>52</sub>H<sub>76</sub>N<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: C, 65.78%; H, 8.07%; N, 5.89%; Found: C, 65.64%; H, 8.16%; N, 5.90%.

#### Compound 5

2-Pyridinecarboxaldehyde **14** (440 μL, 4.55 mmol) and **11** (0.5 g, 0.56 mmol) were dissolved in 40 mL of a EtOH/DMF (1/1) mixture and stirred at room temperature during 2 days. Then, 100 mL of CH<sub>3</sub>CN was added and the white precipitate thus formed was filtrated and washed three times with petroleum ether (3x30 mL). The filtrate was placed during one week in a refrigerator, which caused further precipitation. The solid was filtered and combined with the first batch, affording the desired compound **5** in 1,3-A conformation as a white solid (0.47 g, 63 %). mp = 124 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.23 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 1.47 (8H, m, J = 7.5 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.46 (8H, t, J = 6.0 Hz, =N-CH<sub>2</sub>-), 3.51 (8H, t, J = 8.5 Hz, -O-CH<sub>2</sub>-), 3.81 (8H, s, Ar-CH<sub>2</sub>-Ar), 6.97 (8H, s, Ar-H), 7.26 (4H, m, J = 6.0 Hz, Pyr-H), 7.69 (4H, t, J = 7.5 Hz, Pyr-H), 7.98 (4H, d, J = 7.5 Hz, Pyr-H), 8.23 (4H, s, -CH=N-), 8.60 (4H, d, J = 4.5 Hz, Pyr-H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 30.3, 31.6, 33.9, 58.4, 68.3, 120.8, 124.5, 125.7, 133, 136.4, 143.8, 149.2, 154.6, 154.8, 161.3. MS (ESI), *m/z*: [M]<sup>+</sup>, calculated 1233.66, measured 1233.67. Anal. Calcd. for C<sub>80</sub>H<sub>96</sub>N<sub>8</sub>O<sub>4</sub>: C, 77.89%; H, 7.84%; N, 9.08%; Found: C, 77.76 %; H, 8.00%; N, 8.96%. UV-vis (CHCl<sub>3</sub>/MeOH (1/1)): λ<sub>max</sub> (nm)/ ε (mol<sup>-1</sup>Lcm<sup>-1</sup>) = 238(52064). IR (cm<sup>-1</sup>): ν<sub>C=N</sub>: 1651.

#### Compound 6

2-Pyridinecarboxaldehyde **14** (560 μL, 5.84 mmol) and compound **12** (0.7 g, 0.73 mmol) were dissolved in 40 mL of a EtOH/DMF (1/1) mixture, and stirred at room temperature during 2 days. 100 mL of CH<sub>3</sub>CN was added and the white precipitate thus formed was filtrated and washed several times with petroleum ether (100 mL). The filtrate was placed during one week in a refrigerator to complete the precipitation. The solid was filtered and combined with the first batch, affording the desired compound **6** in 1,3-A conformation as a white solid (0.75 g, 78 %). mp = 182 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.20 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 1.44 (8H, m, J = 7.5 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.45 (8H, t, J = 6.5 Hz, =N-CH<sub>2</sub>-), 4.00 (8H, t, J = 7.5 Hz, -O-CH<sub>2</sub>-), 7.28 (4H, m, J = 5.5 Hz, Pyr-H), 7.33 (8H, s, Ar-H), 7.69 (4H, t, J = 7.5 Hz, Pyr-H), 8.00 (4H, d, J = 7.7 Hz, Pyr-H), 8.24 (4H, s, -CH=N-), 8.59 (4H, d, J = 5.0 Hz, Pyr-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 29.9, 31.3, 31.4, 34.3, 58.3, 66.8, 120.8, 124.5, 127.6, 128, 136.4, 145.6, 149.2, 154.8, 156.8, 161.5. MS (ESI), *m/z*: [M+H]<sup>+</sup> calculated 1306.59, measured 1306.82. Anal. Calcd. for C<sub>76</sub>H<sub>88</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·H<sub>2</sub>O: C, 68.95%; H, 6.85%; N, 8.46%; Found: C, 68.90 %; H, 6.82%; N, 8.22%. UV-vis (CHCl<sub>3</sub>/MeOH (1/1)): λ<sub>max</sub> (nm)/ ε (mol<sup>-1</sup>Lcm<sup>-1</sup>) = 238(37632). IR (cm<sup>-1</sup>): ν<sub>C=N</sub>: 1649.

