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Electrochemical Synthesis and Structural Characterization of Silver(I) Complexes of *N*-2-Pyridyl Sulfonamide Ligands with Different Nuclearity: Influence of the Steric Hindrance at the Pyridine Ring and the Sulfonamide Group on the Structure of the Complexes[§]

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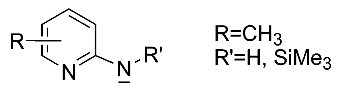
A new series of silver complexes, [AgL], of the anionic forms of potentially bidentate *N*-2-pyridyl sulfonamide ligands [*N*-(3-methyl-2-pyridyl)-*p*-toluenenesulfonamide (HTs3mepy), *N*-(3-methyl-2-pyridyl)mesitylenesulfonamide (HMs3mepy), *N*-(4-methyl-2-pyridyl)-*p*-toluenesulfonamide (HTs4mepy), and *N*-(6-methyl-2-pyridyl)mesitylenesulfonamide (HMs6mepy)] have been prepared by an electrochemical procedure. In addition, heteroleptic complexes of composition [AgLL′] (L′ = 1,10-phenanthroline and 2,2′-bipyridine) were obtained when the coligand L′ was added to the electrolytic phase. The complexes were characterized by microanalysis, IR and ^{1}H NMR spectroscopy, and LSI mass spectrometry. In the cases of the compounds $[Ag(Ts3mepy)]_n$ (**1**), $[Ag_4(Ms3mepy)_4]$ (**2a**), $[Ag(Ms3mepy)]_n$ (**2b**), $[Ag_4(Ms6mepy)_4]$ (**3a**), $[Ag_2(Ms6mepy)_2]_n$ (**3b**), $[Ag_2(Ms3mepy)_2(phen)_2]$ (**5**), $[Ag_2(Ms6mepy)_2phen]$ (**7**), and $[Ag_2(Ts4mepy)_2(bipy)_2]$ (**8**), characterization was also carried out by single-crystal X-ray diffraction. Compounds **1** and **2b** present a polymer structure formed by an $\{AgN_2\}$ digonal core. Compounds **2a** and **3a** are tetranuclear and also have a distorted $\{AgN_2\}$ digonal core. Compound **3b** is based on binuclear distorted $\{AgN_2\}$ digonal units joined by an intermolecular sulfonyl oxygen atom to produce a stairlike polymer structure. The heteroleptic complexes **5** and **8** are dimeric with a distorted $\{AgN_4\}$ tetrahedral geometry, while compound **7** shows two different geometries around the metal, distorted $\{AgN_2\}$ digonal and $\{AgN_4\}$ tetrahedral. The supramolecular structures of all species are organized by π,π-stacking, C–H···π, or C–H···O interactions.

Introduction

The chemistry of metal complexes with pyridine-functionalized amide ligands (Chart 1) has received a great deal of attention,[1−4] which is due, in part, to the fact that such complexes can be made relatively easily. Furthermore, variation of the substituents in these ligands is facile. This latter feature provides the possibility of tailoring the bite angle and degree of steric hindrance present in the ligand, and in addition, it is believed that the presence of bulky substituents on these ligands can stabilize the metal complexes. A particular class of ligands of this type is the pyridine sulfonamide ligands. These ligands are very versatile in terms of their coordination modes; they can act as anionic monodentate systems via the nitrogen pyridine atom (I)[5] or

Chart 1



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[§] Dedicated to Professor J. R. Dilworth, on the occasion of his 60th birthday.

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10.1021/ic0490268 CCC: $30.25

Chart 2

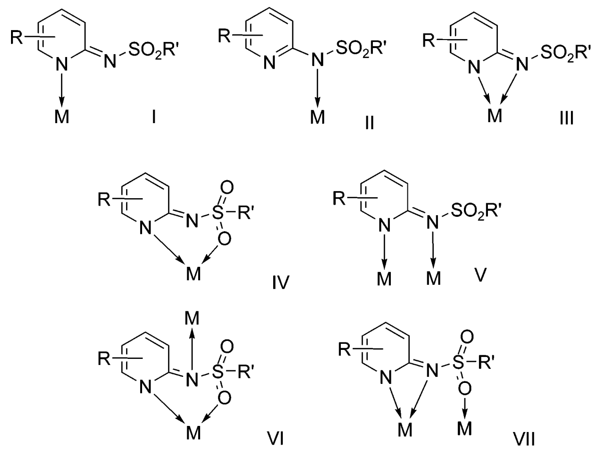
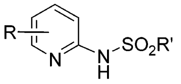


Chart 3



Code	R	R'
HTs3mepy	3-Me	4-MeC$_6$H$_4$
HMs3mepy	3-Me	2,4,6-Me$_3$C$_6$H$_2$
HTs4mepy	4-Me	4-MeC$_6$H$_4$
HMs6mepy	6-Me	2,4,6-Me$_3$C$_6$H$_2$

amide nitrogen atom (II),[6] act as chelates (III,[7,8] IV[9,10]), or act as bridges between two metal atoms (V,[11] VI,[12] VII[12]) (Chart 2). In this way these complexes can have variable nuclearities and great structural diversity.

This versatility, together with the plasticity of the silver(I) ion, which can adopt coordination numbers between 2 and 6 and various geometries ranging from linear through to trigonal, tetrahedral, trigonal pyramidal, and octahedral, can allow the construction of different architectures.[13] Moreover, the presence in these ligands of different substituents on the pyridine ring and on the sulfonic acid group (Chart 3) allows the possibility of investigating whether the position and number of substitutents has any influence on the coordinative behavior of these ligands and, consequently, on the structure of the corresponding amido silver complexes. In addition, we were interested in incorporating coligands such as 1,10-phenanthroline and 2,2′-bipyridine into the coordination sphere of silver to determine whether its presence could lead to novel structures.

Accordingly, we report here the synthesis of a series of a homoleptic and heteroleptic neutral Ag(I) complexes with ligands of the type shown in Chart 3. The complexes were prepared using an electrochemical procedure in which the metal is the anode of a cell containing an acetonitrile solution of differently substituted *N*-2-pyridyl sulfonamide ligands.

Results and Discussion

Synthesis and General Characterization. The homoleptic and some heteroleptic silver(I) sulfonamide complexes, [AgL] and [AgLL′] (L′ = phen or bipy), can be readily prepared in good yield by the electrochemical method described, which is a methodology similar to that reported previously for related systems.[5−10]

Thus, the electrochemical oxidation of anodic silver in a cell containing different substituted *N*-2-pyridyl sulfonamide ligands (HL) in acetonitrile gave the complexes [AgL] in good yields. The compounds were obtained as white crystalline light-sensitive solids by air concentration of the resulting acetonitrile solution.

Coligands such as 1,10-phenanthroline or 2,2′-bipyridine were added to the electrochemical cell with the intention of incorporating them as coligands for silver coordination in an attempt to decrease the nuclearity of the compounds. The electrochemical oxidation of silver in a solution of the *N*-2-pyridyl sulfonamide ligands (HL) and an equimolecular amount of 1,10-phenanthroline in acetonitrile gave the complexes [$Ag_2L_2phen_2$] or [Ag_2L_2phen], showing that the coligand had been incorporated into the complex. Attempts to obtain crystals of complexes **4** and **6** that were suitable for X-ray studies proved unsuccessful, but analytical and spectroscopic data (vide infra) confirmed them to be silver(I) compounds with monoanionic sulfonamide and phenanthroline ligands coordinated to the metal. Presumably these compounds have structures similar to that of complex **5**.

However, when the coligand 2,2′-bipyridine (bipy) was added to the electrochemical cell, only in the case of the *N*-(4-methyl-2-pyridyl)-*p*-toluenesulfonamide ligand was the coligand incorporated into the metal coordination sphere. The complex isolated in this case was [Ag_2(Ts4mepy)$_2$(bipy)$_2$] (**8**), as confirmed by X-ray diffraction. In all other cases, the analytical data and the spectroscopic studies on the resulting products did not show evidence for the incorporation of the additional coligand and the homoleptic compound [AgL] was formed exclusively. This situation was confirmed by X-ray studies on some of these products, **1**, **2b**, and **3b**. The compounds [Ag(Ms3mepy)]$_n$ (**2b**) and [Ag_2(Ms6mepy)$_2$] (**3b**) prepared in this way are supramolecular isomers to complexes **2a** and **3a**, respectively,[14] with an identical stoichiometry formed when the synthesis was carried out in the absence of coligand (see Scheme 1).

The heteroleptic silver(I) sulfonamide compounds were obtained as white crystalline light-sensitive solids by air concentration of the resulting acetonitrile solutions. These complexes were found to be more soluble than the homoleptic analogues in chloroform and a range of other chlorinated organic solvents.

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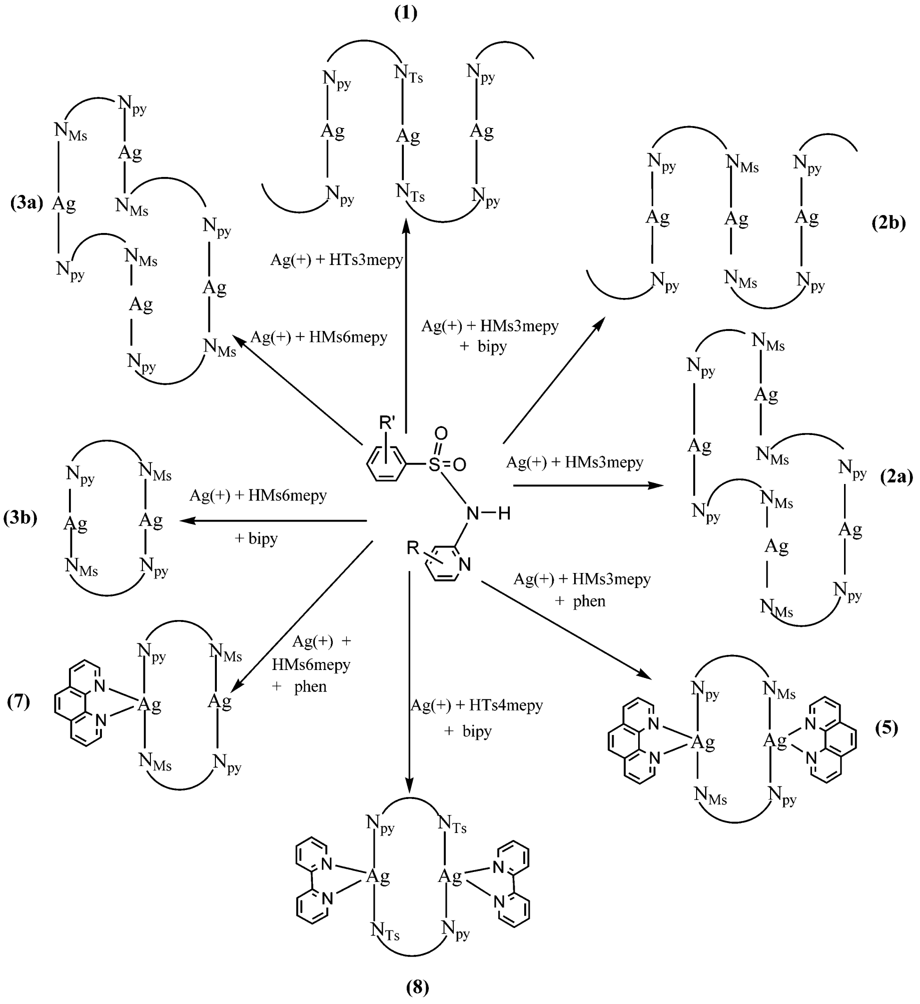
Scheme 1



The electrochemical efficiency, defined as moles of metal dissolved/Faraday of charge, was in all cases close to 1.0 mol·F^{-1}. This fact, together with the evolution of hydrogen at the cathode, is compatible with the occurrence of the following electrode reactions:

$$\text{cathode: } HL + e^{-} \rightarrow 1/2H_2 + L^{-}$$

$$\text{anode: } L^{-} + Ag \rightarrow [AgL] + e^{-}$$

$$L^{-} + Ag + L' \rightarrow [AgLL'] + e^{-}$$

Here HL stands for the corresponding neutral sulfonamide ligand and L′ = phen or bipy.

Spectroscopic Properties of [AgL] Compounds. The IR spectra of these complexes do not contain the band observed in the ligand at 3248−3222 cm^{-1}, which is attributed to ν(N−H) stretching. This difference in the spectra indicates that the ligand is in the anionic amidate form in the complex. The spectra also show bands in the aromatic region that are due to ν(C═N) (1608−1587 cm^{-1}) and ν(C═C) (1580−1555 cm^{-1}). These bands are shifted to lower frequencies with respect the free ligand as a result of coordination through the sulfonamide nitrogen atom. The spectra also show bands in the region 1340−1325 cm^{-1}, which are attributed to ν_{as}(S═O), and bands in the range 1140−1115 cm^{-1}, which are attributed to the ν_{sym}(S═O) vibrations. A band is also observed at 2951−2931 cm^{-1}, and this corresponds to ν(CH_3).

