Synthesis and Spectroscopic, Thermal and Electrochemical Studies of Mixed-ligand Complexes of Silver(I) with Derivatives of Benzoyltrifluoroacetonate and 4,4′-Bipyridine, Including the Crystal Structure of [Ag(4,4′-bpy)(tfcpb)]$_n$

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Three new mixed-ligand complexes of silver(I) with 4,4′-bipyridine and derivates of benzoyltrifluoroacetone (Htfpb: 4,4,4-trifluoro-1-phenyl-1,3-butandione, Htfcpb: 4,4,4-trifluoro-1-(4-chlorophenyl)-1,3-butandione and Htfmpb: 4,4,4-trifluoro-1-(4-methoxyphenyl)-1,3-butandione) were synthesized and characterized by elemental analyses and ^{1}H NMR spectroscopy. Thermal and electrochemical properties were also studied. The single-crystal structure of [Ag(4,4′-bpy)(tfcpb)]$_n$ shows a one-dimensional coordination polymer as a result of 4,4′-bpy bridging. The four-coordinate Ag(I) ions are linked into double chains by Ag···O contacts, which are extended into a 3D supramolecular structure through abundant weak interactions, such as π···π, C–H···F, C–H···O, C–H···Cl and F···F contacts.

Key words: Silver(I), 4,4′-Bipyridine, Benzoyltrifluoroacetone Derivatives

Introduction

Supramolecular chemistry and crystal engineering based upon the self-assembly of metal ions and bridging organic ligands have attracted great interest in recent years due to the novel structural topologies and potential applications in optical and magnetic components, catalysis, and electrical conductivity observed in the materials obtained [1 – 4]. The development of supramolecularly assembled compounds based on coordinative and hydrogen bonding has allowed to rationally design and prepare supramolecular architectures by noncovalent interactions. It is crucial to consider both geometric and energetic features. Lately, many supramolecular assemblies have been designed by carefully selecting building blocks and organic ligands containing appropriate functional groups for supramolecular interactions (hydrogen bonding, π···π interactions *etc.*) [5 – 9]. The self-assembly of multidentate organic ligands and metal ions has resulted in many novel polymeric coordination frameworks.

According to former work, designing and synthesizing MOFs (metal organic frameworks) can use the subtle interplay of many factors such as the geometric preference of the metal ion, the size and shape of the organic building blocks, templates, and solvent systems. It is known that β-diketonates along with neutral bridging ligands are good candidates for the construction of coordination frameworks with specific structures due to their various coordination modes, from which a rich variety of one-, two- and three-dimensional metal-organic polymeric architectures have been constructed.

Coordinatively unsaturated metal complexes of β-diketonates are of particular interest as building blocks of supramolecular structures. In the last few years, several crystalline products have been synthesized using [$M(\beta$-diketonato)$_2$] complexes ($M =$ Pb, Cd) and different bridging and chelating ligands [10]. Silver(I) ions exhibit linear, trigonal, and tetrahedral coordination and have a high affinity for hard donor atoms such as nitrogen or oxygen atoms and soft donor atoms such as sulfur atoms, and are there-
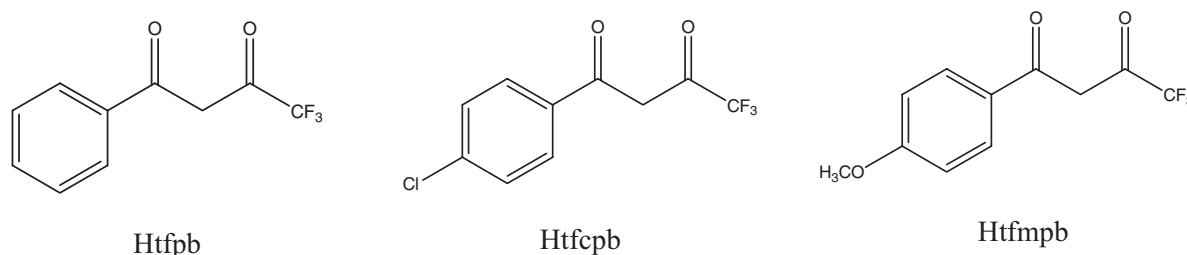
Scheme 1. Structural formulae of the employed ligands. (The acacH-type ligands are shown in their keto forms).

