Inorg. Chem. **2003**, *42*, 5654–5659

Inorganic Chemistry

Article

Crucial Role of the Counteranion on the Templation of Metallomacrocycles and a 3D Network: Synthesis, Characterization, and Structural Analysis

Laurence Raehm, Lamia Mimassi, Carine Guyard-Duhayon, and Hani Amouri*

Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071,
Université Pierre et Marie Curie; 4 place Jussieu, case 42, 75252 Paris Cedex 05, France

Marie Noelle Rager

NMR Services of Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie,
75231 Paris Cedex 05, France

Received January 28, 2003

Two novel supramolecular architectures, $\{[Ag_2L^1{}_2][X]_2\}$ with X = $CF_3SO_3^-$ (**2a**) or X = NO_3^- (**2b**) and $\{[AgL^1{}_2][X]\}_n$ with X = BF_4^- (**3**), were constructed by self-assembly and obtained in quantitative yields, using AgX as a building block and L^1 as the bridging ligand (L^1 = 1,3-bis(benzimidazol-1-ylmethyl)benzene). The X-ray molecular structures of **2a** and **3** are reported. Complex **2a** was identified as a metallomacrocycle in which one ligating triflate anion is coordinated to each of the two unsaturated Ag(I) ions. **2a** crystallizes in monoclinic unit cell $P2_1/n$ with $a = 9.728(6)$ Å, $b = 17.303(4)$ Å, $c = 13.268(3)$ Å, $\beta = 92.52(4)°$, $V = 2231(2)$ Å^3, and $Z = 2$. Remarkably, the X-ray structure of **2a** shows a layered network structure consisting of infinite metallomacrocycles held together through π–π interactions between benzimidazole rings. In dramatic contrast, the product **3** prepared from $AgBF_4$ and L^1 lacks metal–counterion bonding, leading to a supramolecular 3D network with the following three outstanding features: (i) in one dimension, metallomacrocycles containing two Ag centers and two bridging ligands form infinite, double-stranded chains; (ii) neighboring chains are arranged by two distinct π–π interactions, one between substituted benzene rings and the other between benzimidazole rings, leading to a 3D structure; (iii) cavities within the 3D network contain BF_4^- counteranions. **3** crystallizes in monoclinic unit cell $C2/c$ with $a = 25.33(3)$ Å, $b = 11.655(6)$ Å, $c = 18.466(8)$ Å, $\beta = 123.00(8)°$, $V = 4572(8)$ Å^3, and $Z = 4$. Interestingly, electrospray mass spectroscopy suggests in either case that the identified elemental subunit $[AgL^1{}_2]^+$ is the key building block which self-assembles and subsequent anion templation provides either the macrocycles **2a**, **b** or the inorganic polymer **3**. Remarkably, in dichloromethane solvent ligand-to-metal stoichiometries of 2:1 in **3** and 1:1 in **2a**, **b** are obtained even with excess ligand, showing the power of metal–anion interactions in determining the overall supramolecular structure. Anion metathesis, showing supramolecular structural rearrangements from **2a** to **2b** and more spectacularly from **3** to **2b**, smoothly occurred. The crucial effect and the nature of coordinating counteranions (BF_4^-, $CF_3SO_3^-$, NO_3^-) on the supermolecule design are presented and discussed.

Introduction

Metal-driven self-assembly[1] of macrocycles is currently considered as a powerful tool to design various metallomacrocycles of different shapes and geometries,[2] which are often obtained in one step and in higher yields than those obtained by more tedious classical organic methods.[3,4] These metallomacrocycles often have cavities whose size can be readily modified for selective encapsulating properties,[5] and they also show applications in catalysis[6] and as devices for sensing and ion transport.[7] Their preparation can be easily achieved using metal ions which directionally form dative bonds with the adequate bridging ligands, providing the ultimate metallomacrocycle with different shapes.[4,8,9] Very recently, a new

---

* Author to whom correspondence should be addressed. E-mail: amouri@ccr.jussieu.fr.

