The Structural Role of the Triflate Anion in the Non-Covalent Silver Polymer $[Ag(LOH)_2(CF_3SO_3)(CH_3CN)]$ {LOH = α-(4-Pyridyl)benzhydrol}

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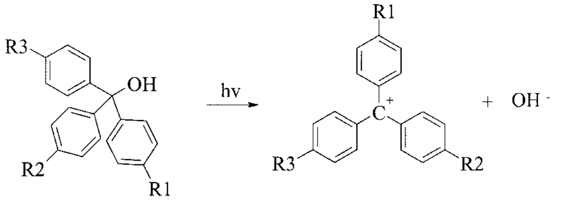
$Ag(CF_3SO_3)$ was reacted with the ligand α-(4-pyridyl)benzhydrol (LOH) in order to build a mixed organic/inorganic analogue of wheel-and-axle diols. In the resulting $[Ag(LOH)_2(CF_3SO_3)(CH_3CN)]$ complex, the metal is four-coordinate, with two pyridines *trans* each other and a triflate and an acetonitrile group completing a sawhorse geometry. The main structural motif is based on the strongest and most directional tectons, the coordination bond Ag–O and the hydrogen bonds –OH···O–S–O···HO–. Secondly, the sixfold phenyl embrace, $CH_3\cdots\pi$, $CH_3\cdots CF_3$ and Ag···F tectons also direct the crystal assembly. A new synthon originating from the combination of the S–O···HO–, the $\pi\cdots CH_3$ and the $CH_3\cdots CF_3$ individual tectons is identified. The structural roles of the anion and of the solvent are discussed.

Introduction

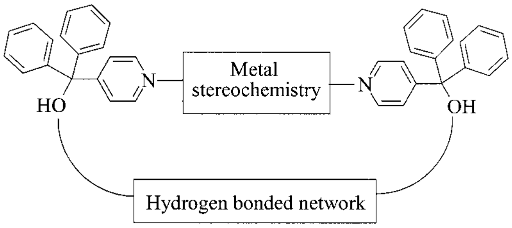
We are currently pursuing the engineering of crystalline systems built by combining photoactivatable triphenylmethanol derivatives with metal centers structured in porous networks.



Scheme 1

Triphenylmethanol derivatives (TPMs) (Scheme 1) are actively studied because they show C−OH photocleavage, accompanied by an intense chromatic change on irradiation by UV/Visible light both in polar solvents and in the solid state.[1] Furthermore, compounds with the general formula Ar_3X-OH (X = C, Si, Ge) have a propensity to crystallize giving trimeric or tetrameric molecular aggregates based on hydrogen-bonded −OH clusters, and they also frequently form clathrate compounds with hydrogen-bond acceptor solvent molecules.[2] Remarkable clathrating properties are shown also by the diol derivatives of the general formula $HOC(Ar)_2$-L-$(Ar)_2COH$, where L is a suitable rigid organic spacer,[3a] the so-called “wheel-and-axle” systems.

Our purpose is to incorporate a metal center into the L spacer of the $HOC(Ar)_2$-L-$(Ar)_2COH$ host framework, in order to combine the clathrating nature of the diol organic matrix with the potential host-guest reactivity triggered by the inorganic functionality (Scheme 2). The coordination of a metal center at the peripheral rim of the TPM molecule could tune the electronic properties of the chromophore and concomitantly drive the organization of the crystal architecture.



Scheme 2

Our approach to the rational design of these architectures is based on the molecular tectonics method,[4] in which the crystal structure is deconvoluted in the contributions of the single inorganic and organic building blocks, which are separately analyzed and optimized.

The first step in modeling these organic-inorganic “wheel-and-axle” complexes consists in the introduction of a transition metal as a bridge between two aromatic rings; this aim is pursued by synthesizing the transition metal complexes of the ligand α-(4-pyridyl)benzhydrol (LOH, Scheme 2).[5] Here, we report and analyze the solid-state arrangement of the new silver complex $[Ag(LOH)_2$-

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(OTf)(CH_3CN)], with the aim of establishing a hierarchy in the importance and robustness of the supramolecular motifs observed in the compound and of elucidating the structural role of the counteranion. Currently, we also report our first results on the supramolecular organization of two $Ag(LOH)_2^+$ complexes with weakly coordinating anions, BF_4^- and PF_6^-.[6]