fore favorable and fashionable building blocks for MOFs [11–16]. Furthermore, silver ions can form short Ag···Ag contacts as well as interactions unsupported by ligands, which have been proven to be two of the most important factors contributing to the formation of such complexes and their special properties [17, 18]. Several complexes of silver(I) with derivates of β-diketonates have been reported from our laboratory [19]. In this article, we report on the synthesis, characterization, thermal and electrochemical properties of Ag(I) complexes with 4,4'-bipyridine and benzoyltrifluoroacetones (Htfpb: 4,4,4-trifluoro-1-phenyl-1,3-butandione, **1**, Htfcpb: 4,4,4-trifluoro-1-(4-chlorophenyl)-1,3-butandione, **2**, and Htfmpb: 4,4,4-trifluoro-1-(4-methoxyphenyl)-1,3-butandione, **3**; see Scheme 1) as co-ligands, and on the crystal structure of [Ag(4,4'-bpy)(tfcpb)]$_n$.

Results and Discussion

NMR spectroscopy, thermogravimetry (TG), and cyclovoltammetry (CV)

The ^{1}H NMR spectra of DMSO solutions of **1**, **2** and **3** display two different protons of the 4,4'-bpy ligand at 8.7 and 7.8 ppm and additionally singlets at 5.97, 5.92 and 5.95 ppm of the central =C- protons of the tfpb$^-$, tfcpb$^-$ and tfmpb$^-$ anions, respectively. In **1** (three distinct peaks of the phenyl group), **2** (two distinct peaks of the 4-chlorophenyl group) and **3** (two distinct peaks of the 4-methoxyphenyl group), peaks of the β-diketonate anions appear at 7.3–7.8 ppm (overlapped with protons of the 4,4'-bpy ligand) for **1** and **2**, and at 6.92 and 7.7–8.0 ppm (also overlapped with signals of protons of the 4,4'-bpy ligand) for **3**. The singlet at 3.76 ppm is assigned to the methoxy group in the mbtfa$^-$ anion.

The TG curves show that the complexes **1**, **2** and **3** exhibit similar decomposition pathways. There is no weight loss up to 220 °C for **1**, up to 235 °C for **2** and up to 225 °C for **3**. The thermal decomposition of the compounds occurs in two steps. The first step (endothermic decomposition) is found in the temperature range of 220–250 °C (almost 68 % weight) for **1**, 235–250 °C (almost 70 % weight) for **2** and 225–250 °C (almost 73 % weight) for **3**. The second step in the temperature range of 250–500 °C (almost 11 % weight for **1**, 9.5 % weight for **2** and 10 % weight for **3**) corresponds to the decomposition of the compounds. The mass loss calculations as well as the microanalyses of the remaining solids suggest that the residue is metallic silver, in agreement with the residual mass of 21.00 % for **1** (calcd. 22.54 %), 20.50 % for **2** (calcd. 21.00 %) and 17.00 % for **3** (calcd. 16.00 %).