The room-temperature ^{1}H NMR spectra of the complexes do not contain the broad signal attributable to the −NH hydrogen, which appears in the free ligand at δ 12.3−9.4 ppm. The absence of this signal in the complex is a result of deprotonation of the ligand. The multiplet resonances in the aromatic region, δ 8.1−6.3 ppm, and also the signals corresponding to the methyl groups, δ 2.9−1.7 ppm, appear slightly shifted with respect to those in the free ligand. This is again due to the coordination of the ligand.

The LSI mass spectra of the silver compounds show the [AgL]$^+$ ion with the appropriate isotope distribution at *m*/*z* 370 for the *p*-toluenesulfonamide derivative and *m*/*z* 398 for the mesitylenesulfonamide complex. The peaks corresponding to the free ligand at *m*/*z* 263 and 291, respectively, are also observed.

Spectroscopic Properties of [$Ag_2L_2phen_2$] and [Ag_2L_2phen] Compounds. The IR spectra of these complexes do not contain the ν(N−H) band observed for the ligand. The absence of this band is indicates that deprotonation of the ligand has taken place. In addition to the bands described above for the homoleptic compounds, the spectra of the mixed complexes show bands at around 1510, 850, and 730 cm^{-1}, which are typical for coordinated 1,10-phenanthroline.[15,16]

The room-temperature ^{1}H NMR spectra of the complexes do not contain the broad signal attributable to the −NH proton. Once again, this is consistent with the deprotonation of the ligand. The multiplet resonances, including those for the 1,10-phenanthroline, appear in the aromatic region (δ 9.5−6.3 ppm). In the complexes the signals of the 1,10-phenanthroline can be distinguished at low field from those due to the aromatic sulfonamide ligand. In these cases the signals attributable to the 2,9- and 3,8-protons of 1,10-phenanthroline, between δ 9.5−9.1 and δ 8.2−7.7 ppm, respectively, experience a small dowfield shift with respect to the corresponding signals in the free ligand. This shift provides evidence for the coordination of the 1,10-phenanthroline molecule.[17] Finally, the signals corresponding to the methyl groups, δ 2.7−2.0 ppm, also appear slightly shifted with respect to those in the free ligand, again due to coordination of the ligand.

The LSI mass spectra show the [AgLphen]$^+$ ion, with the appropriate isotope distribution, at *m*/*z* 551 for the *p*-toluenesulfonamide mixed complex and *m*/*z* 578 for the mesitylenesulfonamide complex. In all cases the peaks corresponding to the free ligands are observed at *m*/*z* 263 and 291, respectively. For complexes **4** and **7** the peak corresponding to the loss of 1,10-phenanthroline are also observed at *m*/*z* 369 and 398, respectively.

Spectroscopic Properties of the [AgLbipy] Compound. The IR spectrum of this complex shows bands and signals similar to those described above for the homoleptic complexes. Additional bands were also observed at 758 and 735 cm^{-1}, and these are typical of coordinated 2,2′-bipyridine.[16] The room-temperature ^{1}H NMR spectrum of **8** shows signals assignable to the hydrogens of 2,2′-bipyridine in addition to the signals corresponding to the hydrogen atoms of the deprotonated sulfonamide ligands. The downfield shift of the signal attributable to the 3,3′-protons (δ 8.2 ppm) and the upfield shift of the signal for the 6,6′-protons (δ 8.7 ppm) provide evidence for the coordination of the 2,2′-bipyridine ligand.[18] The LSI mass spectrum shows a peak corresponding to the [Ag(Ts4mepy)bipy]$^+$ ion, with the appropriate isotope distribution, at *m*/*z* 526. Peaks due to the loss of the 2,2′-bipyridine coligand, [Ag(Ts4mepy)]$^+$, at *m*/*z* 369 and the free ligand at *m*/*z* 263 are also observed.

Description of Structures. The ligand HTs4mepy and the complexes **1**, **2a,b**, **3a,b**, **5**, **7**, and **8** were studied by X-ray diffraction. The crystal parameters, experimental details for data collection, and bond distances and angles for all these compounds are provided as Supporting Information.

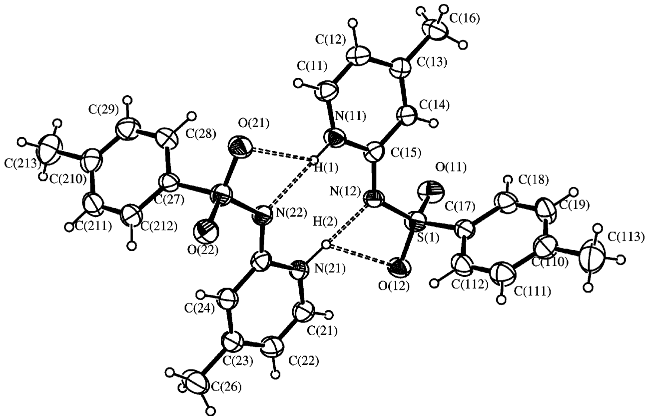
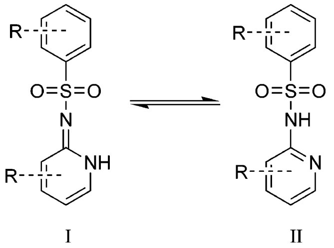


Figure 1. HTs4mepy. Selected bond distances (Å): N(11)−C(11) 1.351(3), N(11)−C(15) 1.365(3), N(11)−H(1) 0.89(2), N(12)−C(15) 1.341(3), N(21)−C(21) 1.356(3), N(21)−C(25) 1.361(3), N(21)−H(2) 0.924(16), N(22)−C(25) 1.348(3).

Scheme 2



Structure of HTs4mepy. A view of the structure of HTs4mepy is shown in Figure 1, together with the atomic numbering scheme.

The molecular structure of this ligand is consistent with an imide tautomer (I) (see Scheme 2) in which the two independent molecules in the unit cell of HTs4mepy are associated by intermolecular hydrogen bonds, through the pyridine nitrogen atom with one of the sulfonyl oxygen atoms and with the sulfonamide nitrogen atom of a neighboring molecule (see figures in Supporting Information).

This situation is similar to that found in HTspy[8] and HMs6mepy[9] but contrasts with the hydrogen network found in HTs3mepy[6] and HMs3mepy,[10] where the presence of the methyl group in position 3 of the pyridine ring precludes, for steric reasons, the involvement of the $N_{sulfonamide}$ atom in the hydrogen bond.

Structures of Polymeric Compounds. Structures of [Ag(Ts3mepy)]$_n$ (1) and [Ag(Ms3mepy)]$_n$ (2b). The polymeric structures of [Ag(Ts3mepy)]$_n$ (**1**) and [Ag(Ms3mepy)]$_n$ (**2b**), together with the atomic numbering schemes adopted, are shown in Figures 2 and 3, respectively. The packing along the *a* axis is provided as Supporting Information.

The structures of these two compounds are similar in that they have a crystallographically imposed symmetry in the unit cell and can be described as one-dimensional helical polymers with pitches of 6.2951(6) and 7.959(6) Å, respectively. All Ag(I) ions adopt a regular digonal geometry (AgN$_2$) and are coordinated by two nitrogen atoms from different sulfonamide ligands with a bond angle of 180° in both cases. In this way the metals are bridged by two anionic sulfonamide molecules that behave in a $\kappa^2(\mu\text{-}N,N')$ manner

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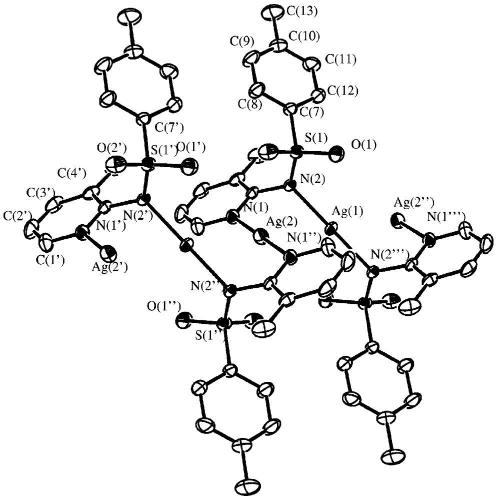

Figure 2. Structure of **1**. Selected bond distances (Å) and angles (deg): Ag(1)−N(2)^a 2.141(3), Ag(1)−N(2) 2.141(3), Ag(1)−Ag(2)^b 3.1476(3), Ag(1)−Ag(2) 3.1476(3), Ag(2)−N(1) 2.128(3), Ag(2)−N(1)^c 2.128(3), N(2)$^{a-}$Ag(1)−N(2) 180.00(11), Ag(2)$^{b-}$Ag(1)−Ag(2) 180.0, N(1)−Ag(2)−N(1)^c 180.0(2), 106.46(12). Key: (a) $-x$, $1-y$, $-z$; (b) $x-1$, y, z.

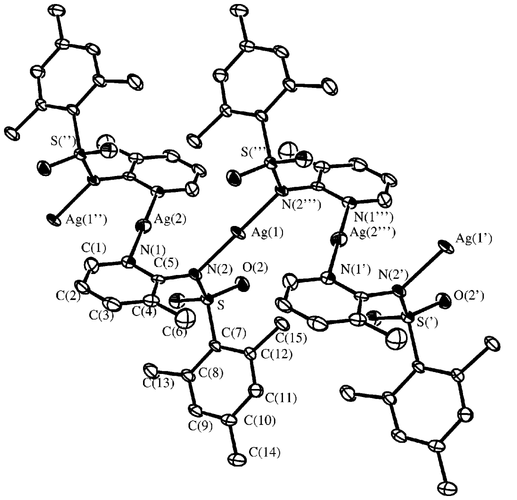

Figure 3. Structure of **2b**. Selected bond distances (Å) and angles (deg): Ag(1)−N(2)^a 2.133(6), Ag(1)−N(2) 2.133(6), Ag(1)−Ag(2) 3.980(3), Ag(2)−N(1)^b 2.125(8), Ag(2)−N(1) 2.125(8), N(2)$^{a-}$Ag(1)−N(2) 180.0, N(1)$^{b-}$Ag(2)−N(1) 180.0(4). Key: (a) $1-x$, $1-y$, $-z$; (b) $-x$, $1-y$, $-z$.

with the sulfonyl oxygen atoms not involved in the coordination. The distances between the Ag atoms and the nearest O of the sulfonyl groups are 2.898(3) and 2.944(3) Å for **1** and 2.900(6) and 2.992(6) Å for **2b**. The sulfonamide ligands dispose themselves in a "*head to head*" and "*tail to tail*" fashion, meaning that the silver atoms can be classified into two different alternate groups according to their coordination environment; one sort of Ag(I) is coordinated by two pyridine nitrogen atoms, N(1)−Ag(1)−N(1′), while the other group is coordinated by two sulfonamide nitrogen atoms, N(2)−Ag(2)−N(2′). The distance between silver atoms in compound **1**, 3.1476(3) Å, is shorter than in **2b**, 3.980(3) Å, but both are too long for the existence of any Ag···Ag interaction.

In both compounds the Ag−N$_{py}$ and Ag−N$_{amide}$ bond lengths, 2.128(3) and 2.141(3) Å for **1** and 2.125(8) and 2.133(6) Å for **2b**, respectively, are similar and are within the normal range observed in other digonal Ag(I) complexes of pyridine and/or sulfonamido ligands.[19] However, these distances are slightly shorter than those found in the dimeric silver(I) complex with 2-pyridyl-*p*-toluenesulfonamide, where the ligands also present a $\kappa^2(\mu\text{-}N,N')$ coordination but are in a trans disposition (head to tail). This situation produces Ag−N$_{py}$ bond distances of 2.150(3) Å, which are shorter than Ag−N$_{amide}$, 2.164(3) Å, due to existence of short Ag···Ag [2.7392(10) Å] and Ag···O [2.733(3) Å] interactions.[11] This Ag···O interaction produces an N$_{py}$−Ag−N$_{amide}$ angle of 165.90(10)°, which is lower that the N−Ag−N angle of 180° found in **1** and **2b**.

Complexes **1** and **2b** have a one-dimensional polymeric structure along the *a* axis (Supporting Information) with intermolecular π,π-stacking interactions between the pyridine rings of two adjacent polymeric chains. These interactions are of the offset or slipped-stacking type. The distances between centroids are 3.6232(3) and 3.610(2) Å for **1** and **2b**, respectively. Both planes are symmetry-imposed parallel, and they are separated by 3.296(4) and 3.346(7) Å, respectively, indicating a respective lateral displacement of 1.504(4) and 1.355(4) Å.

In both cases, nonclassical intermolecular H-bonds are found. One of these occurs between a hydrogen atom of the methyl group in the position *para* to the sulfonyl group [C(13) for **1** and C(14) for **2b**] and one of the oxygen atoms of a sulfonyl group in a neighboring chain. The other intermolecular C−H···O interactions involve the hydrogen atoms of the CH and methyl groups of the pyridine rings in one chain and the oxygen atoms of neighboring chains (Supporting Information). The association of each chain with four other chains through π,π-stacking and C−H···O interactions leads to chains that are parallel to the *a* axis. In this arrangement the sulfonyl groups of each chain intercalate between two sulfonyl groups of two adjacent chains, and in this way, π,π-stacking interactions are established.