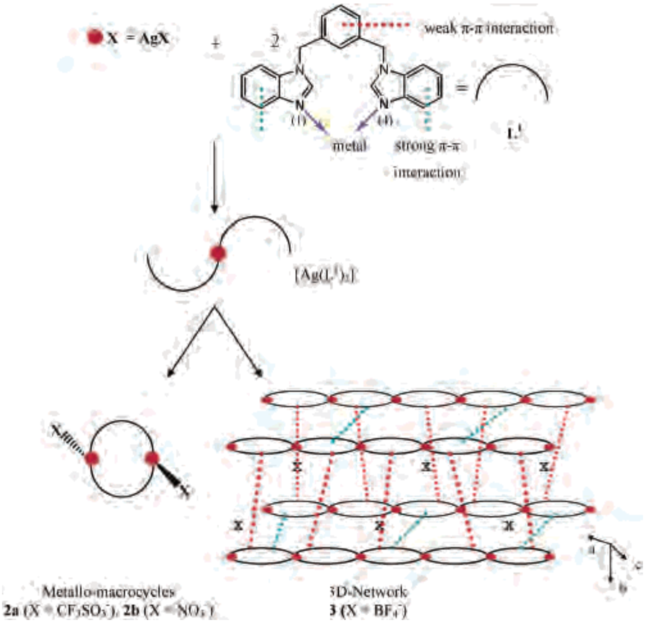
[1] Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.

[2] (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. (b) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52−55. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (d) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502−518. (e) Swiegers, G. F.; Malefeste, T. J. *Chem. Rev.* **2000**, *100*, 3483−3537.

10.1021/ic0340884 CCC: $25.00

© 2003 American Chemical Society
Published on Web 08/05/2003

Scheme 1. Schematic Representation of the Supramolecular Species: Metallomacrocycles **2a,b** and 3D Network **3**, Where Most X Anions Have Been Omitted for Clarity, and Proposed Intermediate $[Ag(L^1)_2]^+$ in the Formation of the Supramolecular Species **2a,b** and **3**



approach utilizing anion templation to construct macrocycles has been used with some success, for instance, Hawthorne's mercuracarboranes templated by two iodides,[10] Ward and McCleverty's cobalt box encapsulating a BF_4^- anion,[11] and very recently Beer and co-workers' rotaxane templated by chloride.[12] We recently reported the self-assembly of iridocryptates which encapsulate BF_4^- anions.[13] Pursuing our research in this area, we report here the synthesis by self-assembly and the structure of a novel metallomacrocycle templated by two triflate anions (Scheme 1). Remarkably, even when the same ligand to metal molar ratio is maintained, the role and nature of the anion crucially modify the structure and the shape of the ultimate supramolecular species. Thus, under the same experimental conditions but using the weaker binding anion BF_4^- a 3D network was obtained (Scheme 1). A complete study in solution and in the solid state of the binding ability of various anions ($CF_3SO_3^-$, BF_4^-, and NO_3^-) and their influence on the formation of the final supramolecular structure are presented and discussed.

Results and Discussion

Synthesis and Characterization of Argentomacrocycles 2a and 2b. X-ray Molecular Structure of 2a. Treatment of $AgCF_3SO_3$ (**1a**) with 2 equiv of L^1 (L^1 = 1,3-bis-(benzimidazol-1-ylmethyl)benzene)[14] in a CH_2Cl_2 solution for several hours gave a white precipitate. This compound was obtained in a quantitative yield and gave elemental analysis consistent with a metallomacrocycle of formula $\{[Ag_2L^1{}_2][CF_3SO_3]_2\}$ (**2a**). Complex **2a** was found to be soluble in polar solvents such as methanol, acetonitrile and dimethyl sulfoxide; hence, the ^1H NMR spectrum was recorded in CD_3CN. The ^1H and ^{13}C NMR data are consistent with the proposed formula. Remarkably, the coordinated ligand L^1 displays a symmetric pattern close to that of the free ligand L^1. The electrospray (ES) mass spectrum shows a peak at m/z = 785.12 which corresponds to the formation of $[Ag(L^1)_2]^+$ species in solution. This suggests that the identified $[Ag(L^1)_2]^+$ subunit is the key building block which leads through self-assembly and subsequent anion templation (vide infra) to the metallomacrocycle **2a**.

It is worth noting that Hawthorne and co-workers[10] have reported that mercurocarboranes are efficiently constructed through anion templation. In this context two supramolecular species identified by X-ray spectroscopy were reported in which one macrocycle is centrally templated by one chloride anion and the other superstructure is templated by two iodide anions lying above and below the average plane of the macrocycle. It is noteworthy that cage structures of the M_3L_2, M_6L_4 or M_4L_6 type are well described in the literature;[9,15] however, less is known about the simplest metallomacrocycles of the M_2L_2 and M_2L_4 types.[16] Although complexes of the type $M_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) exist, the cavities are much smaller, excluding guests.[17]

Suitable crystals of **2a** were obtained by slow evaporation of Et_2O into CH_3CN solution. The complex crystallizes in the monoclinic unit cell space group $P2_1/n$. Crystallographic

---

(3) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972−983.