#### Compound 7

NaBH<sub>4</sub> (0.31g, 8.1 mmol) and **3** (0.5 g, 0.4 mmol) were dissolved in 40 mL of MeOH and refluxed during 2 days. 50 mL of water was added carefully and the product was extracted three times with CHCl<sub>3</sub> (3x50 mL). The organic phases were combined and then evaporated, affording the desired compound **7** in 1,3-A conformation as a white solid (0.42 g,

84 %). mp = 122 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.22 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 1.51 (8H, m, J = 7.0 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.55 (8H, t, J = 7.0 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-NH-), 3.46 (8H, t, J = 7.5 Hz, -O-CH<sub>2</sub>-), 3.69 (8H, s, Ar-CH<sub>2</sub>-Ar), 3.83 (8H, s, Pyr-CH<sub>2</sub>-), 6.93 (8H, s, Ar-H), 7.11 (4H, t, J = 5.5 Hz, Pyr-H), 7.28 (4H, d, J = 7.5 Hz, Pyr-H), 7.59 (4H, m, J = 7.5 Hz, Pyr-H), 8.50 (4H, d, J = 4.5 Hz, Pyr-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 30.5, 31.7, 33.9, 38.7, 46.7, 55.4, 69.4, 121.8, 122.1, 126.3, 133, 136.4, 143.4, 149.2, 154.6, 160.4. MS (ESI), *m/z*: [M+H]<sup>+</sup> calculated 1241.83 measured 1241.82. Anal. Calcd. for C<sub>80</sub>H<sub>104</sub>N<sub>8</sub>O<sub>4</sub>: C, 77.38%; H, 8.44%; N, 9.02%; Found: C, 77.24 %; H, 8.58%; N, 8.83%. UV-vis (CHCl<sub>3</sub>/MeOH (1/1)): λ<sub>max</sub> (nm)/ ε (mol<sup>-1</sup>Lcm<sup>-1</sup>) = 237(56840). IR (cm<sup>-1</sup>): ν<sub>NH</sub>: 3282, 3318.

#### Compound 8

NaBH<sub>4</sub> (0.12g, 3 mmol) and compound **6** (0.2 g, 0.15 mmol) were dissolved in 30 mL of EtOH and refluxed during 2 days before it was allowed to cool to room temperature. 50 mL of water was added carefully and the product was extracted three times with CHCl<sub>3</sub> (3x50 mL). The organic phases were combined and evaporated, affording the desired compound **8** in 1,3-A conformation as a white solid (0.17 g, 85 %). mp = 172 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 1.22 (36H, s, -C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (8H, m, J = 7.0 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.48 (8H, t, J = 7.0 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-NH-), 3.78 (8H, s, -NH-CH<sub>2</sub>-), 3.91 (8H, t, J = 7.5 Hz, -O-CH<sub>2</sub>-), 7.09 (4H, m, J = 5.0 Hz, Py-H), 7.27 (4H, d, J = 7.5 Hz, Py-H), 7.30 (8H, s, Ar-H), 7.57 (4H, J = 5.5 Hz, m, Py-H), 8.48 (4H, d, J = 4.5 Hz, Py-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ(ppm) = 29.7, 31.3, 34.2, 46.4, 55.4, 67.3, 121.7, 121.9, 136.3, 145.5, 149.1, 157.1, 160.3. MS (ESI), *m/z*: [M]<sup>+</sup> calculated 1313.63, measured 1313.89. Anal. Calcd. for C<sub>76</sub>H<sub>96</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>: C, 69.47%; H, 7.36%; N, 8.53%; Found: C, 69.18%; H, 7.46%; N, 8.22%. UV-vis (CHCl<sub>3</sub>/MeOH (1/1)): λ<sub>max</sub> (nm)/ ε (mol<sup>-1</sup>Lcm<sup>-1</sup>) = 261(49560). IR (cm<sup>-1</sup>): ν<sub>NH</sub>: 3280, 3321.