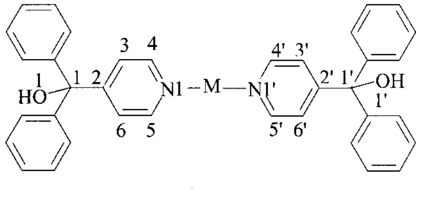
The analysis of the relevant interactions in the crystal packing of [$Ag(LOH)_2$(OTf)(CH_3CN)] will follow the scheme: (i) search for hydrogen bonds involving the −OH donor; (ii) search for short contacts (less than the sum of the van der Waals radii); among the above short contacts, detect weak hydrogen bonds, π interactions, aromatic$\cdots$aromatic association; (iii) heuristic search for other supramolecular long range arrangements, such as multiple phenyl embrace and long F$\cdots$Ag contacts, to complete the metal environment; (iv) analysis of the combination of the patterns to determine recurrent motifs for the structure, in comparison also to other $Ag(LOH)_2^+$ complexes.[6]

Results and Discussion

[$Ag(LOH)_2$(OTf)(CH_3CN)] is obtained by reacting LOH with an excess of $Ag(CF_3SO_3)$. The complex is stable in the solid state in the dark, while its solution slowly releases silver. The spectroscopic characterization does not show any remarkable feature: in the ^1H NMR spectrum, the protons H4 and H5 of the pyridyl ring are deshielded with respect to the free ligand, and the singlet assigned to the acetonitrile molecule is present ($\delta = 2.00$ ppm); in the IR spectrum, there are the typical bands assigned to the triflate anion. Crystals suitable for X ray diffraction analysis were obtained from the mother liquor within a couple of days.

The metal is coordinated to two pyridine N_{py} atoms, one oxygen atom of the anion and to one acetonitrile molecule (Figure 1), in a sawhorse geometry already observed for similar Ag complexes[7] [N2−Ag−O2 = 127.7(4)°]. The acetonitrile molecule is loosely bound, in fact the Ag−N2 distance [2.650(9) Å] is one of the longest ever observed in the solid state for $Ag-N{\equiv}C-CH_3$ coordination. The Ag atom, the CH_3CN and CF_3SO_3 ligands are placed on a symmetry plane that cuts the complex perpendicularly to the $N_{py}-Ag-N_{py}$ vector.

In a related work,[6] we found that in [$Ag(LOH)_2$]BF_4 and [$Ag(LOH)_2$]PF_6 the silver ion coordinates linearly two ligand molecules. In [$Ag(LOH)_2(CF_3SO_3)(CH_3CN)$], a new element is introduced into the organization of the crystal structure around the [$Ag(LOH)_2$]$^+$ unit; namely, the metal atom also employs covalent bonds to expand its supramolecular environment by directly coordinating the anion and the acetonitrile molecule. Scheme 3 shows the geometric descriptors chosen to represent the conformation of the complex. Selected parameters are: the dihedral angle between pyridines (ψ: C4−N1−N1′−C4′), the orientation of the C−OH vectors with respect to the adjacent pyridine (φ: O1−C1−C2−C3 and O1′−C1′−C2′−C3′), and the reciprocal orientation of the two C−OH vectors (χ: O1−C1−C1′−O1′). The classification of the triaryl groups has been made following Dance's analysis of triphenylphosphanes,[8] by calculating the torsion angles $C_{(ortho)}-C_{(ipso)}-C_{(sp3)}-O$ for each ring (labeled so that |torsion| < 90°), and then considering the cases: *rotor* (20° < |T1| ≈ |T2| ≈ |T3| < 70°, same sign), *anti-rotor* (20° < |T1| ≈ |T2| ≈ |T3| < 70°, opposite sign), *parallel flipper* (|T1| < 20°, T2 ≈ −T3), *orthogonal flipper* (70° < |T1| < 90°,



Ψ:C4-N1-N1'-C4'
Φ:O1-C1-C2-C6
O1'-C1'-C2'-C6'
χ:O1-C1-C1'-O1'