(4) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417−425.

(5) (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486−516. (b) Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576−13582. (c) Gale, P. A.; Sessler, J. L.; Král, V. *Chem. Commun.* **1998**, 1−8. (d) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989−997.

(6) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151−1152.

(7) Bélanger, S.; Hupp, J. T.; Stern, C. L.; Slone, R. V.; Watson, D. F.; Carrell, T. G. *J. Am. Chem. Soc.* **1999**, *121*, 557−563.

(8) Beauchamp, D. A.; Loeb, S. J. *Chem. Commun.* **2002**, 2484−2485.

(9) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509−518.

(10) (a) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267−276. (b) Zheng, Z.; Knobler, C. B.; Mortimer, M. D.; Kong, G.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 1235−1243.

(11) Fleming, J. S.; Mann, K. L. V.; Carraz, C.-A.; Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1279−1281.

(12) Wisner, J. A.; Beer, P. D.; Drew, M. G. B.; Sambrook, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 12469−12476.

(13) Amouri, H.; Rager, M. N.; Cagnol, F.; Vaisserman, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3636−3638.

(14) Chawla, S. K.; Gill, B. K. *Polyhedron* **1997**, *16*, 1315−1322.

(15) (a) Saalfranck, R. W.; Stark, A.; Peters, K.; Von Schnering *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 851. (b) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Lissner, F.; Kang, B.-S.; Kaim, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 3371−3375. (c) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. *Org. Lett.* **2002**, *4*, 913−915. (d) Radhakrishnan, U.; Schweiger, M.; Stang, P. J. *Org. Lett.* **2001**, *3*, 3141−3143. (e) Harsthorn, C. M.; Steel, P. J. *Chem. Commun.* **1997**, 541−542. (f) Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics* **1997**, *16*, 3094−3096.

(16) (a) Chand, D. K.; Biradha, K.; Fujita, M. *Chem. Commun.* **2001**, 1652−1653. (b) Harsthorn, C. M.; Steel, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 3935−3940. (c) McMorran, D. A.; Steel, P. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 3295−3297. (d) Owens, T. D.; Hollander, F. J.; Oliver, A. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 1536−1540. (e) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Zhang, H.-X.; Kang, B.-S. *J. Chem. Soc., Dalton Trans.* **2001**, 359−361.

(17) (a) Caruso, F.; Camalli, M.; Rimml, H.; Venanzi, L. M. *Inorg. Chem.* **1995**, *34*, 673−679. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191−243.

Table 1. Crystal Data and Structure Refinement for **2a** and **3**

	2a	**3**
empirical formula	$C_{46}H_{36}Ag_2F_6N_8O_6S_2$	$C_{44}H_{40}AgBF_4N_8O_2$
fw	1190.68	907.53
space group	$P2_1/n$	$C2/c$
a (Å)	9.728(6)	25.33(3)
b (Å)	17.303(4)	11.655(6)
c (Å)	13.268(3)	18.466(8)
β (deg)	92.52(4)	123.00(8)
V (Å^3)	2231(2)	4572(8)
Z	2	4
ρ_{calcd} (g·cm^{-3})	1.77	1.32
temp (°C)	200	295
λ(Mo Kα) (Å)	0.710690	0.710690
μ (cm^{-1})	10.57	5.01
$R(F_o)^a$	0.0498	0.0816
$R_w(F_o)^b$	0.0601	0.0915

^{a} $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Table 2. Selected Atomic Distances (Å) and Angles (deg) for **2a**

Ag(1)−N(1) = 2.095(5)
Ag(1)−N(4) = 2.086(5)
Ag(1)−Ag(1) = 6.257(1)
Ag(1)−O(3) = 2.841(5)
N(1)−Ag(1)−N(4) = 173.12(19)
Ag(1)−N(1)−C(1) = 123.4(4)