The electrochemical behavior of the complexes was studied using cyclovoltammetry in DMSO containing 0.1 M tetrabutylammonium perchlorate. Fig. 1 (curve a) shows the cyclovoltammogram (CV) of AgNO$_3$ in this solution, the curves (b) to (d) of **1**, **2** and **3**, respectively, under the same conditions. All cyclovoltammograms exhibit a cathodic peak (C$_1$) in the negative scan mode and a corresponding anodic peak (A$_1$) in the positive scan mode. The cathodic peaks are due to the reduction of the silver ion (Ag$^+$), and the anodic peaks are related to the oxidation of Ag^0 produced at the electrode surface. The cathodic peak potentials of the complexes are shifted to more negative values, −135, −67 and −84 mV s for **1**, **2** and **3**, respectively, compared to the AgNO$_3$ peak potential. Based on the observed shifts, the formation constants of the complexes were obtained as 200 M^{-1} for **1**, 16 M^{-1} for **2** and 26 M^{-1} for **3** [20]. It should be noted that Ag$^+$ is strongly solvated in DMSO, and its interactions are comparable with those of some cryptands [21]. However, the presence of ligand ions shifts the cathodic peak potentials
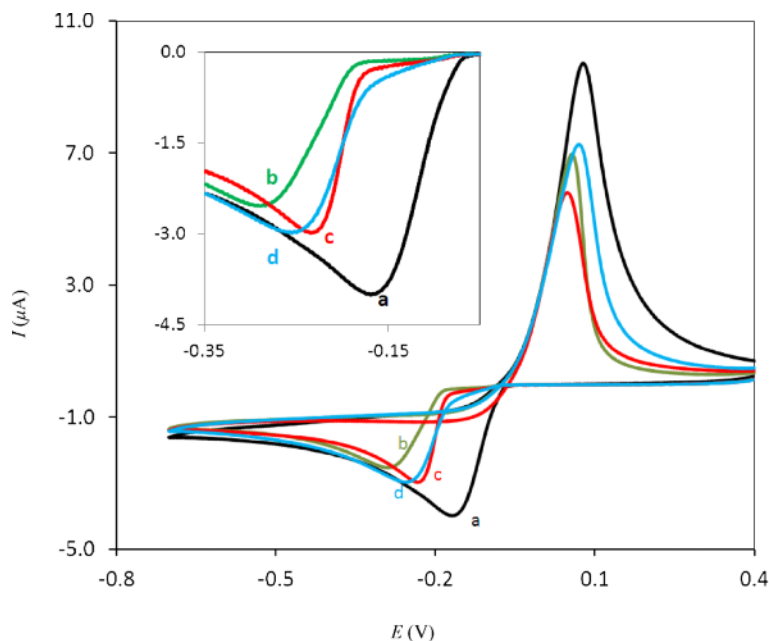
Fig. 1 (color online). Cyclovoltammograms of 1.0 mM (a) AgNO$_3$, (b) **1**, (c) **2** and (d) **3** (glassy carbon electrode in DMSO), supporting electrolyte 0.1 M TBAP, scan rate 100 mV s^{-1}. Inset: expand of cathodic peaks.

to more negative values. Additionally, the voltammetric study of the complexes has shown that they have a high kinetic stability.

Crystal and molecular structure of
[Ag(4,4′-bpy)(tfcpb)]$_n$ (2)

Single-crystal X-ray diffraction analysis reveals that the coordination polymer **2** crystallizes in the orthorhombic space group *Fddd*. The asymmetric unit contains two crystallographically different Ag(I) ions, 4,4′-bpy ligands and tfcpb anions (Fig. 2a). The four-coordinate Ag(I) ions adopt a distorted tetrahedral structure with bond angles ranging from 71.5 to 160.9° for Ag1 and 71.4 to 160.8° for Ag2. Both Ag(I) ions are coordinated by two N atoms from two different μ-4,4′-bpy ligands and two O atoms from one tfcpb anion. The distortion of the tetrahedron is indicated by the calculated value of the τ_4 parameter introduced by Houser and co-workers [22] to describe the geometry of a four-coordinated metal system, which is 0.70 in Ag1 and 0.64 in Ag2 (for a perfect tetrahedral geometry $\tau_4 = 1$). The carboxylate groups of the tfcpb anions are coordinated to the Ag(I) ions in an *O,O′*-chelating mode. The Ag–N$_{bipy}$ bond lengths are 2.186(6) and 2.200(6) Å for Ag1 and 2.200(6) and 2.209(6) Å for Ag2. They are in the same range as