Scheme 3

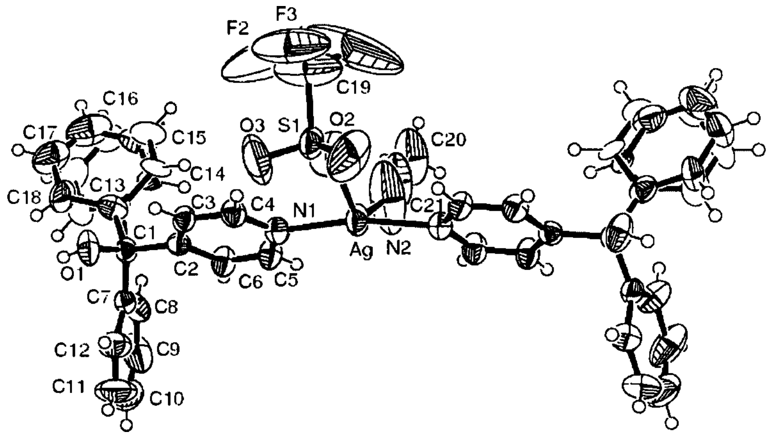


Figure 1. Molecular structure and labelling of the independent unit of [$Ag(LOH)_2(CF_3SO_3)(CH_3CN)$]; Ag, O2, S1, C19, F3, N2, C20 and C21 are on a mirror plane; phenyl C13−C18 is disordered over two orientations

Table 1. Molecular conformation and supramolecular organization of the [Ag(LOH)$_2$(OTf)(CH$_3$CN)] complex; *top*: ψ = reciprocal pyridine orientation, φ = orientation of the C−OH vector relative to the adjacent pyridine ring, χ = reciprocal orientation of the two C−OH vectors, T1, T2, T3 = conformation of the triaryl group, following Dance;[8] T1 refers to the pyridine ring and T2 to the ring involved in the NC−CH$_3$···π contact; T3 is presented for both disordered conformers (a) and (b); *bottom*: supramolecular tectons belong to three classes: metal environment (4+1 coordination), hydrogen bond (−OH···O−S−O···HO− motif), and weak directional interactions [CH$_3$···CF$_3$, CH$_3$···π, sixfold phenyl embrace (6PE)]; symmetry operations: (i) *x*, 3/2 − *y*, *z*; (ii) 1 − *x*, 2 − *y*, −*z*; (iii) *x* + 1, *y*, *z*; (iv) *x* + 1, *y*, *z* + 1; (v) 2 − *x*, 2 − *y*, 1 − *z*; (vi) *x*, 5/2 − *y*, *z*; (vii) 2 − *x*, *y* − 1/2, 1 − *z*

Molecular conformation (°)	ψ (C4−N1−N1′−C4′)	φ (O1−C1−C2−C3)	χ (O1−C1−C1′−O1′)	T1	T2	T3
	0.00	−24.3(5)	0.00	−24.3(5)	−35.1(5)	−69.8(7)(a) −38.0(8)(b)

Supramolecular organization (Å,°)	Metal environment				H-bond	Weak directional interactions		
	Ag−N_{py}	Ag···O	Ag···N_{solv}	Ag···CF_3	O−H···O D···A <DHA	CH_3···F	CH_3···π	6PE O−C1Ar_3···Ar_3C1−O
	Ag···N1 2.191(3)	Ag···O2 2.529(5)	Ag···N2 2.650(9)	Ag···F3(iii) 3.542(6)	O1−H···O3(ii) 2.849(5) 171(5)	C20···F3(iv) 3.00(1)	C20···C9(v) 3.552(7)	C1···C1(v) 6.535(7)
	Ag···N1(i) 2.191(3)	N1−Ag−O2 93.90(8)	N1−Ag−N2 90.86(9)	N1−Ag−F3(iii) 84.56(8)			C20···C9(vii) 3.552(7)	O1−C1···C1(v) 175.9(2)
	N1−Ag−N1(i) 168.7(2)		O2−Ag−N2 127.7(4)	O2−Ag−F3(iii) 117.3(2)				O1(v)−C1(v)···C1 175.9(2)
				N2−Ag−F3(iii) 115.0(3)				

T2 ≈ −T3). Table 1 lists the results of the conformational analysis and contains the key features of the supramolecular arrangement; symmetry operations cited in the text are also reported in Table 1. The pyridine rings are coplanar (Ψ = 0°), while the −OH groups deviate by Φ = −24.3(5)° from the pyridine plane. The complex exhibits the *syn* configuration for the two −OH groups (χ = 0°), in contrast with the *anti* configuration usually found in similar cases;[6,13] this will be related to the crystal packing in the course of the discussion. The triaryl group has a regular rotor conformation, with *T*1, *T*2 and *T*3 values falling in the range indicated by Dance.[8]

The coordination of the anion and acetonitrile group can be considered as the first stage of the supramolecular organization of the [Ag(LOH)$_2$]$^+$ unit; the analysis of the assembly of the [Ag(LOH)$_2$(OTf)(CH$_3$CN)] molecules follows the steps outlined in the introduction.