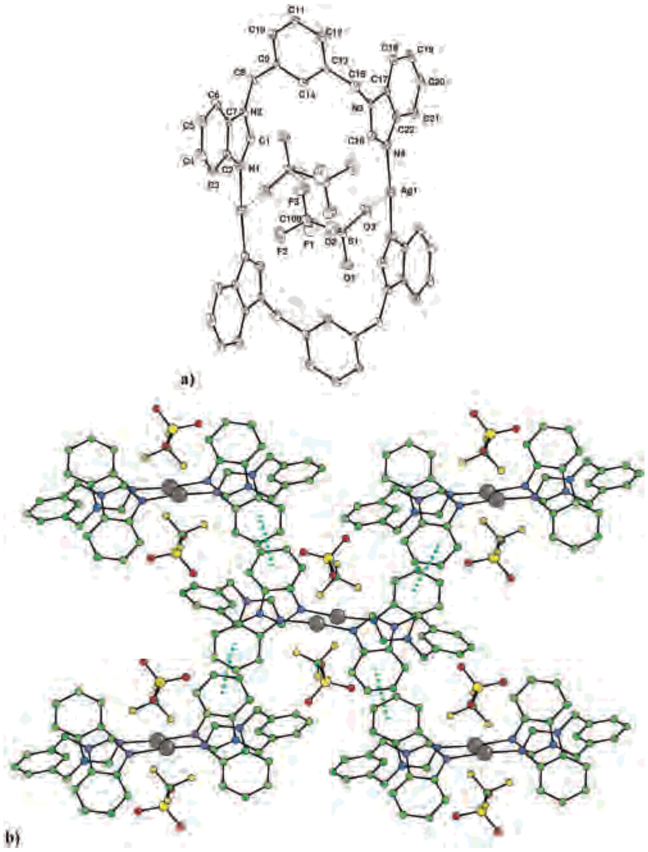


Figure 1. X-ray molecular structure of **2a**: (a) Cameron view showing the atom numbering system; (b) side view showing the two coordinated triflate anions above and below the plane of the metallomacrocycle and $\pi-\pi$ interactions between a macrocycle and its neighbors.

data for **2a** are shown in Table 1. Selected bond distances and angles are shown in Table 2. The structure shows that complex **2a** consists of a metallomacrocycle (Figure 1a). Two ligands L^1 bind to each Ag(I) ion forming a 14-electron species, and therefore a third coordination site is occupied by a coordinated triflate anion that acts as a template to stabilize the whole system. The Ag(1)−O(3) distance is 2.8 Å and is comparable to those reported for triflate anions bonded to Ag(I) ions.[18,19] Each ligand L^1 connects another Ag(I) center through the other benzimidazole arm, generating a metallomacrocycle. The Ag−Ag distance is 6.3 Å, while the distance between the two facing central arene rings is 8.7 Å. Further, we note the presence of a center of symmetry lying halfway between two parallel phenyl rings within the macrocycle. A side view of the molecule shows (Figure 1b) that the two triflate anions lie above and below the cavity of the macrocycle similarly to what has been reported by Hawthorne and co-workers for the iodomercuroborane species. Interestingly, the X-ray determination shows that, in the solid state, **2a** consists of infinite planes in which every macrocycle interacts with its four closest neighbors (Figure 1c). Indeed, a strong $\pi-\pi$ interaction with a plane to plane distance of 3.6 Å between the benzimidazole rings of a macrocycle and the benzimidazole rings of its neighbors has been evidenced. Moreover, these infinite griddle-like planes interact with each other, creating a network of stacked layers of macrocycles. This is also due to $\pi-\pi$ interactions between macrocycles from neighboring planes.

The analogous metallomacrocycle $\{[Ag_2L^1{}_2][NO_3]_2\}$ (**2b**) was also prepared following the same procedure as that for **2a** but using $AgNO_3$ (**1b**) instead of **1a**. Remarkably, **2b** was also successfully obtained in quantitative yield when the starting metallomacrocycle **2a** was treated by an excess of NBu_4NO_3 in CH_3CN. Anion metathesis smoothly occurred (Scheme 2). The infrared, NMR, and elemental analysis data suggested that the two nitrate anions displaced the bonded triflate. Although no X-ray structure was obtained, we feel that, at least in the solid state, the two nitrate anions are now templating the new argentomacrocycle **2b**.[20]

When the reaction between L^1 and a silver ion was repeated using $AgBF_4$ (**1c**) instead of **1a**, a completely different supramolecular species was isolated and fully characterized.

Synthesis, NMR, and X-ray Molecular Structure of a 3D Network (3). Upon treatment of **1c** with the bidentate ligand L^1 in CH_2Cl_2 under conditions similar to those described for **1a**, a white compound was obtained and identified by elemental analysis, NMR, infrared, and X-ray analysis as a coordination polymer, $\{[AgL^1{}_2][BF_4]\}_n$ (**3**). The electrospray (ES) mass spectrum of **3** also shows a peak at $m/z = 785.12$ which corresponds to the formation of $[Ag(L^1)_2]^+$ species in solution and similar to that observed for **2a**. This suggests that in both reactions the identified [Ag-