Structure of Tetranuclear Compounds. Structure of [Ag$_4$(Ms3mepy)$_4$] (2a). The molecular structure of [Ag$_4$(Ms3mepy)$_4$] (**2a**), a supramolecular structural isomer of **2b**, is shown in Figure 4, together with the atomic numbering scheme adopted. For the sake of clarity, a view of the coordination sphere of the metals is represented in Figure 4b.

The structure is formed by discrete molecules and consists of a tetranuclear array of silver atoms, which are on the vertex of an almost planar rhombic parallelogram [Ag−Ag−Ag angles, 64.17(2), 64.68(2), 115.10(3), and 115.62(3)°, rms = 0.0644]. The overall pattern of metal−metal distances is such that there are two shorter and two longer distances. These distances, which are in the range 2.9803(9)−3.3033-

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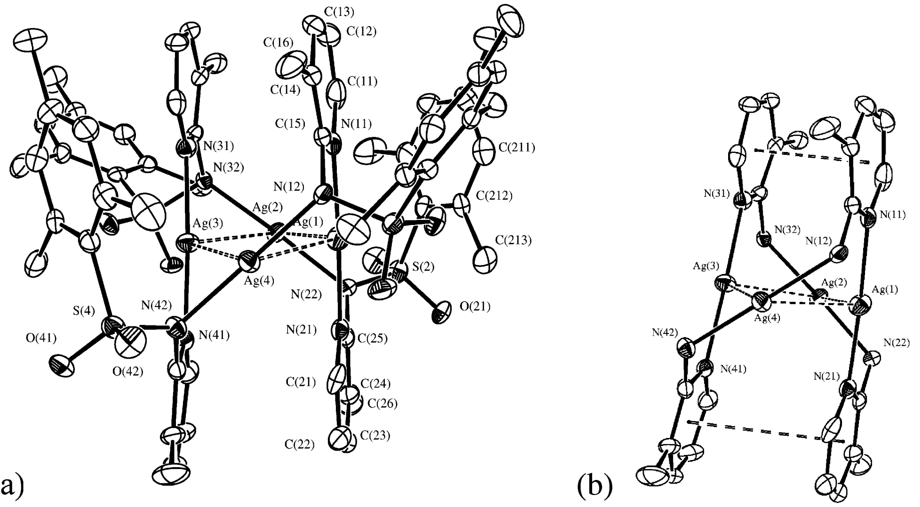

Figure 4. (a) Structure of **2a** and (b) partial view of **2a**. Selected bond distances (Å) and angles (deg): Ag(1)−Ag(2) 2.9932(9), Ag(2)−Ag(3) 3.3033(9), Ag(3)−Ag(4) 2.9803(9), Ag(4)−Ag(1) 3.2736(9), Ag(1)−N(21) 2.117(6), Ag(1)−N(11) 2.146(6), Ag(2)−N(32) 2.097(5), Ag(2)−N(22) 2.107(6), Ag(3)−N(41) 2.132(6), Ag(3)−N(31) 2.142(6), Ag(4)−N(42) 2.074(6), Ag(4)−N(12) 2.092(6), N(21)−Ag(1)−N(11) 175.5(3), N(32)−Ag(2)−N(22) 177.5(2), N(41)−Ag(3)−N(31) 174.5(3), N(42)−Ag(4)−N(12) 179.1(2).

Table 1. Selected Bond Distances (Å) and Angles (deg)

compd	$N_{amide}-C_{py}$	$N_{py}-C_{py}$	Ag⋯O	Ag⋯Ag	$N-Ag-N_{digonal}$	ref
HTs3mepy	1.346(4)	1.362(5)				6
[Ag(Ts3mepy)]$_n$ (**1**)	1.416(5)	1.347(5)	2.898(3) [Ag(1)−O(1)]			this work
			2.944(3) [Ag(2)−O(2)]	3.1476(3)	180	
HMs3mepy	1.326(2)	1.359(2)				10
[Ag(Ms3mepy)]$_n$ (**2b**)	1.407(10)	1.354(10)	2.900(6) [Ag(1)−O(1)]			this work
			2.992(6) [Ag(2)−O(1)]	3.980(3)	180	
[$Ag_4(Ms3mepy)_4$] (**2a**)	1.401(8)	1.349(8)	2.835(5) [Ag(1)−O(11)]	2.9932(9) [Ag(1)−Ag(2)]	175.5(3)	this work
	1.376(8)	1.373(9)	2.855(5) [Ag(2)−O(31)]	3.3033(9) [Ag(2)−Ag(3)]	177.5(2)	
	1.425(8)	1.338(8)	2.749(5) [Ag(3)−O(32)]	3.2736(9) [Ag(1)−Ag(4)]	174.5(3)	
	1.402(8)	1.372(8)	2.973(5) [Ag(4)−O(12)]	3.3549(9) [Ag(1)−Ag(3)]	179.1(2)	
[$Ag_2(Ms3mepy)_2(phen)_2$](**5**)	1.416(7)	1.340(6)	3.084(4) [Ag−O(2)]	3.4221(12)	$N_{amide}-Ag-N_{py}$ Td	this work
HMs6mepy	1.347(2)	1.367(2)				9
[$Ag_4(Ms6mepy)_4$] (**3a**)	1.381(6)	1.350(6)	2.730(4) [Ag−O(2)]	2.8847(6)	171.52(16)	this work
[$Ag_2(Ms6mepy)_2$]$_n$ (**3b**)	1.374(5)	1.358(5)	2.565(3) [Ag−O(2)]$_{inter}$	2.7374(8)	157.46(13)	this work
			2.730(3) [Ag−O(1)]$_{intra}$			
[$Ag_2(Ms6mepy)_2(phen)$] (**7**)	1.350(19)	1.393(18)	2.884(11) [Ag(1)−O(11)]	2.789(2)	178.6(7)	
HTs4mepy	1.341(3)	1.365(3)				
	1.348(3)	1.361(3)				
[$Ag_2(Ts4mepy)_2(bipy)_2$] (**8**)	1.382(4)	1.355(4)	3.097(2) [Ag(1)−O(11)]	2.9166(5)	$N_{amide}-Ag-N_{py}$ Td	this work

(9) Å, are too long to consider the existence of a significant silver−silver interaction.

The silver atoms are coordinated by four anionic sulfonamide molecules that behave in a $\eta^2(\kappa\text{-}N,N')$ manner. The distances between the silver centers and the nearest oxygen atoms of the sulfonyl groups vary from 2.749(5) to 2.973(5) Å. Consequently, if the silver−silver and silver−oxygen interactions are ignored, the coordination geometry around each silver atom can be described as almost linear (AgN_2), with the N−Ag−N angles in the range 174.5(2)−179.1(2)°. It appears that a correlation exists between the Ag⋯O distances and the value of the N−Ag−N angle. The difference in the N−Ag−N angle with respect to the ideal value of 180° increases as the Ag⋯O distance decreases (Table 1), i.e., as the interaction becomes stronger. On the assumption that the four metal atoms show a AgN_2 digonal coordination, the silver centers can be divided into two different pairs according to the nature of the nitrogen atoms coordinated to them. One pair, containing atoms Ag(1) and Ag(3), is coordinated by two pyridine nitrogen atoms from two different ligands, while the other pair, Ag(2) and Ag(4), is coordinated by two sulfonamide nitrogen atoms, also from two different ligands. In this way, the ligands are coordinated in head to head and tail to tail forms.

The lengths of the $Ag-N_{py}$ bonds are in the range 2.117(6)−2.146(6) Å, with an average value of 2.132(6) Å. These are similar to the corresponding bond lengths found in complexes **1** and **2b** but are longer than the $Ag-N_{Ms}$ bond, 2.074(6)−2.107(6) Å [average value of 2.091(3) Å].

The pyridine rings are almost perpendicular to the plane described by the four silver atoms, with an average dihedral angle of 87.5(1)°. This disposition is stabilized by a weak *π*,*π*-stacking interaction between these pyridine rings; the distances between centroids are 3.8686(2) and 3.6282(3) Å, and the average value for the dihedral angle between rings is 6.1(3)°. Intermolecular C−H⋯O interactions are also present in **2a**. Each tetramer interacts with two neighboring units, using one hydrogen atom from a methyl group in the *ortho* position of the mesityl group and one hydrogen atom from the adjacent CH group with one oxygen atom of the

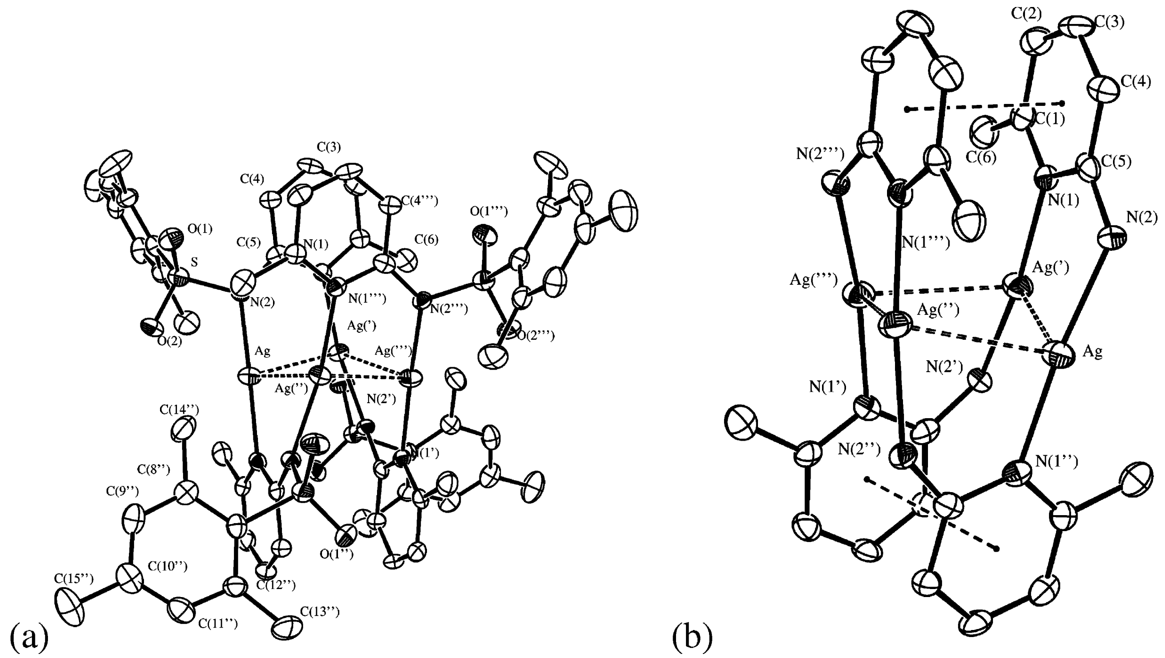

Figure 5. (a) Structure of **3a** and (b) partial view for **3a**. Selected bond distances (Å) and angles (deg): Ag−N(2) 2.144(4), Ag−N(1)^a 2.147(4), Ag−Ag^a 2.8834(7), N(2)−Ag−N(1)^a 171.52(16), Ag^a−Ag−Ag^b 89.187(4). Key: (a) 3/2 − *y*, *x* + 1/2, 3/2 − z; (b) *y* − 1/2, 3/2 − *x*, 3/2 − *z*.

other tetrameric unit. The other interaction is established between one hydrogen atom of CH(py) in the *para* position to the pyridine nitrogen atom and an oxygen atom from another tetranuclear molecule (Supporting Information).

Structure of [Ag$_4$(Ms6mepy)$_4$] (3a). A view of the molecular structure of **3a** with the atom labeling scheme is shown in Figure 5. The structure consists of discrete molecules that have a crystallographically imposed symmetry in the unit cell.

Complex **3a** has a tetranuclear structure different from that described for **2a**. The lattice is formed by discrete molecules with a tetranuclear arrangement of silver atoms on the vertexes of an almost perfect square parallelogram: Ag−Ag−Ag angles are close to 90° (89.19°). This parallelogram is less planar than the one described for **2a** (rms = 0.1718). The distance between contiguous silver atoms, 2.8834(7) Å, is smaller than in compound **2a** [2.9803(9)−3.3033(9) Å] and also slightly shorter than the one in metallic silver (2.888 Å).[20] However, the distance is still significantly less than twice the van der Waals radius for silver (3.44 Å).[21] Consequently, it can be postulated that some intramolecular Ag···Ag interaction exists.

The silver atoms are also bridged by four anionic sulfonamide molecules that behave in a $\eta^2(\kappa\text{-}N,N')$ manner. In this case, the environment around each silver atom is the same, which contrasts to the situation found in complex **2a**. Each silver atom in **3a** is now coordinated by a pyridine nitrogen atom and a sulfonamide nitrogen atom from different ligands. In this way, each ligand spans the metal centers in a head to tail arrangement. The coordination geometry is best described as distorted AgN$_2$ digonal, 171.52(16)°.