(i) The −OH donors are strongly linked to the triflate acceptors of adjacent molecules by OH···O hydrogen bonds [O1···O3(ii) = 2.849(5) Å, O1−H···O3(ii) = 171(5)°]: the [Ag(LOH)$_2$(OTf)(CH$_3$CN)] molecule uses its two −OH groups to hydrogen bond with the two triflate groups of a pair of adjacent molecules related by a twofold screw axis; concomitantly each triflate anion accepts two hydrogen bonds from the −OH groups of two adjacent molecules, generating the −OH···O−S−O···HO− tecton, with a OH···OH(vi) distance of 7.544(6) Å. The overall arrangement consists of a double strand along the *b* axis (Figure 2).

(ii) The short contacts (Table 1) involve the methyl group of the acetonitrile ligand, which is sandwiched between two aromatic rings giving two symmetric CH$_3$···π[9] interactions [C20···C9(v,vii) = 3.552(7) Å, H20···C9(v,vii) = 2.87 Å, H···π = 2.76 Å]. The two aromatic rings belong to a pair of triaryl groups in an adjacent double strand. The same methyl group also interacts with the triflate bridging the two aryl groups by means of a CH$_3$···CF$_3$ interaction [C20···F3(iv) = 3.00(1) Å]. Both interactions connect the double strands in a sheet (Figure 3). A short non-bonded H···H(vi) distance (2.36 Å, vi = *x*, 5/2 − *y*, *z*) between two almost coplanar aromatic rings which belong to the pair of molecules held together by the triflate bridge is also present in the structure. The local mirror symmetry would impose a much shorter contact between the two H atoms facing each other (1.66 Å), but this distance is relaxed by tilting the rings out of the common plane and introducing local disorder.

(iii) A sixfold phenyl embrace[10] [6PE, C1···C1(v) = 6.535(7) Å, O1−C1···C1(v) = 175.9(2)°] is formed between triaryl groups that are also involved in the CH$_3$···π interactions (Figure 4). The rotor conformation of the triaryl groups fits well in the 6PE and dictates the reciprocal orientation of the rings also involved in the H···H contact. Recently it has been shown by Bader and co-workers[11] that short H−H contacts between hydrogen atoms with similar charges can contribute up to 10 kcal/mol to the stabilization of the system where they occur. The assignment of stabiliz-