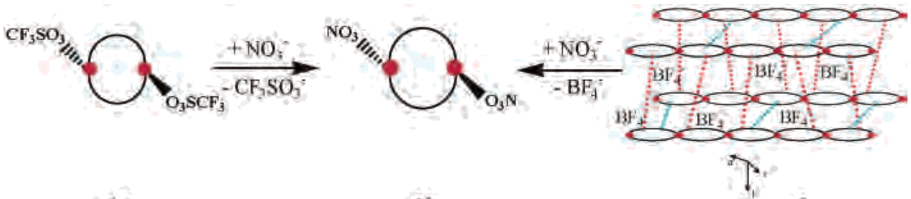
---

(18) McKee, V.; Nelson, J.; Speed, D. J.; Town, R. M. *J. Chem. Soc., Dalton Trans.* **2001**, 3641−3646.

(19) James, S. L.; Mingos, D. M. P.; White, A. J. P.; J., W. D. *Chem. Commun.* **1998**, 2323−2324.

(20) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986. (b) Jung, O.-S.; Park, S. H.; Lee, Y.-A.; Lee, U. *Chem. Lett.* **2000**, 1012−1013. (c) Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, J. K.; Chae, H. K. *J. Am. Chem. Soc.* **2000**, *122*, 9921−9925. (d) Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Chae, H. K.; Jang, H. G.; Hong, J. *Inorg. Chem.* **2001**, *40*, 2105−2110. (e) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, *118*, 295−296.

Scheme 2. Anion Metathesis from **2a** to **2b** and from **3** to **2b**[a]



2a **2b** **3**

[a] Most BF_4^- anions have been omitted for clarity.

Table 3. Selected Atomic Distances (Å) and Angles (deg) for **3**

Ag(1)−N(1) = 2.344(9)	N(1)−Ag(1)−N(1a) = 103.0(5)
Ag(1)−N(4) = 2.265(9)	N(1)−Ag(1)−N(4) = 122.9(3)
	N(1)−Ag(1)−N(4a) = 95.2(3)
	N(4)−Ag(1)−N(4a) = 118.9(5)

$(L^1)_2]^+$ subunit is the key building block which leads through self-assembly to either superstructure (Scheme 1).

The structure of **3** was also confirmed by an X-ray determination. Suitable crystals of **3** were obtained by slow evaporation of Et_2O into CH_3CN solution. The complex crystallizes in the monoclinic unit cell space group $C2/c$. Crystallographic data for **3** are shown in Table 1. Selected bond distances and angles are shown in Table 3. The structure shows that complex **3** consists of infinite doubly stranded chains, whereby every layer interacts with other close layers by extensive intermolecular $\pi-\pi$ interactions, thus describing a 3D network (Figure 2). In each layer four L^1 ligands wrap around the Ag(I) ion to give a tetrahedral coordination geometry and are disposed in a propeller arrangement with a dihedral angle $\theta = 74°$. Each ligand L^1 connects another Ag(I) center through the other benzimidazole arm, generating an infinite doubly stranded chain. Interestingly, the central phenyl rings of two close doubly stranded chains show an offset π-stacking phenomenon with a plane to plane distance of 3.7 Å.[21] This weak π-interaction is observed throughout the infinite chain. In addition, another stronger π-interaction with a plane to plane distance of 3.4 Å between benzimidazole rings of layer A and another doubly stranded chain, i.e., layer B, can be observed. This strong $\pi-\pi$ interaction deforms the shape of the 24-membered ring described by two L^1 ligands and the two Ag(I) centers. In this ring the average Ag−Ag distance is 10.9 Å. Moreover, the distance between the two parallel π-bonded benzimidazole groups is 10.1 Å, while the distance between non-π-bonded benzimidazole groups is 3.6 Å. Finally, the BF_4^- anions are located between two doubly stranded chains. Indeed, they can be found inside the cavities defined by the silver ions and the extensive intermolecular $\pi-\pi$ interactions between the central phenyl rings and the benzimidazole groups of the bridging ligands L^1 (Figure 2). Taken together, this is a rare 3D network for Ag(I) ions connected by benzimidazole ligands whereby two types of bonding, mainly metal-directional dative bonds and intermolecular π-interactions, promote the self-assembly of the **3** supramolecular architecture. In a previous work we reported the self-assembly of 1D infinite polymers of general formula $\{[AgL^2_2][X]\}_n$ $\{X = BF_4^-, CF_3SO_3^-; L^2 =$ 1,3-bis(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6-dimethylbenzene}, but the current supramolecular species **3** has different structure and π-bonding interactions.[22]