#### Crystallisation conditions

**Compound 6:** A CHCl<sub>3</sub> (0.5 mL) solution of compound **6** (5 mg, 3.82 μmol) was placed in a closed beaker containing acetonitrile. Slow vapour diffusion of acetonitrile into the solution of the ligand **6** produced, after several days, colourless crystals suitable for X-ray diffraction (Formula: 2(C<sub>76</sub>H<sub>88</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>)·CHCl<sub>3</sub>).

**Compound 7:** A solution in CHCl<sub>3</sub> (0.5 mL) of compound **7** (5 mg, 4.03 μmol) was placed in a closed beaker containing hexane. Slow vapour diffusion of hexane into the solution of **7** produced colourless, after several days, crystals suitable for X-ray diffraction (Formula: C<sub>80</sub>H<sub>104</sub>N<sub>8</sub>O<sub>4</sub>).

**6-(AgSbF<sub>6</sub>)<sub>2</sub>:** In a crystallization tube (20 x 4 mm), a solution of compound **6** (3.00 mg, 2.29 μmol) in CHCl<sub>3</sub> (1 mL) was layered with a CHCl<sub>3</sub>/ iso-PrOH (1/1) mixture (0.1 mL). A solution of AgSbF<sub>6</sub> (1.70 mg; 4.95 μmol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (3.39 mg, 63 % yield). Anal. Calcd. for C<sub>76</sub>H<sub>88</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·2(AgSbF<sub>6</sub>)·(CHCl<sub>3</sub>): C, 43.78%; H, 2.25%; N, 5.30%. Found: C, 43.42%; H, 2.20%; N, 5.26%.

**6-(AgAsF<sub>6</sub>)<sub>2</sub>:** In a crystallization tube (20 x 4 mm), a solution of **6** (3.00 mg; 2.29 μmol) in CHCl<sub>3</sub> (1 mL) was layered with a CHCl<sub>3</sub>/iso-PrOH (1/1) mixture (0.1 mL). A solution of AgAsF<sub>6</sub> (2.02 mg; 6.80 μmol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (2.60 mg, 60 % yield). Anal. Calcd. for

C<sub>76</sub>H<sub>88</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·2(AgAsF<sub>6</sub>)·2(H<sub>2</sub>O): C, 47.16%; H, 4.79%; N, 5.79%. Found: C, 47.06%; H, 4.56%; N, 5.76%.

**6-(AgBF<sub>4</sub>)<sub>2</sub>**: In a crystallization tube (20 x 4 mm), a solution of the ligand **6** (3.00 mg; 2.29  $\mu$ mol) in CHCl<sub>3</sub> (1 mL) was layered with a CHCl<sub>3</sub>/ iso-PrOH (1/1) mixture (0.1 mL). A solution of AgBF<sub>4</sub> (1.30 mg; 6.67  $\mu$ mol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (2.00 mg, 51 % yield). Anal. Calcd. for C<sub>76</sub>H<sub>88</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·2(AgBF<sub>4</sub>)·2(H<sub>2</sub>O): C, 52.73%; H, 5.36%; N, 6.47%. Found: C, 52.65%; H, 5.16%; N, 6.50%.

**6-(AgNO<sub>3</sub>)<sub>2</sub>**: In a crystallization tube (20 x 4 mm), a solution of compound **6** (3.00 mg; 2.29  $\mu$ mol) in CHCl<sub>3</sub> (1 mL) was layered with a CHCl<sub>3</sub>/ iso-PrOH (1/1) mixture (0.1 mL). A solution of AgNO<sub>3</sub> (1.00 mg; 6.9  $\mu$ mol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced, after several days, colourless crystals suitable for X-ray diffraction (2.00 mg, 51 % yield). Anal. Calcd. for C<sub>76</sub>H<sub>88</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·2(AgNO<sub>3</sub>): C, 55.47%; H, 5.39%; N, 8.51%. Found: C, 55.30%; H, 5.44%; N, 8.41%.