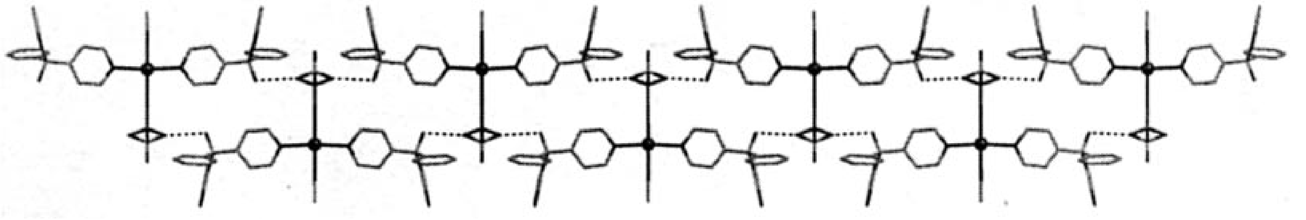


Figure 2. Association of the −OH···O−S−O···HO− tectons in double strands

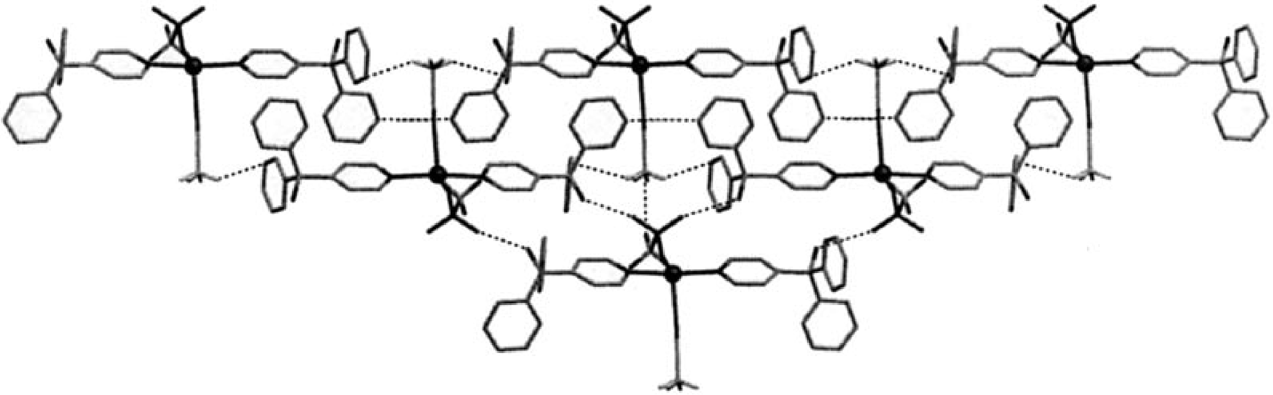


Figure 3. Association of the hydrogen-bonded double strands in sheets, via $CH_3\cdots\pi$ and $CH_3\cdots CF_3$ interactions (dashed); the short H···H contacts are also dashed (2.36 Å)

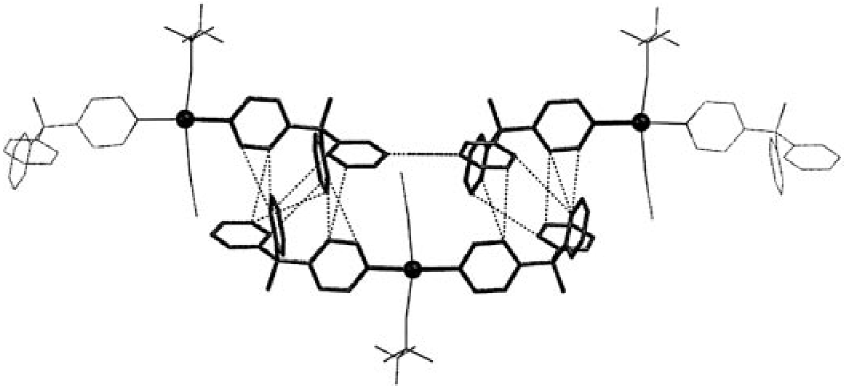


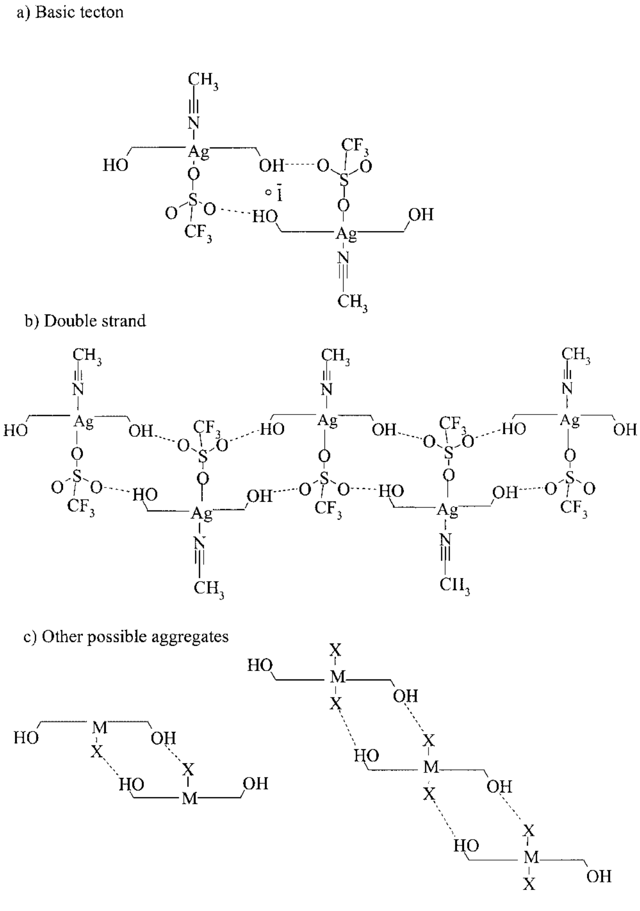
Figure 4. Sixfold phenyl embrace (6PE) involving molecules in the sheets shown in Figure 3; C···C contacts are dashed; the H···H short interaction is also shown

ing character to a short H−H interaction relies on the analysis of the experimental electron-density topology; in the absence of such evidence, it can be noted that the observed contact results from the balance of a local compression required to optimize the 6PE geometry in the presence of mirror symmetry, and a consequent rearrangement due to local overcrowding. The stabilization arising from the 6PE geometry can equal up to 20 kcal mol^{-1},[12] and this could counterbalance the possible repulsion between symmetry-related aromatic rings, whilst the H−H stabilization could justify a slight distortion from the best 6PE geometry.