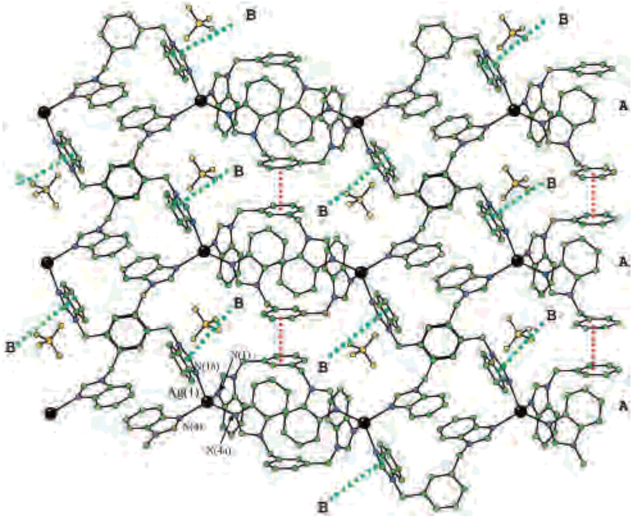


Figure 2. X-ray molecular structure of the 3D network **3**: Cameron view showing the numbering system, the strong $\pi-\pi$ interaction (dashed lines) between two benzimidazole rings of double-stranded infinite chains A and B (B chains have been omitted for clarity), and the weak $\pi-\pi$ interaction (dotted lines) between substituted benzene rings of several infinite chains A. Note that the two $\pi\angle\pi$ interactions are not in the same plane.

In an effort to understand the crucial role of the anion in the formation of the metallomacrocycles **2a** and **2b** relative to that of the 3D network **3**, where the BF_4^- is not coordinated to the metal center, we added excess $[NBu_4][NO_3]$ to a stirred solution of **3** in CH_3CN and monitored the reaction. After 5 min a white precipitate was formed, and the reaction was allowed to proceed for 30 min. The compound was isolated and characterized by elemental analysis, NMR, and infrared as metallomacrocycle **2b**. This result confirms the templating effect of the coordinated anion NO_3^- on the formation of the ultimate supramolecular structure. Spectacularly, in this case, the anion metathesis leads to a complete rearrangement of the structure from a 3D architecture to a macrocycle, underlining once again the crucial role of the anion. This transformation can easily be explained if the key $[Ag(L^1)_2]^+$ subunit is indeed obtained when the complexes are in solution. These experiments also imply that the coordinating effect of these anions decreases in the order $NO_3^- > CF_3SO_3^- > BF_4^-$.

---

(21) (a) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393−401. (b) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885−3896.

(22) Mimassi, L.; Guyard-Duhayon, C.; Raehm, L.; Amouri, H. *Eur. J. Inorg. Chem.* **2002**, 2453−2457.

Attempts to study the anion binding in solution by ^{19}F NMR for **2a** were not successful due to solubility limitation in CD_3CN and to the low $\Delta\delta$ value for bonded and free $CF_3SO_3^-$ anion.[19] For instance, the ^{19}F NMR spectrum of **2a** shows the presence of a singlet at $\delta = -77.5$ ppm, identical to that of $[NBu_4][CF_3SO_3]$. Upon addition of 5 equiv of $[NBu_4][CF_3SO_3]$ to **2a** only one signal was observed at $\delta = -77.5$ ppm. This suggests either that a rapid exchange occurs between bonded and free triflate or that in solution the triflate anions of **2a** are loosely bound. Despite these inconclusive NMR studies, we feel that the final structure of these supramolecular structures is governed by the templating effect of the anion.

Concluding Remarks

In summary, this work illustrates the power of anion template self-assembly in determining the final structure of a supermolecular species: with the coordinating triflate or nitrate ions, layered structures of argentomacrocycles are formed, whereas, with BF_4^-, a 3D network is created. In the latter case both metal-directed self-assembly and $\pi-\pi$ interactions allow the construction of an inorganic polymer, displaying as an outstanding feature the formation of large cavities where BF_4^- anions are located. These cavities are large enough to acquire not only small guest molecules but also large oligomer species. Moreover, anion metathesis allows the rearrangement of a 3D network into a macrocyclic structure. Currently, we are extending our research to prepare other supramolecular species with chiral cavities in view of using these materials to resolve chiral guests.

Experimental Section

Unless otherwise stated, all reactions were performed under an argon atmosphere using standard Schlenk techniques, but products were handled in the air. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. NMR spectra were recorded using Bruker AM 300 and Avance 400 MHz instruments. NMR chemical shifts are reported in parts per million referenced to the residual solvent proton/carbon resonance [(^{1}H) CD_3CN, 1.95; DMSO, 2.5/(^{13}C) CD_3CN, 1.3; DMSO, 39.7]. The numbering system used for protons and carbons is shown in Figure 1a. Infrared spectra were obtained on a Bio-Rad Win-IR spectrometer version 2.04 A from samples prepared on KBr disks. Elemental analyses were performed by the Microanalytical Laboratory of the Université Paris VI.