As in **2a**, compound **3a** has an additional weak interaction with the oxygen atom of the sulfonyl group. Once again, this interaction introduces modifications in the N−Ag−N angle and the Ag···Ag distance. The Ag···O distance [2.730(4) Å] is shorter than the Ag···O average distance of 2.853(5) Å in **2a**, which indicates that the Ag···O interaction in **3a** is stronger than that in complex **2a**. As a consequence, the N−Ag−N angle in **3a** [171.49(16)°] is smaller than in **2a** [174.5(2)−179.1(1)°].

The values of the different Ag−N bond lengths are very similar at 2.147(4) and 2.146(4) Å for Ag−N$_{py}$ and Ag−N$_{Ms}$, respectively. These values are similar to those found for the polymeric complexes **1** and **2b** described above, but the Ag−N$_{Ms}$ bond distances in **3a** are slightly shorter than those found in complex **2a**.

The pyridine rings and the plane described by the four silver atoms, Ag$_4$, form a dihedral angle with an average value 88.7(1)°, i.e., almost perpendicular. As in the case of **2a**, this disposition is stabilized by a strong π,π-stacking interaction between these pyridine rings, with the average value of distances between centroids being 3.5153(3) Å and a dihedral angle between the rings of 2.7(2)°. In **3a** a weak intermolecular C−H···π interaction [C(6)−H···π, 3.500(4) Å, C−H···π 139.4°] exists between one hydrogen atom of the methyl group of the pyridine ring and the π-cloud of one of the pyridine rings of other tetranuclear molecule (Supporting Information).

Structure of Dinuclear Compounds. Homoleptic Complexes: Structure of [Ag$_2$(Ms6mepy)$_2$]$_n$ (3b). The product obtained in the synthesis of the Ag(I) complex with *N*-(6-methyl-2-pyridyl)mesitylenesulfonamide (HMs6mepy) and 2,2′-bipyridine was found to be [Ag$_2$(Ms6mepy)$_2$]$_n$ (**3b**), a

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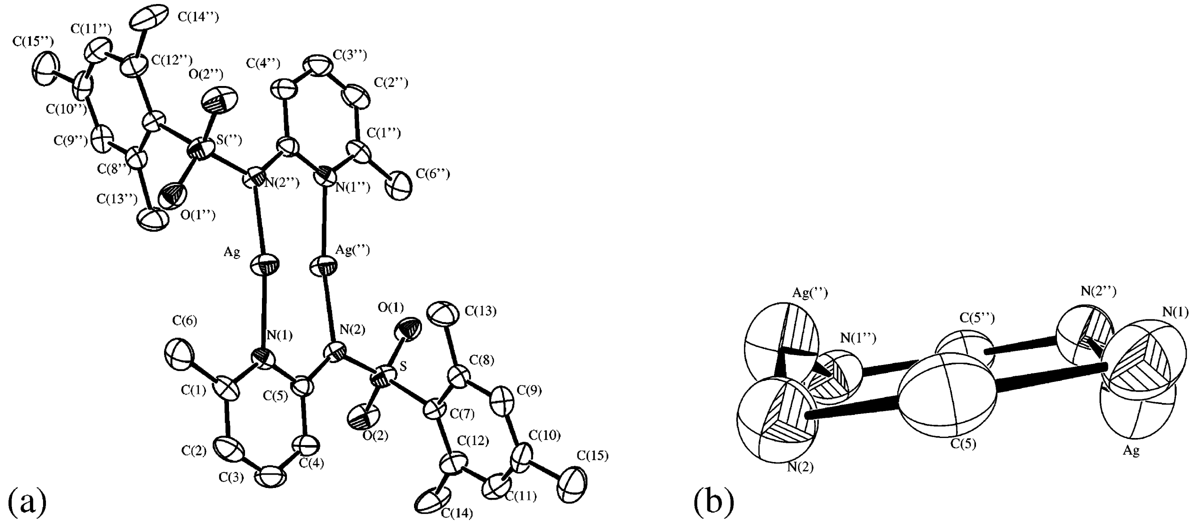

Figure 6. (a) Structure of **3b** and (b) partial view of **3b**. Selected bond distances (Å) and angles (deg): Ag−N(1) 2.188(4), Ag−N(2)^a 2.187(4), Ag−Ag^a 2.7374(8), N(2)^a−Ag−N(1) 157.46(13). Key: (a) 1/2 − *x*, 3/2 − *y*, 1 − *z*.

supramolecular structural isomer to **3a**. The bipy coligand was not incorporated into the coordination sphere of the metal.

The molecular structure of this complex, along with the atom numbering scheme, is shown in Figure 6.

The complex presents a dimeric structure that has a crystallographically imposed symmetry in the unit cell. The dimer units contain two anionic ligands that act as bidentate bridges through the two nitrogen atoms $\kappa^2(\mu\text{-}N,N')$ in a head to tail disposition. The coordination of the sulfonamide molecules generates an eight-membered $Ag_2N_4C_2$ ring analogous to others described in the literature.[22]

In addition, the dimer units are intermolecularly joined across the *b* axis by a sulfonyl oxygen atom bonded to a silver atom of a neighboring molecule (Figure 7). The Ag···O(2′) (′: *x*, *y* − 1, *z*) bond distance, 2.565(3) Å, is 0.68 Å (21%) shorter than twice the van der Waals radius (3.24 Å)[21] and similar to that found for other Ag(I) complexes with sulfonyl oxygen intermolecular interactions.[23] Thus, the structure can be described as a stairlike polymer formed by self-assembly of sulfonyl-O bridged dimers and is similar to that found in other Ag(I) complexes with some amino acids.[24]

As a consequence of this intermolecular interaction with the oxygen sulfonyl atom, the core atoms in the eight-membered ring $Ag_2N_4C_2$ (rms = 0.1538) are not coplanar. The silver atoms are located 0.396(3) Å above and below the N_4C_2 plane (rms = 0.0142). This fact, along with the presence of the weak intramolecular Ag···O [2.730(3) Å] interactions, produces an N−Ag−N angle of 157.46(13)°, which is the lowest of all the complexes studied here. In addition, the distance between the silver atoms is 2.7374(8) Å, similar to that of the dimeric silver(I) complex with the 2-pyridyl-*p*-toluenesulfonamide ligand,[11] and shorter than in metallic silver, 2.888 Å, indicating a significant intermetallic interaction.[20]

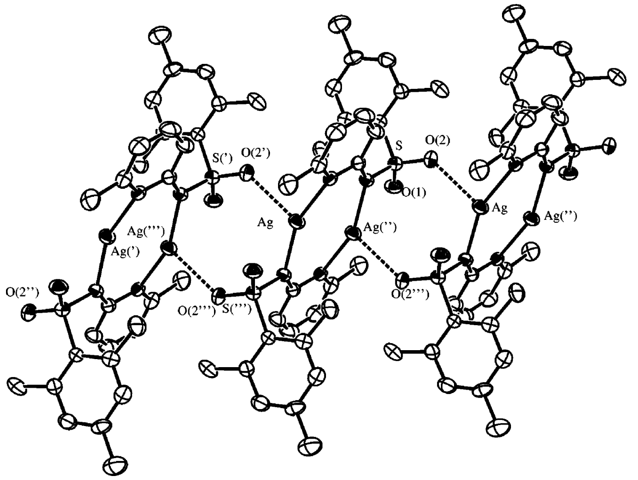

Figure 7. Polymeric structure of **3b**.

The geometry of the Ag(I) ion can therefore be considered as highly distorted AgN_2 digonal or, alternatively, as a trigonal arrangement AgN_2O if the intermolecular coordination with the oxygen atom is considered [N(1)−Ag−N(2′) = 157.46(13)°, N(2′)−Ag−O(2″) = 117.70(11)°, and N(1)−Ag−O(2″) = 84.83(12)°; ′, 1/2 − *x*, 3/2 − y, 1 − z; ″, *x*, *y* − 1, *z*]. The N−Ag−N angle is splayed wider compared to the normal trigonal arrangement but deviates significantly from a linear arrangement owing to the presence of the coordinated oxygen atom. Therefore, in this complex the ligand can be considered to act as a bridge between three metal atoms (Scheme 3). As far as we are aware, this is the

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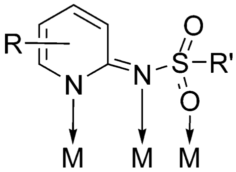
Scheme 3. Coordination Mode of *N*-2-Pyridyl-Sulfonamide Ligand in $[Ag_2(Ms6mepy)_2]_n$ (**3b**)



first example of this type of ligational mode for an *N*-2-pyridyl sulfonamide ligand.

The Ag−N bond distances, 2.188(4) and 2.187(4) Å for Ag−N_{py} and Ag−N_{Ms}, respectively, are longer than that found in the digonal complex with 2-pyridyl-*p*-toluenesulfonamide ligand[11] and those in other dicoordinated Ag(I) complexes with pyridine and/or sulfonamido ligands.[19] This situation is as one would expect given the higher coordination number.

In **3b** an intermolecular C−H···π interaction is observed between a hydrogen atom of one methyl group in the *ortho* position of the mesityl group and one phenyl ring of the neighboring molecule. In addition, **3b** presents a weak intermolecular C−H···O interaction involving the methyl group of the pyridine ring and one oxygen atom. C−H···O and S−O···Ag interactions connect the dimer units, producing a stairlike linear chain. These chains are connected to one another through C−H···π interactions (Supporting Information).

Heteroleptic Phenanthroline Complexes. Structure of $[Ag_2(Ms3mepy)_2(phen)_2]$ (5). The synthesis of heteroleptic complexes with 1,10-phenanthroline allowed the crystal structure of the Ag(I) mixed complex with the *N*-(3-methyl-2-pyridyl)mesitylenesulfonamide ligand to be determined.

The molecular structure of $[Ag_2(Ms3mepy)_2(phen)_2]$ (**5**) is shown in Figure 8, together with the atomic numbering scheme adopted. The structure contains discrete molecules that have a crystallographically imposed symmetry. For the sake of clarity, a view of the coordination sphere of the metals is represented in Figure 8b.

The structure consists of a dimer in which each silver atom has an AgN_4 tetracoordinated environment and is bonded by two anionic sulfonamide ligands—one through the sulfonamide nitrogen and the other through the pyridyl nitrogen atom. The coordination sphere is completed by a bidentate phenanthroline molecule. The dihedral angle between the planes N_{Ms}−Ag−N_{py} and N_{phen}−Ag−N_{phen} is 84.7(2)°, which is close to the ideal value of 90° for a tetrahedral geometry. The restricted “bite” of the phenanthroline, N−Ag−N = 69.11(18)°, represents the one major deviation from the ideal geometry. The shortest Ag···O separation between the silver atom and the nearest O atoms of the sulfonyl group is 3.084(4) Å, suggesting a weak interaction between them.

The anionic sulfonamide ligands behave as a bidentate bridge, $\kappa^2(\mu\text{-}N,N')$, and are situated in a trans disposition. In a similar way to **3b**, the coordination of the sulfonamide molecules generates an $Ag_2N_4C_2$ eight-membered ring in a “*chair*” disposition (see Figure 8b). This situation means that the silver atoms are located 1.111(4) Å above and below the C_2N_4 plane (rms = 0.1551) (see Figure 8b). The distance between the silver atoms is 3.4221(12) Å, similar to twice the van der Waals radius for silver (3.44 Å).[21] This distance is too long to consider the existence of a significant Ag···Ag interaction.

There are four different Ag−N bond distances. The Ag−N_{py} bond length is 2.223(5) Å, which is shorter than that found in the complex $[Ag(py)_4]^+$, 2.322 Å,[25] and other AgN_4 tetracoordinated Ag(I) complexes with ligands derived from substituted pyridine (2.402−2.299 Å).[26] The Ag−N_{Ms} bond distance, 2.398(5) Å, is greater than those found in the aforementioned complexes of silver(I), in which the silver atom is diagonally coordinate, but is similar to the corresponding value found in **7** (vide infra) for the bond involving the amide nitrogen and four-coordinated silver atoms.

Finally, the Ag−N bonds to the phenanthroline ligands are 2.394(5) and 2.409(5) Å, i.e., similar to those in other AgN_4 bidentate phenanthroline chelate complexes with tetracoordinated Ag(I) (2.411−2.266 Å).[27]

The crystal packing of compound **5** is such that one of the phenanthroline units in one molecule interacts with that on a neighboring molecule through π,π-stacking interactions[28] [distances between centroids = 3.5176(3) Å]. The rings of the phenanthroline molecules that are involved in such interactions are not totally eclipsed by one another, meaning that an offset or slipped stacking situation is observed as shown in Figure 9. This interaction is quite surprising since it is produced between the benzene ring of one phenanthroline moiety and the pyridine ring of another phenanthroline. The third ring, also a pyridine ring, is not involved in this interaction, meaning that there is a slippage from one phenanthroline molecule to another of exactly the size of a six-membered ring (benzene).

Other intermolecular interactions are also observed, and these are nonclassical C−H···O interactions between the hydrogen atoms on the phenanthroline of one molecule and the sulfonyl oxygen of another. The π,π-stacking interactions and the nonclassical hydrogen bonds lead a macromolecular network similar to a stairlike polymer (Supporting Information).