in other Ag(I)-bpy complexes [23]. The Ag–O bond lengths (2.490(6) and 2.623(6) Å for Ag1 and 2.521(7) and 2.584(7) Å for Ag2) are compatible with those in Ag(I) complexes containing oxygen ligator atoms [24]. In addition to the strong coordinative bonds, there are weak Ag···O interactions [Ag1–O32 ($3/4 - x$, $3/4 - y$, z) and Ag2–O12 ($3/4 - x$, $3/4 - y$, z)] with distances of 3.120 and 3.144 Å (Figs. 2b, 2c). These are slightly longer than the reported Ag···O distances in reference [19], but still fall in the secondary bonding range (the sum of van der Waals radii of Ag and O is 3.24 Å). The separation Ag$^+$···Ag$^+$ is 3.306 Å, which is longer than the Ag···Ag distance in metallic silver, but obviously shorter than twice the van der Waals radius of Ag(I) [25]. Each Ag atom is linked by two different 4,4′-bipyridine molecules (the two aryl ring planes form angles of 5.95 and 30.99°) to two other Ag atoms. In comparison with reported structures [19], in **2**, the tfcpb anions have two different orientations (up and down) relative to the "Ag(I)-4,4′-bpy" part of the coordination polymer (Fig. 3). As shown in Fig. 4, a pair of adjacent Ag-bpy single chains are linked into a double chain by weak Ag···O and Ag···Ag interactions.

Intermolecular, intramolecular and $\pi \cdots \pi$ stacking interactions are observed in **2**. They seem to be responsible for the packing of the coordination polymer. An inspection of the data of **2** for weak directional inter-

(a)
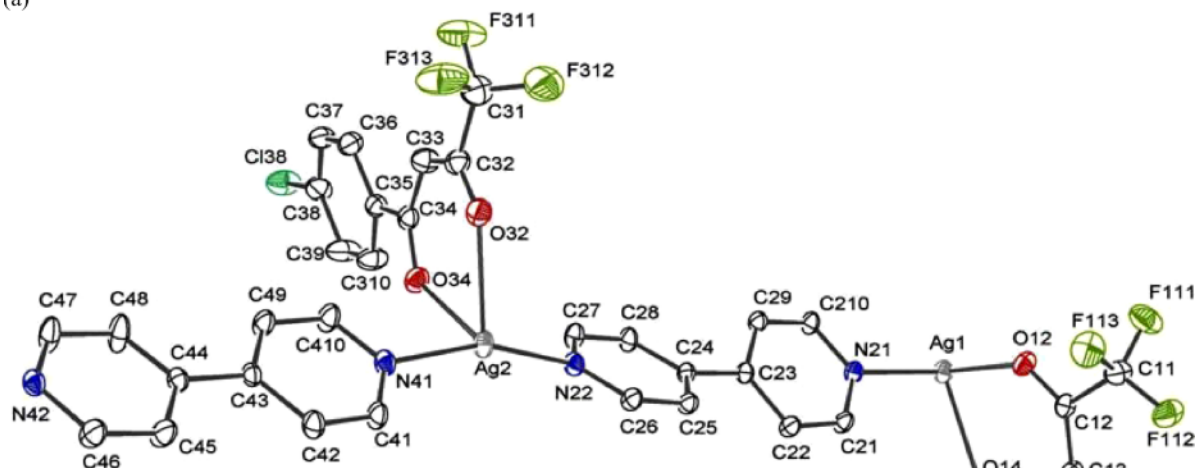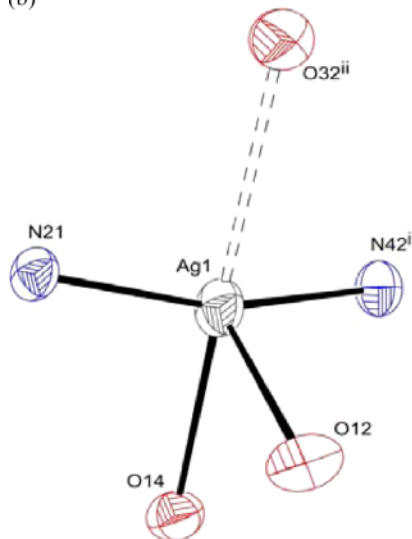
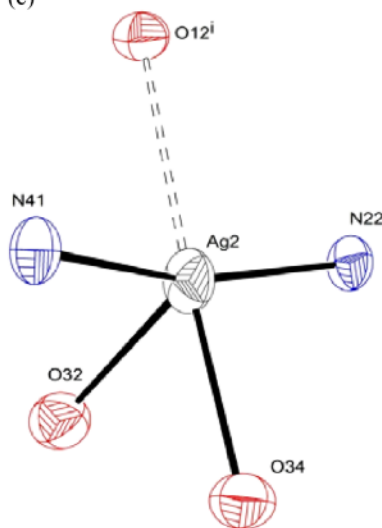(b)   (c)