**8-(AgAsF<sub>6</sub>)<sub>2</sub>**: In a flask, 3.0 mg of the ligand **8** (2.19  $\mu$ mol) dissolved in 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with 2.00 mg of AgAsF<sub>6</sub> (4.74  $\mu$ mol) dissolved in 0.5 mL of MeOH. Slow vapour diffusion of Et<sub>2</sub>O produced, after several days, colourless crystals suitable for X-ray diffraction studies (2.70 mg, 66 % yield). Anal. Calcd. for C<sub>76</sub>H<sub>96</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·2(AgAsF<sub>6</sub>)·H<sub>2</sub>O: C, 47.41%; H, 5.13%; N, 5.82%; Found: C, 47.38%; H, 5.08%; N, 5.62%.

**8-(AgPF<sub>6</sub>)<sub>2</sub>**: In a flask, 3.0 mg of the ligand **8** (2.19  $\mu$ mol) dissolved in 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with 1.20 mg of AgPF<sub>6</sub> (6.57  $\mu$ mol) dissolved in 0.5 mL of MeOH. Slow vapour diffusion of Et<sub>2</sub>O produced, after several days, colourless crystals suitable for X-ray diffraction studies (1.80 mg, 49 % yield). Anal. Calcd. for C<sub>76</sub>H<sub>96</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>·2(AgPF<sub>6</sub>): C, 50.17%; H, 5.32%; N, 6.16%; Found: C, 49.86%; H, 5.28%; N, 6.08%.

**7-(AgBF<sub>4</sub>)<sub>2</sub>**: In a flask, 3.0 mg of the ligand **7** (2.41  $\mu$ mol) dissolved in 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with 1.40 mg of AgBF<sub>4</sub> (7.25  $\mu$ mol) dissolved in 0.5 mL of MeOH. Slow vapour diffusion of Et<sub>2</sub>O produced, after several days, colourless crystals suitable for X-ray diffraction studies (2.20 mg, 52 % yield). Anal. Calcd. for C<sub>80</sub>H<sub>104</sub>N<sub>8</sub>O<sub>4</sub>·2(AgBF<sub>4</sub>)·2(CH<sub>2</sub>Cl<sub>2</sub>): C, 54.69%; H, 6.04%; N, 6.22%; Found: C, 53.16%; H, 6.13%; N, 6.35%.

**7-(AgPF<sub>6</sub>)<sub>2</sub>**: In a flask, 3.0 mg of compound **7** (2.41  $\mu$ mol) dissolved in 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with 1.20 mg of AgBF<sub>4</sub> (6.16  $\mu$ mol) dissolved in 0.5 mL of MeOH. Slow vapour diffusion of Et<sub>2</sub>O produced, after several days, colourless crystals suitable for X-ray diffraction studies (2.20 mg, 52 % yield). Anal. Calcd. for C<sub>80</sub>H<sub>104</sub>N<sub>8</sub>O<sub>4</sub>·2(AgPF<sub>6</sub>)·2(CH<sub>3</sub>OH): C, 54.37%; H, 6.23%; N, 6.18%; Found: C, 53.86%; H, 6.33%; N, 6.30%.

**7-(AgNO<sub>3</sub>)<sub>4</sub>**: In a flask, 3.0 mg of ligand **7** (2.41  $\mu$ mol) dissolved in 0.5 mL of CHCl<sub>3</sub> was mixed with 1.70 mg of AgNO<sub>3</sub> (9.67  $\mu$ mol) dissolved in 0.5 mL of CH<sub>3</sub>CN. Slow vapour diffusion of Et<sub>2</sub>O produced, after several days, colourless crystals suitable for X-ray diffraction studies (2.7 mg, 50 % yield). Anal. Calcd. for C<sub>80</sub>H<sub>104</sub>N<sub>8</sub>O<sub>4</sub>·4(AgNO<sub>3</sub>)·2(C<sub>2</sub>H<sub>5</sub>OH): C, 51.07%; H, 6.04%; N, 8.12%; Found: C, 51.19%; H, 5.97%; N, 7.95%.