Structure of $[Ag_2(Ms6mepy)_2phen]$ (7). The product from the synthesis of the silver complex with *N*-(6-methyl-2-pyridyl)mesitylenesulfonamide and 1,10-phenanthroline gave crystals of $[Ag_2(Ms6mepy)_2phen]$ (**7**) that were suitable for X-ray studies. Unfortunately, the crystal data are of poor quality and non-hydrogen atoms could not be refined with

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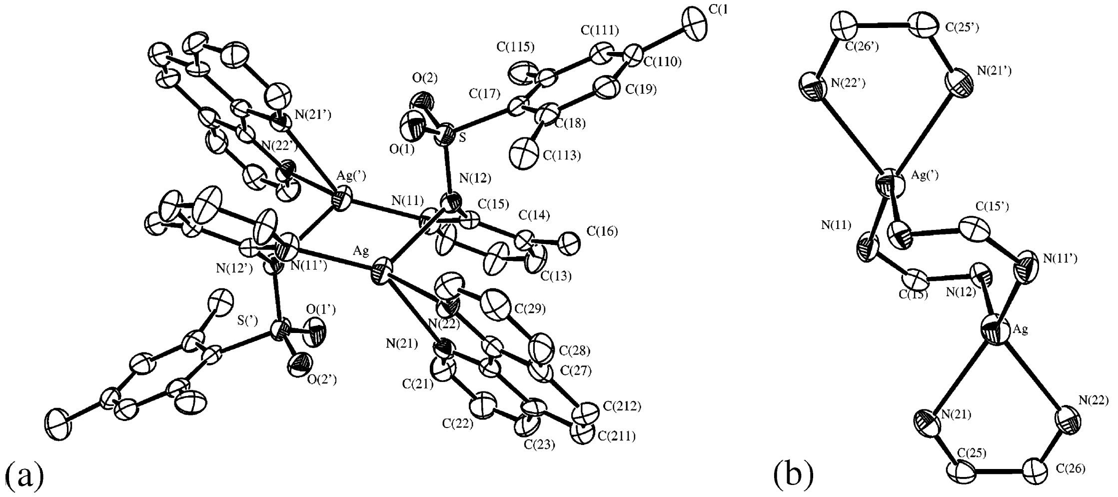

Figure 8. (a) Structure of **5** and (b) partial view of **5**. Selected bond distances (Å) and angles (deg): Ag−N(11)[a] 2.223(5), Ag−N(12) 2.398(5), Ag−N(21) 2.394(5), Ag−N(22) 2.409(5), Ag−Ag[a] 3.4221(12), N(11)[a]−Ag−N(21) 143.27(17), N(11)[a]−Ag−N(12) 122.30(17), N(21)−Ag−N(12) 88.66(15), N(11)[a]−Ag−N(22) 121.61(19), N(21)−Ag−N(22) 69.11(18), N(12)−Ag−N(22) 94.31(17). Key: (a) $-x$, $2 - y$, $-z$.

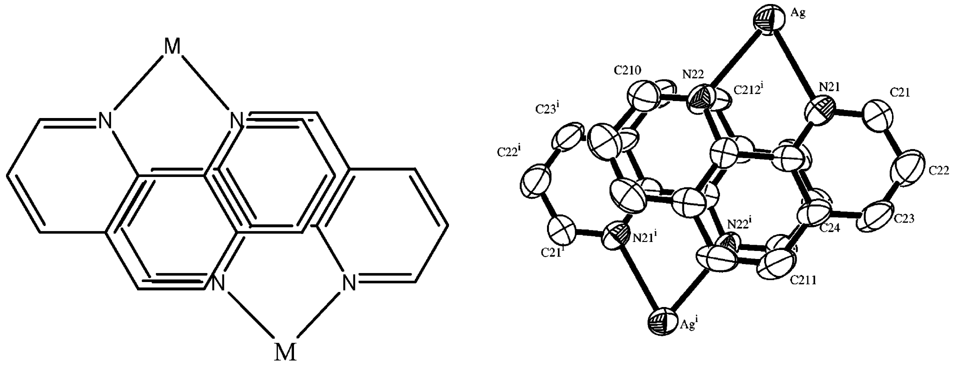

Figure 9. Overlapping between phenanthroline rings of two neighboring molecules of **5**.

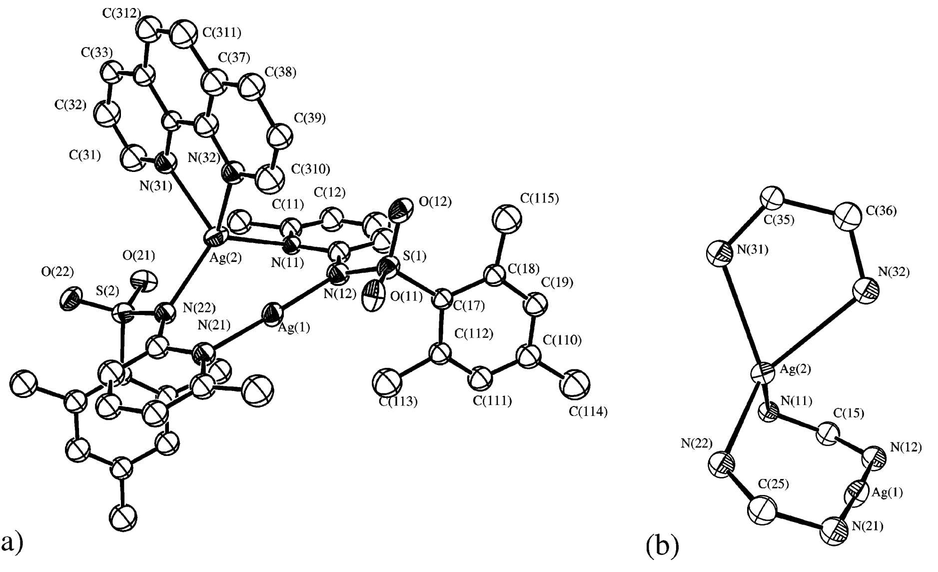

Figure 10. (a) Structure of **7** and (b) partial view of **7**. Selected bond distances (Å) and angles (deg): Ag(1)−N(21) 2.106(12), Ag(1)−N(12) 2.113(12), Ag(1)−Ag(2) 2.789(2), Ag(2)−N(31) 2.324(9), Ag(2)−N(22) 2.377(12), Ag(2)−N(11) 2.385(12), Ag(2)−N(32) 2.426(8), N(21)−Ag(1)−N(12) 178.6(7), N(31)−Ag(2)−N(22) 112.9(4), N(31)−Ag(2)−N(11) 118.3(4), N(22)−Ag(2)−N(11) 117.5(4), N(31)−Ag(2)−N(32) 69.5(5), N(22)−Ag(2)−N(32) 121.2(4), N(11)−Ag(2)−N(32) 108.7(4).

anisotropic displacement parameters. Nevertheless, the final atom locations are shown in Figure 10a.

The structure is based on dimeric molecules, but two silver atoms, two sulfonamide ligands, and only one phenanthroline molecule form this time the dimer. This arrangement causes the two metal atoms to exist in different environments. The sulfonamide ligands again behave as bidentate bridges, κ^2-(μ-*N*,*N*′), in a trans disposition that generates a nonplanar

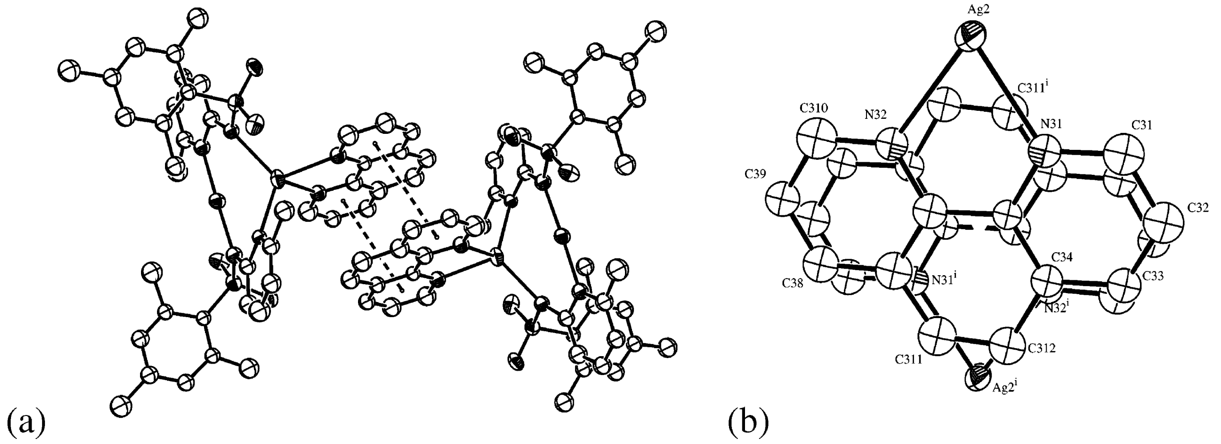

Figure 11. (a) Crystal structure of **7** showing the π,π-stacking interactions as dotted lines and (b) overlap between phenanthroline rings of two neighboring molecules of **7**.

eight-membered $Ag_2N_4C_2$ ring. However, in this case one of the silver atoms, Ag(1) at a distance from the plane of only 0.012(7) Å, is in the plane described by N_4C_2 (rms = 0.0617) and the other silver atom, Ag(2), is out of this plane [by 1.251(8) Å] due the coordination of the phenanthroline ligand (see Figure 10b). The Ag−Ag distance is 2.789(2) Å. This is slightly longer than the distance found for complex **3b** [2.7374(8) Å] but is markedly shorter than that described above for complex **5** [3.4221(12) Å]. In any case, the distance is slightly shorter than the 2.888 Å required for an Ag−Ag metal bond and we can therefore we can envisage the existence of a significant Ag···Ag interaction.

The geometry of Ag(1) can best be described as slightly distorted AgN_2 digonal. One of the nitrogen atoms is a pyridine nitrogen from one anionic sulfonamide ligand, and the other is a sulfonamide nitrogen provided by another ligand, N(21)−Ag(1)−N(12) = 178.6(7)°. The other silver atom, Ag(2), presents a distorted AgN_4 tetrahedral geometry and is bonded to one sulfonamide and one pyridine nitrogen atom from the different sulfonamide ligands as well as a bidentate phenanthroline molecule. In addition, each silver atom in the dimer shows a weak intramolecular interaction with an oxygen atom of the sulfonyl group, Ag(1)···O(11) = 2.884(11) and Ag(2)···O(21) = 2.911(10) Å. Once again, the Ag(1)···O(11) interaction gives rise to an N−Ag(1)−N digonal angle of less than 180°.

All of the pyridine and sulfonamide Ag−N bond distances are different, and as one would expect, these are shorter for digonal Ag(1) [2.106(12) and 2.113(12) Å] than for tetracoordinated Ag(2) [2.385(12) and 2.377(12) Å] as a consequence of the change in coordination number from 2 to 4.

Finally, in the phenanthroline ligand one Ag−N bond length, 2.324(9) Å, is considerably shorter and the other significantly longer, 2.426(8) Å, than expected. This indicates a certain degree of distortion. The bond lengths are of the same order as those found in **5**.

The supramolecular arrangement found in **7** is different from that described above for **5**. In this case (Figure 11) each phenanthroline molecule only interacts with one phenanthroline on a neighboring molecule and this interaction consists of π,π-stacking in such a way that only two rings of the phenanthroline interact. Moreover, the π,π-stacking interaction is produced between the two pyridine rings of the phenanthroline units. The planes are not exactly above one another, but there is slippage of 1.775(9) Å. The distance between centroids is 3.9926(5) Å and the distance between planes is 3.576(9) Å. Hydrogen bonds were not found between different units.

Heteroleptic Bipyridine Complex: Structure of [Ag_2(Ts4mepy)$_2$(bipy)$_2$] (8). The molecular structure of the only heteroleptic compound obtained with 2,2′-bipyridine as a coligand, i.e., [Ag_2(Ts4mepy)$_2$(bipy)$_2$] (**8**), is shown in Figure 12a together with the atomic numbering scheme adopted. For the sake of clarity, a view of the coordination sphere of the metals is represented in Figure 12b.

The structure of **8** is similar to that described for **5** and consists of discrete dimeric molecules in which each silver atom is tetracoordinated, bonding to two anionic sulfonamide ligands that again behave as $\kappa^2(\mu\text{-}N,N')$ bidentate bridges in a trans disposition. The coordination sphere is completed by a bidentate bipyridine molecule, and the main source of distortion of the tetrahedral polyhedron of the silver atom is the small bite of the five-membered chelate rings, N_{bipy}−Ag−N_{bipy} angles of 67.33(8)°.

The coordination of the sulfonamide molecules generates a puckered eight-membered $Ag_2N_4C_2$ ring that is not coplanar, with the silver atoms located 0.875(2) Å out of the plane described by C_2N_4 (rms = 0.0232) (see Figure 12b). The distance between the silver atoms is 2.9166(5) Å, which is longer than in **3b** and **7** but shorter than in **5**. The distance between the silver and nearest oxygen atom, 3.097(2) Å, is too great for this interaction to be considered as bond.