Finally, an examination of the metal environment shows that a long Ag···F3(iii) [3.542(6) Å] contact completes the silver environment giving a distorted trigonal bipyramidal geometry [O2−Ag···F3(iii) = 117.3(2)°, N2−Ag···F3(iii) = 115.0(3)°].

(iv) The main structural motif, the double strand, is based on the strongest and most directional tectons, the coordination bond Ag−O and the hydrogen bonds −OH···O−S−O···HO− involving the cation and the anion. The first useful observation to interpret and rationalize the supramolecular arrangement of $[Ag(LOH)_2(OTf)(CH_3CN)]$ is that the coordination of the anion to the $[Ag(LOH)_2]^+$ structural unit sets the concomitant presence of a pair of hydrogen-bond donors (LOH) and a pair of hydrogen-bond acceptors ($-SO_3^-$) on the complex neutral molecule. The molecule is divided into two halves, each one bearing a −OH and a −S−O$^-$ function and behaving as a self-complementary moiety. Each half of the $[Ag(LOH)_2(OTf)]$ unit

[−Ag(OSO)(LOH)] thus presents the requirements for self-association, which may be triggered by an inversion center or by some twofold rotation relating two adjacent molecules (see a in Scheme 4). Also the basic $[Ag(LOH)_2]^+$ cation, found in $[Ag(LOH)_2]BF_4$ and $[Ag(LOH)_2]PF_6$, bears two −OH groups, both potential hydrogen bond donors and acceptors, but in that case the self-association could be disfavored for two reasons: cation···cation repulsion, and the relatively poor accepting nature of alcoholic −OHs. We can consider the dimeric system defined by the association of two centrosymmetric [−Ag(OSO)(LOH)] moieties as the basic tecton for building the structural motif based on hydrogen bonds. The association of the tectons in the double strands of collinear complexes (see b in Scheme 4) is governed by the nature of the anion: since the triflate fuses two $-S-O^-$ acceptors together, in the *cis* position relative to the metal, the complex must present a *syn* configuration of the C−OH vectors ($\chi = 0°$, Table 1) in order to pair all the donors and all the acceptors in the self-complementary structure. Different motifs could be engineered by choosing a single hydrogen-bond acceptor X (formation of dimers, with unsaturated terminal −OH groups) or a pair of single hydrogen-bond acceptors as *trans* ligands (formation of chains with *anti* configuration of the complex, $\chi = 180°$) (see c in Scheme 4). Both cases have been studied for Pd complexes.[13]



Scheme 4

The association of the double strands described above, built by the coordination bond Ag−O and the hydrogen bonds −OH···O−S−O···HO−, is governed by the formation of a 6PE tecton, which holds the strands together in sheets. The sheets are also held together by the solvent, which adopts a structuring role, through the coordination bond Ag−N and the short $CH_3\cdots\pi$ and $CH_3\cdots CF_3$ interactions .

Finally, the sheets interact using the Ag···F tecton, involving the anion. To investigate the role of the anion and of the solvent in the crystal organization of $[Ag(LOH)_2(OTf)(CH_3CN)]$, the local environment of the triflate anion was examined, see Figure 5. It appears that the combination of the S−O···HO−, the $\pi\cdots CH_3$, and the $CH_3\cdots CF_3$ individual tectons gives rise to a tetrafunctional cyclic pattern that is very similar to the one already observed in the related complexes $[Ag(LOH)_2]BF_4$ and $[Ag(LOH)_2]PF_6$ (Scheme 5).[6] In these complexes there are two basic independent supramolecular tectons (the OH···F−X−F···HO pattern and the cyclic pattern involving Ag···F, Ag···π and −OH···F interactions around the metal), which concur in creating two packing motifs: a chain motif, generated by hydrogen bonds around the anions $[\cdots F-X-F\cdots HO\cap Ag\cap OH\cdots F-X-F\cdots]_n$, and a layer motif, generated by the repetition of the Ag···F···HO−C-π cycle around the metal centers.