**7-(AgBF<sub>4</sub>)<sub>4</sub>**: In a flask, 3.0 mg of ligand **7** (2.41  $\mu$ mol) dissolved in 0.5 mL of CH<sub>3</sub>CN was mixed with 1.90 mg of AgBF<sub>4</sub> (9.75  $\mu$ mol) dissolved in 0.5 mL of CH<sub>3</sub>CN/H<sub>2</sub>O (9/1) mixture. Slow vapour diffusion of Et<sub>2</sub>O produced, after several days, colourless crystals suitable for X-ray diffraction studies (3.60 mg, 71 % yield). Anal. Calcd. For

C<sub>80</sub>H<sub>104</sub>N<sub>8</sub>O<sub>4</sub>·4(AgBF<sub>4</sub>)·6(H<sub>2</sub>O): C, 45.14 %; H, 5.49%; N, 5.26%; Found: C, 44.80%; H, 5.40%; N, 5.24%.

## Acknowledgements

We thank the University of Strasbourg, the C.N.R.S, the International centre for Frontier Research in Chemistry (icFRC), the Labex CSC (ANR-10-LABX- 0026 CSC) within the Investissement d'Avenir program ANR-10-IDEX-0002-02, the Institut Universitaire de France, the Ministère de l'Enseignement Supérieur et de la Recherche for financial support and the Tunisian government for a PhD fellowship to M. H. N.

**Keywords:** Calix[4]arene • Thialix[4]arene • tetranuclear complexes • Silver • Argentophilic

- [1] (a) C.D. Gutsche in *Calixarenes Revised: Monographs in Supramolecular Chemistry* Vol. 6, The Royal Society of Chemistry, Cambridge, **1998**; (b) Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens in *Calixarenes 2001*, (Eds. Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens) Kluwer Academic, Dordrecht, **2001**.
- [2] (a) H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, S. Miyano, *Tetrahedron Lett.*, **1997**, 38, 3971-3972; (b) H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. De Cian, J. Fischer, *Tetrahedron Lett.*, **1998**, 39, 2311-2314; c) M. W. Hosseini in *Calixarenes 2001*, (Eds. Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens) Kluwer Academic, Dordrecht, **2001**, pp.110.
- [3] G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, J. Fischer, *Tetrahedron Lett.*, **1999**, 40, 1129-1132.
- [4] G. Mislin, E. Graf, M. W. Hosseini, A. De Cian *J. Chem. Soc., Chem. Commun.*, **1998**, 1345-1346.
- [5] (a) S. J. Dalgarno, P. K. Thallapally, L. J. Barbour, J. L. Atwood, *Chem. Soc. Rev.*, **2007**, 36, 236-245; (b) L. Baldini, A. Casnati, F. Sansone, R. Ungaro, *Chem. Soc. Rev.* **2007**, 36, 254-266; (c) E. Hadjoudis, I. M. Mavrids, *Chem. Soc. Rev.*, **2004**, 33, 579-588; (d) R. Lalor, H. Baillie-Johnson, C. Redshaw, S. E. Matthews, A. Mueller, *J. Am. Chem. Soc.*, **2008**, 130, 2892-2893.
- [6] (a) V. Böhmer, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 713-745; (b) C. Wieser, C. B. Dielman, D. Matt, *Coord. Chem. Rev.*, **1997**, 165, 93-161; (c) S. M. Biros, J. Jr. Rebek, *Chem. Soc. Rev.*, **2007**, 36, 93-104; (d) M. D. Pluth, K. N. Raymond, *Chem. Soc. Rev.*, **2007**, 36, 161-171.
- [7] D. M. Homden, C. Redshaw *Chem. Rev.*, **2008**, 108, 5086-5130
- [8] (a) M. W. Hosseini, ACS Series, Eds G. J. Lumetta, R. D. Rogers, A. S. Gopalan, **2000**, 557, 296; (b) T. Kajiwara, N. Iki, M. Yamashita, *Coord. Chem. Rev.*, **2007**, 251, 1734-1746; (c) J. Harrowfield, G. Koutsantonis. "Calixarenes as cluster keepers, Calixarenes in the Nanoworld" Springer Netherlands, **2007**, pp. 197-212. (d) N. Iki, in *Calixarenes and Beyond*, Springer International Publishing, **2016**, pp. 335-362; (e) M. Coletta, E. K. Brechin, S. J. Dalgarno in *Calixarenes and Beyond* Springer International Publishing, **2016**, pp. 671-689.
- [9] (a) G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. M. Harrowfield, B. W. Skelton, A. H. White, *Chem. Commun.*, **1999**, 373-374; (b) A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Aust. J. Chem.*, **2000**, 53, 895-898; (c) H. Akdas, E. Graf, M. W. Hosseini, A. De Cian, A. Bilyk, B. W. Skelton, G. A. Koutsantonis, I. Murray, J. M. Harrowfield, A. H. White, *Chem. Commun.*, **2002**, 1042-1043; (d) G. Pilet, S. A. Borsch, S. Parola, D.