Fig. 2 (color online). a) ORTEP diagram of the asymmetric unit of **2**; b), c) representation of the hole in the coordination sphere of the silver atoms.

molecular interactions using the program MERCURY has shown that there are O···H–C, C–H···F and C–H···Cl interactions [26 – 28] (see Table 3). Fig. 5 shows the packing of the molecules of **2** in the crystal highlighting some of the weak intermolecular interactions. The H···O and H···F separations range from 2.457 to 2.636 Å, which indicates moderate-to-strong hydrogen bonds [29]. The packing of the molecules of **2** in the solid state exhibits interesting self-assembled structure topologies through different π···π stacking modes with interlayer distances of 3.331 Å (see also ref. [30]). The centroid-to-centroid separations between neigh-
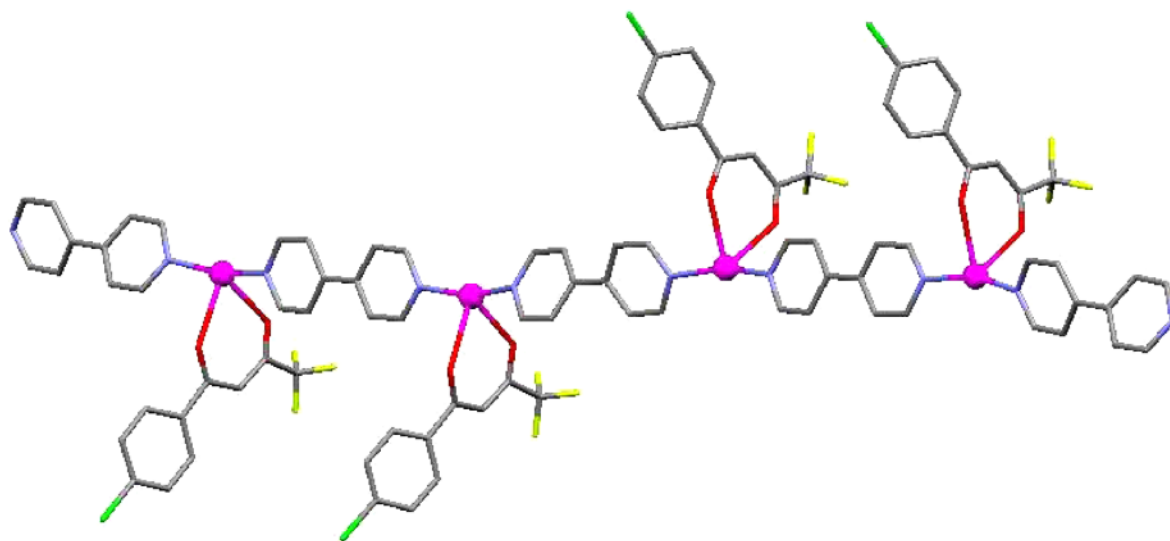
Fig. 3 (color online). Positions of the tfcpb anions relative to the Ag(I)-4,4′-bpy chain in the 1D coordination polymer of **2**.
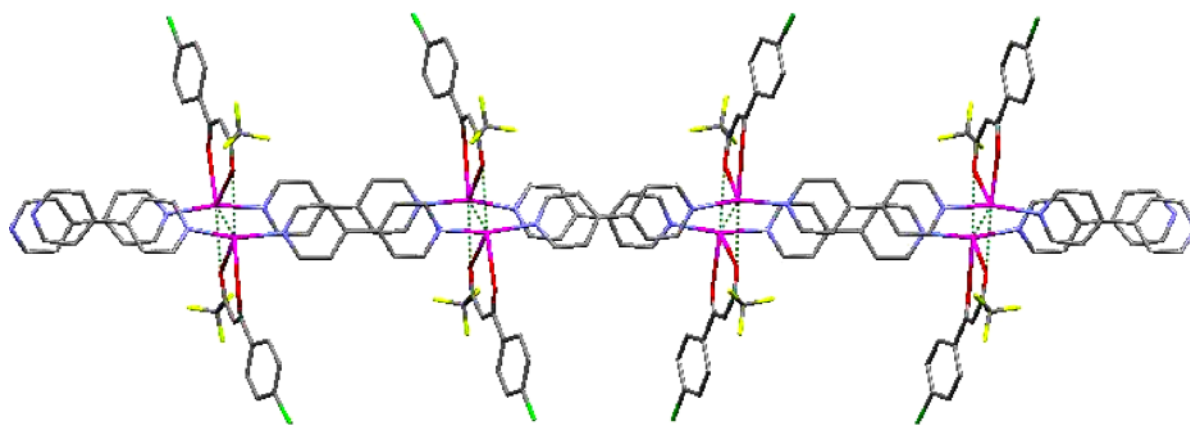