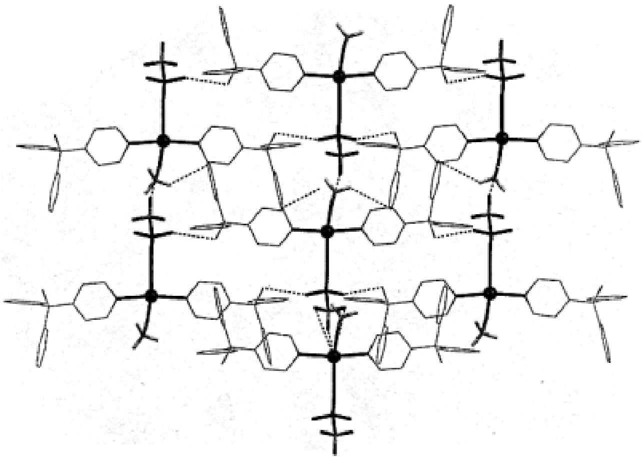
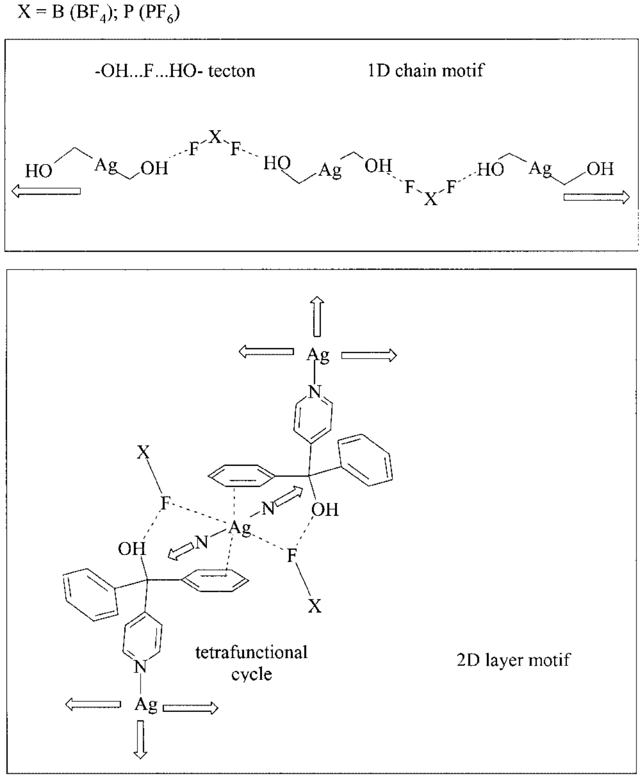
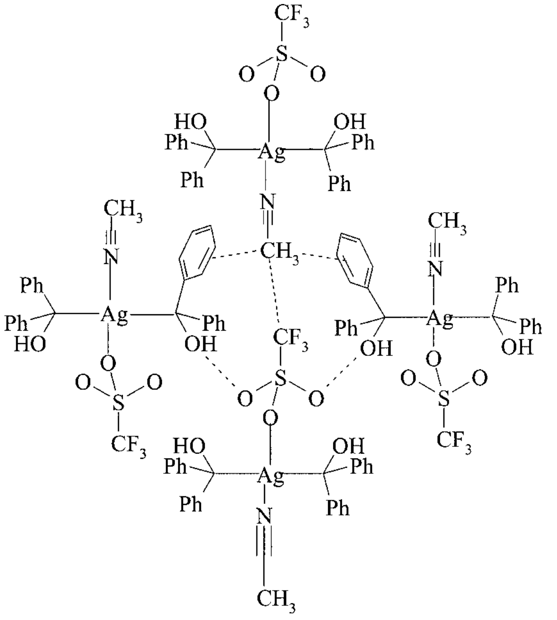


Figure 5. Structural role of the coordinated triflate anion; two mirror-related tetrafunctional cyclic patterns are organized by combining the S−O···HO−, the $\pi\cdots CH_3$ and the $CH_3\cdots CF_3$ individual tectons

In the present case, the methyl group of the acetonitrile plays the structural function of the Ag atoms in the above complexes, by bridging a triarylcarbinol group and the related hydrogen-bonded anion (Scheme 6). A pair of tetrafunctional cyclic patterns surround the anion in a mirror symmetry linking five molecules together: one covalently coordinated to the anion, two coordinated through hydrogen bonds, one through $CF_3\cdots CH_3$ interactions, and one through a $CF_3\cdots Ag$ long contact. The long axes of the five $Ag(pyridine)_2$ systems are approximately parallel.