Synthesis of 1,3-Bis(benzimidazol-1-ylmethyl)benzene (L^1). α,α′-dibromo-*m*-xylene (2.234 g, 8.46 mmol), benzidimidazole (2.111 g, 1.78 mmol), and potassium carbonate (5.75 g, 42 mmol) were put in suspension in 50 mL of acetonitrile. The mixture was stirred at room temperature for 1 h before being refluxed for 15 h at 80 °C. The remaining beige precipitate was filtered off and rinsed with acetonitrile. The solvent was removed from the filtrate, and the beige product was taken up in chloroform and washed three times with water before being dried over Na_2SO_4. The removal of the solvent left an off-white powder. Yield: 2.781 g, 97%.

^{1}H NMR (CD_3CN, 400.13 MHz): δ 8.04 (s, 2H, H_1), 7.66 (dd, 2H, H_3), 7.30−7.22 (dd, 1H, H_{11}), 7.30−7.20 (dd, 2H, H_6), 7.23 (s, 1H, H_{14}), 7.22−7.15 (m, 2H, H_4), 7.20−7.13 (m, 4H, H_5 and H_{10}), 5.35 (s, 4H, H_8). ^{13}C NMR (CD_3CN, 100.62 MHz): δ 145.0 (C_2), 144.7 (C_1), 138.4 (C_9), 134.8 (C_7), 130.3 (C_{11}), 127.9 (C_{10}), 127.6 (C_{14}), 123.6 (C_5), 122.7 (C_4), 120.7 (C_3), 111.4 (C_6), 49.0 (C_8). IR (KBr disk, cm^{-1}): ν(C=C) 1669, 1613; ν(CH_2) 1495, 1458; ν(C−N) 1200−1100; ν(C−H) 776, 740.

Synthesis of $\{[Ag_2L^1{}_2](CF_3SO_3)_2\}$ (2a). To a suspension of $AgCF_3SO_3$ (81 mg, 0.315 mmol) in 10 mL of CH_2Cl_2 was added ligand **L**^{1} (151 mg, 0.446 mmol) in 15 mL of CH_2Cl_2 using standard cannula transfer techniques. A white precipitate appeared rapidly. The mixture was stirred at room temperature for a further 24 h. The white precipitate (170 mg) was collected by filtration, washed with CH_2Cl_2, and dried under vacuum. Yield: 90%.

Anal. Calcd for $C_{46}H_{36}N_8F_6S_2O_6Ag_2$ (1189.7 g·mol^{-1}): C, 46.40; H, 3.05; N, 9.41. Found: C, 46.26; H, 3.24; N, 9.25. ^{1}H NMR (CD_3CN, 400.13 MHz): δ 8.20 (s, 4H, H_1), 7.75 (dd, 4H, H_3), 7.42 (m, 4H, H_4), 7.40 (m, 6H, H_{10} and H_{11}), 7.30 (m, 4H, H_6), 7.23 (td, 4H, H_5), 6.77 (s, 2H, H_{14}), 5.47 (s, 8H, H_8). ^{13}C NMR (CD_3CN, 100.62 MHz): δ 145.8 (C_1), 143.2 (C_2), 137.8 (C_9), 134.0 (C_7), 130.5 (C_{11}), 128.4 (C_{10}), 126.5 (C_{14}), 124.8 (C_5), 124.1 (C_4), 120.3 (C_3), 112.0 (C_6), 49.4 (C_8).^{19}F NMR (CD_3CN, 376.47 MHz, reference δ($CFCl_3$/$CDCl_3$) = 0 ppm): δ −77.6 (s, CF_3SO_3). IR (KBr disk, cm^{-1}): ν(C−F) 1280. ES-MS: *m*/*z* calcd for $C_{44}H_{36}N_8$ $[M + 2L^1]^+$ 785.21, found 785.12. Single crystals were grown from an acetonitrile solution of the complex by slow diffusion of ether.

Synthesis of $\{[Ag_2L^1{}_2](NO_3)_2\}$ (2b). This compound was prepared in a manner similar to that of **2a** but using $AgNO_3$ instead of $AgCF_3SO_3$. Yield: 80%.