Fig. 4 (color online). Fragment of the double chain of the 1D coordination polymer in **2**.

boring aromatic rings exhibit typical slipped $\pi\cdots\pi$ stacking interactions in an offset fashion. Thus, a three-dimensional hydrogen-bonded and layer-packed network is constructed (Fig. 5).

Experimental

Materials and physical measurements

All reagents purchased commercially were used without further purification. Elemental analyses (C, H, N) were performed using a Carlo Erba model EA 1108 analyzer. Solution ^{1}H NMR spectra were recorded on a Bruker DRX-250 Avance spectrometer at 250 MHz using [D$_6$]DMSO as solvent. Thermogravimetrical analyses (TGA) were performed in N$_2$ atmosphere with a flow rate of 20 mL min^{-1} on a Seiko Instruments thermal analyzer from 20 to 800 °C, with a heating rate of 10 °C min^{-1} in ceramic crucibles. Cyclovoltammetry was performed using an Autolab potentiostat/galvanostat 101. The working electrode was a glassy carbon disk (2.0 mm diameter). A Pt wire was used as a counter electrode. The working electrode potentials were measured *versus* a quasi-reference electrode of a platinum wire (all electrodes from Azar Electrode).

Preparation of [Ag(4,4′-bpy)(tfpb)] (1)

A mixture of Ag$_2$O (116 mg, 0.5 mmol), 4,4′-bpy (156 mg, 1 mmol) and Htfpb (216 mg, 1 mmol) was stirred
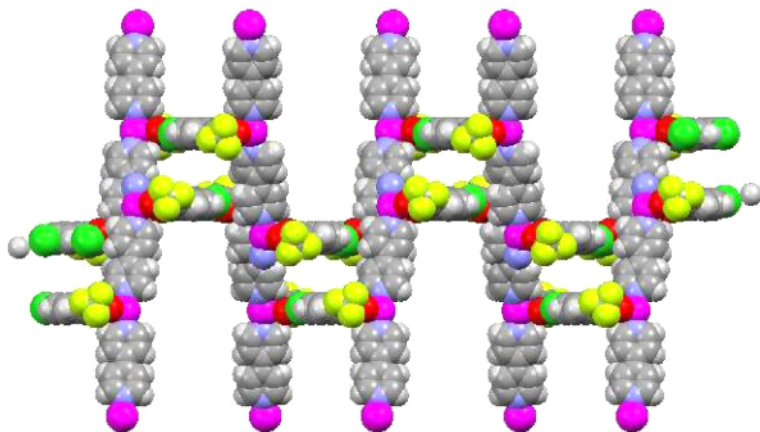
Fig. 5 (color online). Packing diagram of **2** viewing down the *a* axis with intermolecular interactions (especially Cl···H interactions). The crystal structure contains large voids of *ca.* 573 Å^3 (PLATON).