The dihedral angle formed by the bipyridine donor atoms and the plane described by N(11)−Ag(1)−N(22) is 89.4(5)°, and with the plane N(21)−Ag(1)−N(12) this angle is 87.2(6)°. Both of these values are close to the theoretical 90° for a tetrahedral geometry.

All of the Ag−N bond distances are different; the Ag−N_{py} bond lengths are 2.284(3) Å, longer than in **5** but shorter than in **7**. the Ag−N_{Ts} distances are 2.277(3) Å, shorter than in **5** and **7**. Finally, the bipyridine nitrogen atoms are asymmetrically coordinated with distances 2.439(3) and

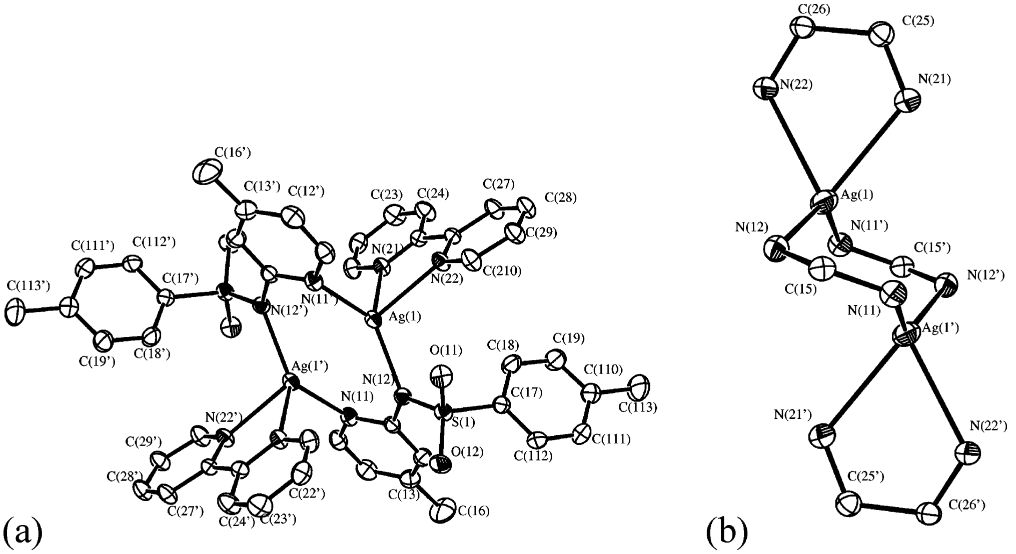

Figure 12. (a) Structure of **8** and (b) partial view of **8**. Selected bond distances (Å) and angles (deg): Ag(1)−N(12) 2.277(3), Ag(1)−N(11)^a 2.284(3), Ag(1)−N(21) 2.439(3), Ag(1)−N(22) 2.455(2), Ag(1)−Ag(1)^a 2.9166(5), N(12)−Ag(1)−N(11)^a 134.85(10), N(12)−Ag(1)−N(21) 119.32(9), N(11)^a−Ag(1)−N(21) 102.87(9), N(12)−Ag(1)−N(22) 109.40(9), N(11)^a−Ag(1)−N(22) 100.73(9), N(21)−Ag(1)−N(22) 67.33(8). Key: (a) $1 - x$, $1 - y$, $1 - z$.

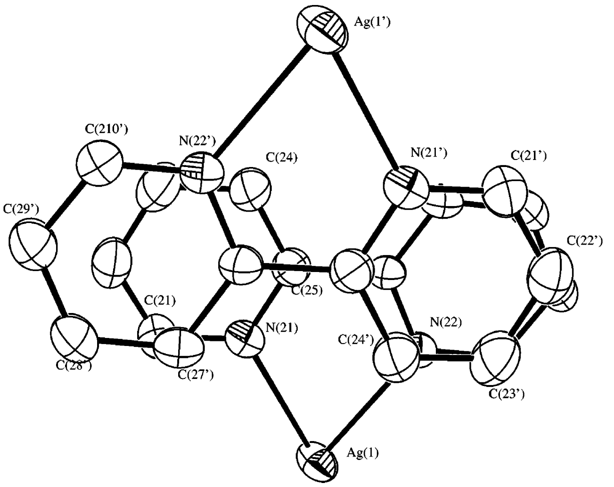

Figure 13. (a) Overlapping between bipyridine rings of two neighboring molecules of **8**.

2.455(2) Å. These bond lengths are typical for bidentate bipyridine chelate Ag(I) compounds (2.467−2.26 Å).[29]

In complex **8**, π,π-stacking interactions exist between the bipyridine rings of different neighboring molecules. These rings are displaced with respect to the ideal situation for "perfect facial alignment". The centers of the rings are separated by 3.8372(3) Å, but the planes are not exactly parallel and are offset by about 3.53 Å with some degree of slippage, as shown in Figure 13.

These π,π-stacking interactions, together with the CH(bipy)−O interactions, produce a macromolecular network similar to a stairlike polymer (Supporting Information).

Conclusions

A number of new Ag(I) complexes with *N*-pyridyl sulfonamide ligands have been prepared and characterized. It was found that these sulfonamide ligands always act as two-electron-pair donor $\kappa^2(\mu\text{-}N,N')$ bridges, with donation occurring through the amido and pyridyl nitrogen atoms regardless of the positions of the methyl groups. This situation produces homoleptic compounds of different nuclearities, helical one-dimensional polymer, tetranuclear, and dinuclear, with a digonal environment around the silver atoms. In the heteroleptic systems only dinuclear complexes with Ag(I) in a tetrahedral (or tetrahedral and digonal) environment were found. It is also noteworthy that on using 2,2′-bipyridine as a coligand, only in the case of the silver complex with *N*-(4-methyl-2-pyridyl)-*p*-toluenesulfonamide was the bipy moiety incorporated into the complex. In the other cases the complexes corresponding to the homoleptic species [AgL] were obtained, albeit with different nuclearities.

The structure of the silver homoleptic complexes with these ligands seems to depend on the position of the methyl group in the pyridine ring and on the number and position of the methyl groups in the benzene ring of the sulfonamide group; see Scheme 4. For example, when the ligand used contains a methyl substitutent in position 3 of the pyridine ring, the resulting compound, $[Ag(Ts3mepy)]_n$ (**1**), has a polymeric structure. However, the substitution of the mesityl group for the tosyl group produces two different supramolecular isomeric compounds: $[Ag(Ms3mepy)]_n$ (**2b**), a polymeric compound; $[Ag_4(Ms3mepy)_4]$ (**2a**), a tetranuclear compound. It seems that the increase in the steric hindrance produced by the mesityl sulfonic group makes the stability of both the polymer and the tetranuclear compound very similar.

An increase in the steric effect produced by a methyl group in position 6 as opposed to 3 on the pyridine ring, and also the presence of three methyl groups in the benzene ring of the sulfonamide group, lead to supramolecular isomeric complexes $[Ag_4(Ms6mepy)_4]$ (**3a**) and $[Ag_2(Ms6mepy)_2]_n$ (**3b**). The first complex has a tetranuclear structure, but **3b**

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[29] Constable, E. C.; Edwards, A. J.; Haire, G. R.; Hannon, M. J.; Raithby, P. R. *Polyhedron* **1998**, *17*, 243−253. Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Commun.* **1998**, 2659−2660.

can be considered as a dimeric compound. Once again, it appears that the steric hindrance is not sufficiently great to make the stability of the two compounds significantly different.

The presence of an additional ligand typically reduces the nuclearity of the complexes. For this reason the heteroleptic complexes are only dimeric. However, the steric hindrance of the sulfonamide ligand plays some role in this respect. In the case of the heteroleptic phenanthroline compounds, the complexes $[Ag_2(Ms3mepy)_2(phen)_2]$ (**5**) and $[Ag_2(Ms6mepy)_2(phen)]$ (**7**) are both dimers. However, in the case of **7** the greater hindrance produced by the methyl group in position 6 of the pyridine ring precludes the incorporation of a second phenanthroline molecule. In addition, the structural determinations reveal that the sulfonyl groups are canted with respect to the adjacent N−Ag−N plane in such a way that the oxygen atoms can form weak intramolecular interactions with the silver atoms. The strength of this interaction is reflected in the fact that the N−Ag−N angles are less obtuse and the Ag···Ag distances generally shorter in the complexes in which silver is digonally coordinated (Table 1).

In the case of complex **3b**, adjacent dimer units are linked to give a 1-D network by linkages between the silver(I) atoms of a dimer unit and the oxygen atom of the sulfonyl group of the neighboring dimer. Therefore, each ligand acts as a bridge between three metal atoms (Scheme 3). This is a new form of coordination for pyridine-functionalized amido ligands of the type represented in Chart 2.

In all complexes the sulfonyl ligand is coordinated as an anion in the amide form and the $N_{amide}-C_{py}$ bond distances in the complexes are greater than the corresponding distances in the free ligands (Table 1).

Experimental Section

General Considerations. Silver (Ega Chemie) was used as plates (ca. 2 × 2 cm). All other reagents, including acetonitrile, dichloromethane, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-6-methylpyridine, *p*-toluenesulfonyl chloride, 2-mesitylenesulfonyl chloride, 1,10-phenanthroline monohydrate, and 2,2′-bipyridine, were commercial products and were used as supplied.

Microanalysis was performed using a Carlo-Erba EA 1108 microanalyzer. IR spectra were recorded as KBr disks with a Bruker Vector-22 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker ARX-400 MHz instrument using $CDCl_3$ as solvent; chemical shifts were determined against TMS as internal standard. EI and LSI mass spectra were recorded on a VG Autospec-M Micromass instrument.

Preparation of the Ligands. Ligands were prepared by reaction of the corresponding amine with the sulfonyl chloride in a 1:1 molar ratio. Details are given for a representative example.

HTs4mepy. 2-Amino-4-methylpyridine (2.0 g, 18.4 mmol) and *p*-toluenesulfonyl chloride (3.51 g, 18.4 mmol) were dissolved in dichloromethane. To this solution was added dropwise an aqueous solution of sodium carbonate (1.95 g, 18.4 mmol in 20 mL). The reaction mixture was stirred overnight, and water (100 mL) was added. The organic layer was dried over anhydrous magnesium sulfate, the solvent was evaporated, and the crude product (an oil) was treated with ethanol. The resulting white solid was isolated by filtration and identified as HTs4mepy. Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.5; H, 5.4; N, 10.7; S, 12.2. Found: C, 59.2; H, 5.3; N, 10.5; S, 11.8. ^{1}H NMR ($CDCl_3$; δ, ppm): 2.29 [s, 3H, CH_3(tolyl)]; 2.36 [s, 3H, CH_3(py)]; 6.61 (d, 1H, py); 7.20 (s, 1H, py); 7.23 (d, 2H, tolyl); 7.79 (d, 2H, tolyl); 8.11 (d, 1H, py); 11.8 (br, 1H, NH). IR (KBr, cm^{-1}): 3228 (m), 2920 (w), 1612 (s), 1513 (s), 1392 (s), 1147 (s). EI MS: *m*/*z*: 262 (100%, M^+).

Data for the Other Ligands. HMs6mepy. Anal. Calcd for $C_{15}N_2H_{18}O_2S$: C, 62.1; H, 6.2; N, 9.6; S, 11.0. Found: C, 61.3; H, 6.4; N, 9.5; S, 10.9. ^{1}H NMR ($CDCl_3$; δ, ppm): 2.37 (s), 3H, CH_3(py); 2.24 (s) 3H, CH_3(*p*-tolyl); 2.69 (s) 6H, CH_3(*o*-tolyl); 6.55 (d), 1H, py; 6.74 (d) 1H, py; 6.88 (s), 2H, tolyl; 7.37 (d) 1H, py; 12.33 (b) 1H, NH. IR (KBr, cm^{-1}): 3236 (w), 2931 (w), 1616 (vs), 1533 (m), 1362 (vs), 1136 (vs). EI MS: *m*/*z* 291 (4%, M^+), 108 (13%, $M^+ - \{O_2S\text{-mesityl}\}$).

HMs3mepy. Anal. Calcd for $C_{15}N_2H_{18}O_2S$: C, 62.1; H, 6.2; N, 9.6; S, 11.0. Found: C, 61.3; H, 6.0; N, 9.3; S, 11.2. ^{1}H NMR ($CDCl_3$; δ, ppm): 2.15 (s), 3H, CH_3(py); 2.25 (s) 3H, CH_3(*p*-tolyl); 2.71 (s) 6H, CH_3(*o*-tolyl); 6.47 (d), 1H, py; 6.89 (s), 2H, tolyl; 7.36 (d) 1H, py; 7.42 (d) 1H, py; 12.3 3 (b) 1H, NH. IR (KBr, cm^{-1}): 3222 (m), 2940 (w), 1595 (s), 1544 (s), 1338 (s), 1098 (s). EI MS: *m*/*z* 291 (100%, M^+), 108 (10%, $M^+ - \{O_2S\text{-mesityl}\}$).