- Luneau, *Inorg. Chem.*, **2005**, *44*, 9112-9120; (e) C. Desroches, J. Zeller, I. J. Hewitt, U. Radius, *Z. Anorg. Allg. Chem.*, **2006**, *632*, 243-245; (f) N. Morohashi, F. Narumi, N. Iki, T. Hattori, S. Miyano, *Chem. Rev.*, **2006**, *106*, 5291-5316; (g) M. Wu, D. Yuan, Y. Huang, W. Wei, Q. Gao, F. Jiang, M. Hong, *Cryst. Gr. & Des.*, **2007**, *7*, 1446-1451; (h) B. Yanfeng, L. YanlingHongjie, L. Deqian, *Inorg. Chem.*, **2008**, *47*, 9733-9735; (i) Y. Bi, W. Liao, X. Wang, R. Deng, H. Zhang *Eur. J. Inorg. Chem.*, **2009**, 4989-4994; (j) Y. F. Bi, X. T. Wang, W. P. Liao, X. W. Wang, R. P. Deng, H. J. Zhang, S. Gao, *Inorg. Chem.*, **2009**, *48*, 11743-11747.
- [10] (a) A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, A. N. Sobolev, R. L. Stamps, A. H. White, *Eur. J. Inorg. Chem.*, **2010**, 2106-2126; (b) Y. Bi, X-T. Wang, W. Liao, X. Wang, X. Wang, H. Zhang, S. Gao, *J. Am. Chem. Soc.*, **2009**, *131*, 11650-11651; (c) A. Gehin, S. Ferlay, J. M. Harrowfield, D. Fenske, N. Kyrtsakas, M. W. Hosseini, *Inorg. Chem.*, **2012**, *51*, 5481-5486.
- [11] (a) H. Schmidbaur *Chem. Soc. Rev.*, **1995**, *24*, 391-400; (b) P. Pyykkö *Chem. Rev.*, **1997**, *97*, 597-636; (c) M. J. Katz, K. Sakai, D. B. Leznoff, *Chem. Soc. Rev.*, **2008**, *37*, 1884-1895.
- [12] (a) G. C. Van Stein, G. Van Koten, B. De Bok, L. C. Taylor, K. Vrieze *Inorg. Chim. Acta*, **1984**, *89*, 79-87; (b) R. E. Riilke, J. M. Ernsting, A. L. Spelt, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vrieze *Inorg. Chem.*, **1993**, *32*, 5769-5778; (c) W. Gan, S. B. Jones, J. H. Reibenspies, R. D. Hancock *Inorg. Chim. Acta*, **2005**, *358*, 3958-3966; (d) C. Maxim, F. Tuna, A. M. Madalan, N. Avarvari, M. Andruh *Cryst. Growth Des.* **2012**, *12*, 1654-1665; (e) A. Switlicka-Olszewska, B. Machura, J. Mrozinski, B. Kalinska, R. Kruszynskic, M. Penkala *New J. Chem.*, **2014**, 38,1611-1626.
- [13] (a) G. D. Enright, K. A. Udachin, J. A. Ripmeester, *Chem. Commun.*, **2004**, 1360-1361; (b) X. Hu, Y. Li, H. Yang, Y. Luo, *Tetrahedron Lett.* **2006**, *47*, 7463-7465; (c) X.L. Ni, X. Zeng, C. Redshaw, T. Yamato *Tetrahedron* **2011**, *67*, 3248-3253.