Anal. Calcd for $C_{46}H_{36}N_{10}O_6Ag_2$ (1016.56 g·mol^{-1}): C, 51.99; H, 3.57; N, 13.98. Found: C, 52.30; H, 3.80; N, 13.30. ^{1}H NMR (d_6-DMSO, 400.13 MHz): δ 8.62 (s, 4H, H_1), 7.78 (dd, 4H, H_3), 7.54 (dd, 4H, H_6), 7.39 (s, 2H, H_{14}), 7.40−7.30 (dd, 2H, H_{11}), 7.30 (m, 4H, H_{10}), 7.27 (m, 4H, H_4), 7.25 (td, 4H, H_5), 5.56 (s, 8H, H_8). ^{13}C NMR (CD_3CN, 100.62 MHz): δ 145.3 (C_1), 142.4 (C_2), 137.2 (C_9), 133.1 (C_7), 129.6 (C_{11}), 127.5 (C_{10}), 127.1 (C_{14}), 123.5 (C_5), 122.8 (C_4), 119.5 (C_3), 111.5 (C_6), 48.0 (C_8). IR (KBr disk, cm^{-1}): ν(N−O) 1384.

Synthesis of $\{[AgL^1{}_2](BF_4)\}_n$ (3). This compound was prepared in a manner similar to that of **2a** but using $AgBF_4$ instead of $AgCF_3SO_3$. Yield: quantitative.

Anal. Calcd for $C_{44}H_{36}AgBF_4N_8$ (870.21 g·mol^{-1}): C, 60.64; H, 4.16; N, 12.86. Found: C, 60.03; H, 4.26; N, 12.99. ^{1}H NMR (CD_3CN, 400.13 MHz): δ 8.15 (s, 4H, H_1), 7.72 (dd, 4H, H_3), 7.39 (dd, 2H, H_{11}), 7.30 (m, 8H, H_6 and H_{10}), 7.29 (m, 4H, H_4), 7.21 (td, 4H, H_5), 6.97 (s, 2H, H_{14}) 5.43 (s, 8H, H_8). ^{13}C NMR (CD_3CN, 100.62 MHz): δ 145.5 (C_1), 143.7 (C_2), 138.0 (C_9), 134.2 (C_7), 130.4 (C_{11}), 128.3 (C_{10}), 126.9 (C_{14}), 124.5 (C_5), 123.7 (C_4), 120.4 (C_9), 111.8 (C_6), 49.3 (C_8).^{19}F NMR (CD_3CN, 376.47 MHz): δ −150.0 (s, BF_4). IR (KBr disk, cm^{-1}): ν(B−F) 1060. ES-MS: *m*/*z* calcd for $C_{44}H_{36}N_8$ $[M + 2L^1]^+$ 785.21, found 785.12. Single crystals were grown from an acetonitrile solution of the complex by slow diffusion of ether.

Anion Exchange: From 2a to 2b. To a colorless solution of **2a** (72 mg, 60.5 μmol) in 20 mL of CH_3CN was added tetrabutylammonium nitrate (185 mg, 0.6 mmol). A white precipitate immediately appeared. The mixture was stirred at room temperature for a further 30 min. The white solid was then collected by membrane filtration. Yield: quantitative. Analytical and spectroscopic data are identical to those obtained for **2b** by direct synthesis.

Anion Exchange: From 3 to 2b. 3 (119 mg, 0.129 mmol) was dissolved in 20 mL of CH_3CN by heating the mixture at 40 °C for a few minutes. The solution was then cooled at room temperature, and tetrabutylammonium nitrate (394 mg, 1.29 mmol) was added to the solution. A white precipitate rapidly appeared. The mixture was stirred at room temperature for a further 2 h. The white solid was then filtered on a membrane to afford a white solid. Yield: quantitative. Analytical and spectroscopic data are identical to those obtained for **2b** by direct synthesis.

X-ray Crystal Structure Determination for 2a and 3. Suitable crystals of **2a** or **3** were obtained using slow diffusion techniques from acetonitrile/ether solution. The selected crystal of complex **2a** or **3** was mounted on the top of a glass rod at room temperature. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. Complete crystallographic data and collection parameters for **2a** and **3** are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[23] The structures of these compounds were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. Fractional parameters, anisotropic thermal parameters, and all bond lengths and angles are given in the Supporting Information for complexes **2a** and **3**.

Acknowledgment. We thank CNRS and the Université Pierre et Marie Curie (Paris) for supporting this work.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0340884

---

(23) Watkin, D. J.; Prout, C. K.; Carruthers, R. J.; Betteridge, P. W. *CRYSTALS*; Oxford, 1996; Issue 10.