HTs3mepy. Anal. Calcd for $C_{13}N_2H_{14}O_2S$: C, 59.5; H, 5.4; N, 10.7; S, 12.2. Found: C, 58.7; H, 5.7; N, 10.2; S, 11.8. ^{1}H NMR ($CDCl_3$; δ, ppm): 2.15 (s), 3H, CH_3 (py); 2.35 (d) 3H, CH_3 (tolyl); 6.50 (d), 1H, py; 7.40 (d), 1H, py; 7.49 (d), 1H, py; 7.85 (d), 2H, tolyl; 7.21 (d), 2H, tolyl; 12.14 (b) 1H, NH. IR (KBr, cm^{-1}): 3248 (m), 2951 (w), 1594 (s), 1544 (s), 1342 (s), 1126 (s). EI MS: *m*/*z* 262 (8%, M^+); 108 (20%, $M^+ - \{O_2S\text{-tolyl}\}$).

Electrochemical Synthesis. The electrochemical method used in the synthesis of the silver complexes is similar to that described previously.[5−10] An acetonitrile solution (50 mL) of either the sulfonamide ligand (HL) or a mixture of the sulfonamide and a coligand (L′ = phen or bipy), with a small amount of tetramethylammonium perchlorate (ca. 10 mg) as the supporting electrolyte, was electrolyzed using a sacrificial silver anode and a platinum cathode. All syntheses were carried out with the electrochemical cell protected from direct light.

Direct current was supplied by a purpose-built dc power supply. Applied voltages of 5−10 V allowed sufficient current flow for smooth dissolution of the silver metal. The current was maintained at 10 mA during 1.5 h. In all cases, hydrogen was evolved at the cathode. These cells can be summarized as $Ag_{(+)}/CH_3CN + HL + L'/Pt_{(-)}$, where L and L′ represent the corresponding sulfonamide ligand and the coligand, respectively. After completion of the electrolysis, the clear solutions were filtered to remove any particles of metal and then left to concentrate protected from direct light. This procedure yielded crystalline products. The solids were washed with acetonitrile and diethyl ether and dried at room temperature.

$[Ag(Ts3mepy)]_n$ (1). Method A. Electrolysis of an acetonitrile solution (50 mL) containing *N*-(3-methyl-2-pyridyl)-*p*-toluenesulfonamide (HTs3mepy) (0.150 g, 0.565 mmol) at 7 V and 10 mA for 1.5 h dissolved 67.6 mg of metal ($E_f = 1.12$ mol·F^{-1}). During the electrolysis hydrogen was evolved at the cathode. Air concentration of the resulting solution yielded white crystals (0.18 g, 86%) of $[Ag(Ts3mepy)]_n$ (**1**) suitable for X-ray studies.

Method B. Electrochemical oxidation of a silver anode in an acetonitrile solution (50 mL) containing *N*-(3-methyl-2-pyridyl)-*p*-toluenesulfonamide (0.150 g, 0.572 mmol) and 2,2′-bipyridine (0.089 g, 0.570 mmol), using a current of 10 mA (6 V) for 1.5 h, resulted in the dissolution of 56.6 mg of metal ($E_f = 0.93$ mol·F^{-1}). Air concentration of the resulting solution yielded white crystals (0.18 g, 86%) corresponding to the homoleptic [Ag(Ts3mepy)] complex, with no evidence for the incorporation of bipy into the complex. Crystals suitable for X-ray studies were confirmed to be

[Ag(Ts3mepy)]$_n$ (**1**). Anal. Calcd for $C_{13}H_{13}AgN_2O_2S$: C, 42.4; N, 7.6; H, 3.6; S, 8.7. Found: C, 42.6; N, 7.5; H, 3.8; S, 8.6. IR (KBr, cm^{-1}): 2920 (m), 1587 (m), 1416 (s), 1268 (vs), 1132 (vs). ^{1}H NMR (CDCl$_3$; δ, ppm): 7.92−6.96 (m, 7H, aromat), 2.39 [s, 3H, *p*-Me(Ts)], 2.10 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 370, [Ag(Ts3mepy)]$^+$; 263, [Ts3mepy]$^+$.

[Ag$_4$(Ms3mepy)$_4$] (**2a**). Electrochemical oxidation of a silver anode in a solution of *N*-(3-methyl-2-pyridyl)mesitylenesulfonamide (HMs3mepy) (0.165 g, 0.565 mmol) in acetonitrile (50 mL), at 6 V and 10 mA for 1.5 h, caused 60.4 mg of silver to be dissolved (E_f = 1.00 mol·F^{-1}). Hydrogen was evolved at the cathode during the electrolysis process. Air concentration of the resulting solution yielded white crystals (0.19 g, 84%) of [Ag$_4$(Ms3mepy)$_4$] (**2a**) suitable for X-ray studies. Anal. Calcd for $C_{15}H_{17}AgN_2O_2S$: C, 45.4; N, 7.1; H, 4.3; S, 8.1. Found: C, 45.6; N, 7.1; H, 4.3; S, 8.1. IR (cm^{-1}): 2928 (m), 1587 (m), 1416 (s), 1274 (vs), 1120 (vs). ^{1}H NMR (CDCl$_3$; δ, ppm): 8.42−6.63 (m, 5H), 2.60 [s, 6H, Me(Ms)], 2.39 [s, 3H, *p*-Me(Ms)], 2.54 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 398, [Ag(Ms3mepy)]$^+$; 291, [Ms3mepy]$^+$.

[Ag(Ms3mepy)]$_n$ (2b). A similar experiment (10 mA, 9 V, 1.5 h) using *N*-(3-methyl-2-pyridyl)mesitylenesulfonamide (HMs3mepy) (0.165 g, 0.568 mmol) and 2,2′-bipyridine (0.089 g, 0.570 mmol) dissolved 58.7 mg of silver from the anode (E_f = 0.97 mol·F^{-1}). The solution was air concentrated to yield a white solid (0.18 g, 86%). Crystals suitable for X-ray studies were found to be [Ag(Ms3mepy)]$_n$ (**2b**), with no evidence for the incorporation of bipy into the complex. Anal. Calcd for $C_{15}H_{17}AgN_2O_2S$: C, 45.4; N, 7.1; H, 4.3; S, 8.1. Found: C, 45.1; N, 7.0; H, 4.2; S, 7.9%. IR (cm^{-1}): 2928 (m), 1585 (m), 1415 (s), 1277 (vs), 1129 (vs). ^{1}H NMR (CDCl$_3$; δ, ppm): 7.66−6.63 (m, 5H, aromat), 2.60 [s, 6H, Me(Ms)], 2.39 [s, 3H, *p*-Me(Ms)], 2.54 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 398 [Ag(Ms3mepy)]$^+$; 291 [Ms3mepy]$^+$.

[Ag$_4$(Ms6mepy)$_4$] (3a). A similar experiment (7 V, 10 mA, 1.5 h) with silver as the anode and *N*-(6-methyl-2-pyridyl)mesitylenesulfonamide (HMs6mepy) (0.165 g, 0.565 mmol) in acetonitrile (50 mL) dissolved 62.2 mg of metal (E_f = 1.03 mol·F^{-1}). Air concentration of the resulting solution yielded crystals (0.20 g, 89%) of [Ag$_4$(Ms6mepy)$_4$] (**3a**) suitable for X-ray studies. Anal. Calcd for $C_{15}H_{17}AgN_2O_2S$: C, 45.4; N, 7.1; H, 4.3; S, 8.1. Found: C, 46.2; N, 6.9; H, 4.1; S, 8.2%. IR (KBr, cm^{-1}): 2932 (m), 1600 (m), 1456 (s), 1287 (s), 1126 (vs). ^{1}H NMR (CDCl$_3$; δ, ppm): 7.26−6.55 (m, 5H), 2.72 [s, 6H, Me(Ms)], 2.17 [s, 3H, *p*-Me(Ms)], 2.57 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 398 [Ag(Ms6mepy)]$^+$; 291 [Ms6mepy]$^+$.

[Ag$_2$(Ms6mepy)$_2$]$_n$ (3b). A solution of *N*-(6-methyl-2-pyridyl)mesitylenesulfonamide (HMs6mepy) (0.165 g, 0.568 mmol) and 2,2′-bipyridine (0.089 g, 0.570 mmol) in acetonitrile (50 mL) was electrolyzed at 5 V and 10 mA during 1.5 h, and 55.4 mg of silver metal was dissolved from the anode (E_f = 0.92 mol·F^{-1}). The solution was air concentrated to yield a white solid (0.17 g, 81%). Crystals suitable for X-ray studies were identified as [Ag$_2$(Ms6mepy)$_2$]$_n$ (**3b**). Anal. Calcd for $C_{15}H_{17}AgN_2O_2S$: C, 45.4; N, 7.1; H, 4.3; S, 8.1. Found: C, 45.2; N, 7.3; H, 4.1; S, 8.2. IR (KBr, cm^{-1}): 2932 (m), 1596 (m), 1455 (s), 1269 (s), 1118 (vs). ^{1}H NMR (CDCl$_3$; δ, ppm): 7.26−6.55 (m, 5H), 2.72 [s, 6H, Me(Ms)], 2.17 [s, 3H, *p*-Me(Ms)], 2.57 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 398, [Ag(Ms6mepy)]$^+$; 291, [Ms6mepy]$^+$.

[Ag(Ts3mepy)(phen)] (4). A similar experiment (10 mA, 6 V, 1.5 h) using *N*-(3-methyl-2-pyridyl)-*p*-toluenesulfonamide (HTs3mepy) (0.150 g, 0.565 mmol) and 1,10-phenanthroline (0.102 g, 0.565 mmol) dissolved 66.7 mg of silver from the anode (E_f = 1.10 mol·F^{-1}). Air concentration of the resulting solution yielded a white crystalline product (0.25 g, 81%). Anal. Calcd for $C_{25}H_{21}AgN_4O_2S$: C, 54.7; N, 10.2; H, 3.8; S, 5.8. Found: C, 54.6; N, 9.9; H, 3.5; S, 5.7. IR (KBr, cm^{-1}): 2924 (m), 1590 (s), 1509 (m), 1417 (s), 1256 (s), 1135 (s), 841 (s), 728 (m). ^{1}H NMR (CDCl$_3$; δ, ppm): 9.52 (m, 2H, phen), 8.55 (m, 2H, phen), 8.25 (s, 2H, phen), 8.11 (m, 2H, phen) 8.02−6.96 (m, 7H, aromat), 2.53 [s, 3H, *p*-Me(Ts)], 2.33 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 551, [Ag(Ts3mepy)phen]$^+$; 370, [Ag(Ts3mepy)]$^+$; 263, [Ts3mepy]$^+$.

[Ag$_2$(Ms3mepy)$_2$(phen)$_2$] (5). A similar experiment (10 mA, 9 V, 1.5 h) using *N*-(3-methyl-2-pyridyl)mesitylenesulfonamide (HMs3mepy) (0.165 g, 0.565 mmol) and 1,10-phenanthroline (0.102 g, 0.565 mmol) dissolved 69.6 mg of silver from the anode (E_f = 1.15 mol·F^{-1}). Suitable crystals of [Ag$_2$(Ms3mepy)$_2$(phen)$_2$] (**5**) for X-ray studies were obtained by crystallization from acetonitrile. Yield: 0.28 g (86%). Anal. Calcd for $C_{27}H_{25}AgN_4O_2S$: C, 56.2; N, 9.7; H, 4.3; S, 5.5. Found: C, 55.7; N, 10.4; H, 4.1; S, 5.6. IR (KBr, cm^{-1}): 2927 (s), 1588 (s), 1507 (m), 1414 (s), 1265 (s), 1130 (vs), 844 (s), 731 (m). ^{1}H NMR (CDCl$_3$; δ, ppm): 9.15 dd, 8.21, 8.19, 7.72 (m, 8H, phen), 7.60−6.53 (m, 5H, aromat), 2.05 [s, 3H, *p*-Me(Ms)], 2.41 [s, 6H, Me(Ms)], 1.87 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 578, [Ag(Ms3mepy)(phen)]$^+$; 291, [Ms3mepy]$^+$.

[Ag(Ts4mepy)(phen)] (6). A similar experiment (10 mA, 8V, 1.5 h) using *N*-(4-methyl-2-pyridyl)-*p*-toluenesulfonamide (HTs4mepy) (0.150 g, 0.565 mmol) and 1,10-phenanthroline (0.102 g, 0.565 mmol) dissolved 55.4 mg of silver from the anode (E_f = 0.91 mol·F^{-1}). Air concentration of the resulting solution yielded a white crystalline product (0.22 g, 78%). Anal. Calcd for $C_{25}H_{21}AgN_4O_2S$: C, 54.7; N, 10.2; H, 3.8; S, 5.8. Found: C, 54.4; N, 10.3; H, 3.6; S, 5.6%. IR (KBr, cm^{-1}): 2920 (s), 1611 (vs), 1513 (m), 1393 (vs), 1271 (s), 1148 (vs), 881 (s), 734 (s). ^{1}H NMR (CDCl$_3$; δ, ppm): 9.23 (m, 2H, phen), 8.35 (m, 2H, phen), 8.18−6.57 (m, 11H, phen + aromat), 2.40 [s, 3H, *p*-Me(Ts)], 2.29 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 551, [Ag(Ts4mepy)(phen)]$^+$; 263, [Ts4mepy]$^+$.