- [14] (a) A. Ovsyannikov, M. N. Lang, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyrtsakas, M. W. Hosseini *Dalton Trans.*, **2013**, 116-126; (b) A. Ovsyannikov, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyrtsakas, M. W. Hosseini *Dalton Trans.*, **2013**, 9946-9953; (c) A. Ovsyannikov, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyrtsakas, M. W. Hosseini *Inorg. Chem.*, **2013**, *52*, 6776-6778; (d) A. Ovsyannikov, S. Ferlay, S. E. Solovieva, I. S. Antipin, A. I. Konovalov, N. Kyrtsakas, M. W. Hosseini *Macrocyclics*, **2016**, *9*, 17-22.
- [15] (a) C. Danila, M. Bolte, V Böhmer *Org. Biomol. Chem.*, **2005**, *3*, 172-184; (b) S. Barbosa, A. Garcia Carrera, S. E. Matthews, F. Arnaud-Neu, V. Böhmer, J- F. Dozol, H. Rouquette, M-J. Schwing-Weill *J. Chem. Soc., Perkin Trans. 2*, **1999**, 719-724; (c) N. I. Nikishkin, J. Huskens, S. A. Ansari, P. K. Mohapatra, W. Verboom *New J. Chem.*, **2013**, *37*, 391-402.
- [16] L. Liang, G. Weiwei, Y. Chaoguo, *Chinese Journal of Chemistry*, **2009**, *27*, 1975-1980.
- [17] I. I. Stoikov, A. V. Galukhin, E. N. Zaikov, I. S. Antipin *Mendeleev Commun.*, **2009**, *19*, 193-195.
- [18] A. V. Galukhin, K. V. Shabalin, I. S. Antipin, A. I. Konovalov, I. I. Stoikov *Mendeleev Commun.*, **2013**, *23*, 41-43.
- [19] (a) E. Méta, M-C. Duclos, S. Pellet-Rostaing, M. Lemaire, J. Schulz, R. Kannappan, C. Bucher, E. Saint-Aman, C. Chaix, *Supramol. Chem.*, **2009**, *21*, 68-80; (b) S. Erdemir, P. Deveci, B. Taner, O. Kocyigit *Tetrahedron*, **2012**, *68*, 642-646.
- [20] A. L. Spek, *J. Appl. Crystallogr.*, **2003**, *36*, 7-13.
- [21] Sheldrick, G. M.: *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, **1997**.

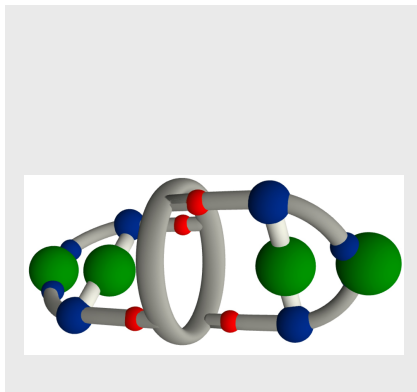
---

## Entry for the Table of Contents

### FULL PAPER

---

Formation of tetranuclear silver complexes in the solid state with short Ag-Ag distance displaying argentophilic interactions.



#### Supramolecular chemistry, Calixarene

*M. H. Noamane, S. Ferlay,\* R. Abidi, N. Kyritsakas and M. W. Hosseini\**

**Page No. – Page No.**

Discrete binuclear and tetranuclear silver complexes based on *ortho*-imino- or *ortho*-amino-methylpyridyl appended *p*-*tert*-butyl-calix[4]arene or *p*-*tert*-butyl-thiacalix[4]arene in 1,3-alternate conformation