Scheme 5



Scheme 6

Conclusions

In [Ag(LOH)$_2$(OTf)(CH$_3$CN)], the structural role of the anion is expressed through the coordination to the metal, with the concomitant presence of the acetonitrile molecule. We have uncoupled the function of the two LOH ligands by observing that the anion triggers the formation of the double strands of collinear complexes in the *syn* configuration: this results in a non-covalent supramolecular polymer.[14] The solvent assists in the stabilization of the association of the strands in sheets. The most striking feature of the solid-state arrangement of [Ag(LOH)$_2$(OTf)(CH$_3$CN)] is the plasticity of the molecule in response to the structural function of the anion, which allows for the tuning of both the coordination geometry and the configuration of the terminal −OH groups in order to achieve the best self-complementary shape, thus giving the multitude of diverse interactions highlighted in the course of the analysis.

Experimental Section

Synthesis: A solution of LOH (62 mg, 0.237 mmol) in THF (40 mL) was added to a solution of Ag(CF$_3$SO$_3$) (61 mg, 0.237 mmol) in CH$_3$CN (10 mL). The solution was stirred for 3 hours; diethyl ether was added until a white precipitate formed. The mixture was filtered and the precipitate was washed with diethyl ether. Yield 72%, m.p. > 123 °C (dec.). Colorless crystals suitable for X-ray analysis were obtained by cooling mother liquors. C$_{39}$H$_{33}$Ag F$_3$N$_3$O$_5$S (820.372): calcd. C 57.09, H 4.02, N 5.12, S 3.90; found C 56.61, H 4.11, N 5.55, S 3.94. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ= 8.57 (d, $^3J_{H,H}$ = 6 Hz, 4 H, C(4)−H + C(5)−H), 7.57 (d, $^3J_{H,H}$ = 6 (Hz), 4 H, C(3)−H + C(6)−H), 7.33−7.23 (m, 20 H, Ar), 3.09 (br., 2 H, −OH), 2.00 (s, 3 H, CH$_3$CN). IR [KBr (cm^{-1})]: ν(OH): 3458 (m), ν(CN): 2255 (m), ν(SO): 1267 (m).

Crystallographic Analysis: Mo-K_α radiation (λ = 0.71073 Å), T = 293 K (SMART AXS 1000 CCD diffractometer). Lorentz and polarization corrections were applied.[15] Structure solved by direct methods using SIR97 [16] and refined by full-matrix least-squares on all F^2 using SHELXL-97,[17] implemented in the WingX package.[18] Hydrogen atoms located on Fourier difference maps and refined isotropically except for the disordered parts, where they have been introduced in idealized positions. Anisotropic displacement parameters refined for all non-hydrogen atoms. The phenyl group C13−C18 is disordered over two equally populated orientations, in order to release steric overcrowding due to a crystallographic mirror plane passing close to C17. The removal of the mirror plane and the modeling of the structure in the corresponding $P2_1$ space group did not result in a unique conformation of the ring. Hydrogen bonds have been analyzed with SHELXL-97[17] and PARST97.[19] Crystal data: C$_{39}$H$_{33}$AgF$_3$N$_3$O$_5$S, 0.10 × 0.08 × 0.03 mm, monoclinic, space group $P2_1/m$, a = 8.4826(7), b = 21.475(2), c = 10.5455(9) Å, β = 101.144(2)°, V = 1884.8(3) Å^3, ρ = 1.446 Mg·m^{-3}, 2369 unique reflections, 1958 observed [$I > 2\sigma(I)$], 318 parameters, $R1$ = 0.0355, $wR2$ = 0.0933 [on $I > 2\sigma(I)$] and $R1$ = 0.0453, $wR2$ = 0.0978 (on all data). For the analysis of the organization of supramolecular tectons in the observed structures and for comparison with literature data, extended use has been made of the software of the Cambridge Structural Database (CSD).[20] The van der Waals radii used for assigning threshold values to intermolecular contacts are (Å): Ag 1.72, C 1.70, F 1.47, H 1.20, N 1.55, O 1.52, S 1.80 (taken from CSD reference values). CCDC-226532 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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