[Ag$_2$(Ms6mepy)$_2$(phen)] (7). A similar experiment (10 mA, 6 V, 1.5 h) using *N*-(6-methyl-2-pyridyl)mesitylenesulfonamide (HMs6mepy) (0.165 g, 0.565 mmol) and 1,10-phenanthroline (0.102 g, 0.565 mmol) dissolved 58.7 mg of silver from the anode (E_f = 0.97 mol·F^{-1}). Air concentration of the resulting solution yielded a white crystalline product (0.24 g, 75%). Suitable crystals of [Ag$_2$(Ms6mepy)$_2$(phen)] (**7**) for X-ray studies were obtained. Anal. Calcd for $C_{42}H_{42}Ag_2N_6O_4S_2$: C, 51.8; N, 8.6; H, 4.3; S, 6.6. Found: C, 51.4; N, 9.2; H, 4.1; S, 6.7%. IR (KBr, cm^{-1}): 2931 (m), 1592 (m), 1510 (w), 1453 (vs), 1278 (m), 1124 (vs), 847 (s), 729 (m). ^{1}H NMR (CDCl$_3$; δ, ppm): 9.47 (m, 2H, phen), 8.21 (m, 2H, phen), 8.18 (s, 2H, phen), 7.68 (m, 2H, phen), 7.16−6.40 (m, 10H, aromat.), 2.16 [s, 6H, *p*-Me(Ms)], 2.71 [s, 12H, Me(Ms)], 2.58 [s, 6H, Me(py)]. LSIMS (*m*/*z*): 578, [Ag(Ms6mepy)(phen)]$^+$; 398, [Ag(Ms6mepy)]$^+$; 291, [Ms6mepy]$^+$.

[Ag$_2$(Ts4mepy)$_2$(bipy)$_2$] (8). Electrochemical oxidation of a silver anode in a solution of *N*-(4-methyl-2-pyridyl)-*p*-toluenesulfonamide (HTs4mepy) (0.150 g, 0.565 mmol) and 2,2′-bipyridine (0.089 g, 0.565 mmol) in acetonitrile (50 mL) using a current of 10 mA, 9 V, for 1.5 h resulted in the dissolution of 56.0 mg of metal (E_f = 0.92 mol·F^{-1}). Crystals obtained by crystallization from acetonitrile were studied by X-ray diffraction and were found to be [Ag(Ts4mepy)(bipy)]$_2$ (**8**). Yield: 0.22 g (81%). Anal. Calcd for $C_{23}H_{21}AgN_4O_2S$: C, 52.6; N, 10.7; H, 4.0; S, 6.1. Found: C, 54.3; N, 10.3; H, 4.2; S, 6.4. IR (KBr, cm^{-1}): 2922 (w), 1610 (vs), 1394 (s), 1278 (vs), 1148 (s), 758 (m), 735 (s). ^{1}H NMR (CDCl$_3$; δ, ppm): 8.66 (d, 2H, bipy), 8.27 (m, 2H, bipy), 8.06 (m, 2H, bipy), 7.80 (m, 2H, bipy), 7.68−6.47 (m, aromat), 2.31 [s, 3H, *p*-Me(Ts)], 2.19 [s, 3H, Me(py)]. LSIMS (*m*/*z*): 526, [Ag(Ts4mepy)(bipy)]$^+$; 370, [Ag(Ts4mepy)]$^+$; 263, [Ts4mepy]$^+$.

Table 2. Crystal and Structure Refinement Data for X-ray Studies

	HTs4mepy	$[Ag(Ts3mepy)]_n$ (**1**)	$[Ag(Ms3mepy)]_n$ (**2b**)	$[Ag_4(Ms3mepy)_4]$ (**2a**)	$[Ag_4(Ms6mepy)_4]$ (**3a**)
empirical formula	$C_{13}H_{14}N_2O_2S$	$C_{13}H_{13}AgN_2O_2S$	$C_{15}H_{17}AgN_2O_2S$	$C_{60}H_{68}Ag_4N_8O_8S_4$	$C_{60}H_{68}Ag_4N_8O_8S_4$
fw	262.32	369.18	397.24	1588.94	1588.94
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	triclinic	triclinic	orthorhombic	tetragonal
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Fdd2$	$I4_1/a$
unit cell dimens (Å, deg)	$a = 10.8901(9)$	$a = 6.2951(6)$	$a = 7.960(6)$	$a = 32.464(4)$	$a = 15.6997(13)$
	$b = 15.5093(13)$	$b = 8.2405(8)$	$b = 8.294(6)$	$b = 58.645(7)$	$b = 15.6997(13)$
	$c = 15.8472(14)$	$c = 13.7554(13)$	$c = 12.598(10)$	$c = 13.3568(14)$	$c = 25.219(3)$
	$\alpha = 90$	$\alpha = 95.041(2)$	$\alpha = 97.131(15)$	$\alpha = 90$	$\alpha = 90$
	$\beta = 102.689(2)$	$\beta = 94.465(2)$	$\beta = 93.498(14)$	$\beta = 90$	$\beta = 90$
	$\gamma = 90$	$\gamma = 102.787(2)$	$\gamma = 108.003(15)$	$\gamma = 90$	$\gamma = 90$
V (Å^3)	2611.2(4)	689.68(11)	780.5(10)	25429(5)	6216.0(11)
Z	8	2	2	16	4
D(calcd) (Mg/m^3)	1.335	1.778	1.690	1.660	1.698
abs coeff (mm^{-1})	0.243	1.611	1.430	1.404	1.436
F(000)	1104	368	400	12800	3200
cryst size (mm^3)	0.33 × 0.22 × 0.15	0.22 × 0.14 × 0.12	0.29 × 0.16 × 0.06	0.33 × 0.12 × 0.12	0.14 × 0.14 × 0.06
θ range for data collcn (deg)	1.86−28.03	1.49−28.00	1.64−28.08	1.43−28.07	1.53−28.03
index ranges	$-14 \le h \le 13$	$-6 \le h \le 8$	$-10 \le h \le 9$	$-42 \le h \le 42$	$-20 \le h \le 18$
	$-20 \le k \le 15$	$-10 \le k \le 10$	$-7 \le k \le 10$	$-40 \le k \le 77$	$-14 \le k \le 20$
	$-19 \le l \le 20$	$-18 \le l \le 13$	$-16 \le l \le 16$	$-17 \le l \le 17$	$-33 \le l \le 30$
reflns collcd	13 925	4292	4621	35 385	16 429
indep reflns	5785 [R(int) = 0.0509]	2995 [R(int) = 0.0233]	3241 [R(int) = 0.0638]	14105 [R(int) = 0.0861]	3684 [R(int) = 0.1212]
completeness to θ (%)	95.5 (θ = 25.00°)	94.7 (θ = 25.00°)	91.1 (θ = 25.00°)	99.3 (θ = 26.00°)	98.9 (θ = 26.00°)
max and min transm	0.964 and 0.928	0.824 and 0.732	0.918 and 0.681	0.845 and 0.629	0.917 and 0.818
data/restraints/params	5785/1/337	2995/0/177	3241/0/197	14105/1/773	3684/0/195
GOF on F^2	0.806	0.955	0.917	0.645	0.730
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0447$	$R_1 = 0.0410$	$R_1 = 0.0818$	$R_1 = 0.0398$	$R_1 = 0.0407$
	$wR_2 = 0.0619$	$wR_2 = 0.0997$	$wR_2 = 0.1886$	$wR_2 = 0.0459$	$wR_2 = 0.0463$
R indices (all data)	$R_1 = 0.1905$	$R1 = 0.0543$	$R_1 = 0.1219$	$R_1 = 0.1413$	$R_1 = 0.1991$
	$wR_2 = 0.0774$	$wR2 = 0.1038$	$wR_2 = 0.2056$	$wR_2 = 0.0609$	$wR_2 = 0.0642$
absolute struct param				−0.019(19)	10(10)
largest diff peak and hole (e·Å^{-3})	0.168 and −0.203	1.959 and −0.561	1.728 and −2.632	0.323 and −0.478	0.455 and −0.439

	$[Ag_2(Ms6mepy)_2]_n$ (**3b**)	$[Ag_2(Ms3mepy)_2(phen)_2]$ (**5**)	$[Ag_2(Ms6mepy)_2phen]$ (**7**)	$[Ag_2(Ts4mepy)_2(bipy)_2]$ (**8**)
empirical formula	$C_{15}H_{17}AgN_2O_2S$	$C_{27}H_{25}AgNO_2S$	$C_{42}H_{42}Ag_2N_6O_4S_2$	$C_{23}H_{21}AgN_4O_2S$
fw	397.24	577.44	974.68	525.37
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	triclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimens (Å, deg)	$a = 24.007(4)$	$a = 10.6773(12)$	$a = 10.3032(13)$	$a = 9.6451(10)$
	$b = 6.9006(12)$	$b = 10.8816(11)$	$b = 13.0738(18)$	$b = 10.4805(10)$
	$c = 21.052(4)$	$c = 12.1176(12)$	$c = 17.166(3)$	$c = 12.5890(13)$
	$\alpha = 90$	$\alpha = 84.481(3)$	$\alpha = 77.842(5)$	$\alpha = 71.869(2)$
	$\beta = 115.226(4)$	$\beta = 88.170(3)$	$\beta = 75.228(4)$	$\beta = 76.127(2)$
	$\gamma = 90$	$\gamma = 62.599(2)$	$\gamma = 89.953(13)$	$\gamma = 66.900(2)$
V (Å^3)	3155.0(10)	1244.0(2)	2182.3(6)	1102.29(19)
Z	8	2	2	2
D(calcd) (Mg/m^3)	1.673	1.542	1.483	1.583
abs coeff (mm^{-1})	1.415	0.926	1.039	1.037
F(000)	1600	588	988	532
cryst size (mm^3)	0.23 × 0.08 × 0.06	0.16 × 0.15 × 0.07	0.11 × 0.07 × 0.04	0.30 × 0.25 × 0.20
θ range for data collcn (deg)	1.88−28.06	1.69−27.99	1.60−28.01	1.72−28.04
index ranges	$-25 \le h \le 31$	$-13 \le h \le 13$	$-5 \le h \le 4$	$-12 \le h \le 12$
	$-8 \le k \le 9$	$-14 \le k \le 13$	$-17 \le k \le 13$	$-13 \le k \le 13$
	$-27 \le l \le 15$	$-15 \le l \le 9$	$-22 \le l \le 20$	$-15 \le l \le 16$
reflns collcd	8432	7048	6438	6919
indep reflns	3496 [R(int) = 0.0622]	4879 [R(int) = 0.0573]	4191 [R(int) = 0.0654]	4822 [R(int) = 0.0442]
completeness to θ (%)	94.9 (θ = 26.00°)	90.2 (θ = 24.00°)	44.3 (θ = 26.00°)	95.0 (θ = 26.00°)
max and min transm	0.919 and 0.873	0.937 and 0.862	0.959 and 0.916	0.813 and 0.740
data/restraints/params	3496/0/194	4879/0/320	4191/0/251	4822/0/282
GOF on F^2	0.800	0.703	0.854	0.895
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0422$	$R_1 = 0.0505$	$R_1 = 0.0608$	$R_1 = 0.0392$
	$wR_2 = 0.0481$	$wR_2 = 0.0634$	$wR_2 = 0.1184$	$wR_2 = 0.0788$
R indices (all data)	$R_1 = 0.1551$	$R_1 = 0.1713$	$R_1 = 0.1958$	$R_1 = 0.0556$
	$wR_2 = 0.0590$	$wR_2 = 0.0812$	$wR_2 = 0.1362$	$wR_2 = 0.0827$
largest diff peak and hole (e·Å^{-3})	0.498 and −0.476	0.415 and −0.352	0.379 and −0.356	0.416 and −0.867

X-ray Crystallography. Compounds **1**, **2a,b**, **3a,b**, **5**, **7**, and **8** and the ligand HTs4mepy were mounted on a glass fiber and studied at room temperature on a SIEMENS Smart CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The crystal parameters and experimental details for data collection are summarized in Table 2. Absorption corrections were carried out using SADABS.[30] All the structures were solved by direct methods, except for [Ag_4(Ms6mepy)$_4$] (**3a**), which was solved by the Patterson method. All structures were refined by full-matrix least-squares based on F^2.[31] All non-hydrogen atoms were refined with anisotropic displacement parameters, except for [Ag_2(Ms6mepy)$_2$phen] (**7**) due to the poor quality of the crystal. In this case the Squeeze program was used to correct the reflection data for the diffuse scattering due to disordered solvent.[32] In all cases the hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except for the hydrogen atoms bonded to pyridine nitrogen atoms on the HTs4mepy ligand, which were located on a difference electron density map and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from ref 33

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 241798−241806 (HTs4mepy, **1**, **2a,b**, **3a,b**, **5**, **7**, and **8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (/44) 1223-336-033; E-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data in CIF format and additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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