in a mixed CH_3CN/H_2O solvent (15 mL, v/v: 1/4). Then, an aqueous NH_3 solution (25 %) was poured into the mixture to give a clear solution. The resultant solution was allowed to evaporate slowly in the dark at room temperature for several days to give colorless crystals of **1** (yield, 60 %). The crystals were washed with small volumes of cold CH_3CN and diethyl ether. – Anal. for $C_{20}H_{14}AgF_3N_2O_2$: calcd. C 50.00, H 2.08, N 5.83; found C 49.72, H 2.40, N 5.59. – ^{1}H NMR ([D_6]DMSO) $\delta = 8.73$ (d, 4H, pyridyl), 7.88 (d, 4H, pyridyl), 7.76 (d, 2H, phenyl), 7.24–7.41 (m, 3H, phenyl), 5.97 (s, 1H, =CH– of tfpb$^-$).

Preparation of [Ag(4,4′-bpy)(tfcpb)]$_n$ (2)

Complex **2** was synthesized in the same way as complex **1** using Htfcpb (250 mg, 1 mmol) in place of Htfpb; yield: 72 %. – Anal. for $C_{20}H_{13}AgClF_3N_2O_2$: calcd. C 46.72, H 5.06, N 5.45; found C 46.47, H 4.92, N 5.69. – ^{1}H NMR ([D_6]DMSO) $\delta = 8.72$ (d, 4H, pyridyl), 7.70–8.00 (m, 6H, pyridyl and phenyl), 7.45 (d, 2H, phenyl), 5.92 (s, 1H, =CH- of tfcpb$^-$).

Preparation of [Ag(4,4′-bpy)(tfmpb)] (3)

Complex **3** was synthesized in the same way as complex **1** using Htfmpb (246 mg, 1 mmol) in place of Htfpb; yield: 65 %. – Anal. for $C_{31}H_{24}AgF_3N_4O_3$: calcd. C 55.94, H 4.06, N, 8.42; found C 55.37, H 4.29, N 8.59. – ^{1}H NMR ([D_6]DMSO) $\delta = 8.70$ (d, 4H, pyridyl), 7.84 (d, 4H, pyridyl), 7.75 (d, 2H, phenyl), 6.92 (d, 2H, phenyl), 5.95 (s, 1H, =CH- of tfmpb$^-$), 3.76 (s, 3H, methoxy).

X-Ray structure determination

The data collection (Table 1) was performed on a Stoe IPDS II diffractometer using graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). The data were corrected

Table 1. Crystal data and structure refinement for **2**.

Compound	[Ag(4,4′-bpy)(tfcpb)]$_n$
Empirical formula	$C_{40}H_{26}Ag_2Cl_2F_6N_4O_4$
Formula weight	1027.29
Crystal system	orthorhombic
Space group	*Fddd*
a, Å	21.887(2)
b, Å	29.461(2)
c, Å	53.737(4)
Volume, Å^3	34 650(4)
Z	32
Density (calcd.), g cm^{-1}	1.58
μ(Mo K_α), mm^{-1}	1.1
F(000), e	16 256
θ range, deg	1.22 – 25.26
hkl index ranges	$\pm25, \pm35, -64 \rightarrow 63$
Completeness to θ_{max}, %	98.5
Reflections coll./indep./R_{int}	79 003/7744/0.0633
Data/ref. parameters	4089/524
$R1/wR2$ [$I > 2\sigma(I)$]	0.0649/0.1896
$R1/wR2$ (all data)	0.1053/0.2045
Goodness of fit on F^2	1.172
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.64/ − 0.44

Table 2. Selected bond lengths (Å) and angles (deg) for **2**[a].

Ag1–N42^i	2.186(6)	Ag2–N22	2.201(6)
Ag1–N21	2.200(6)	Ag2–N41	2.210(6)
Ag1–O12	2.489(6)	Ag2–O32	2.521(7)
Ag1–O14	2.623(6)	Ag2–O34	2.584(6)
Ag1···O32^{ii}	3.120	Ag2···O12^i	3.144
Ag1···Ag2	3.306(1)		
N42–Ag1–N211	161.0(2)	N41–Ag2–O32	89.8(2)
N42–Ag1–O12	100.7(2)	N22–Ag2–O34	93.0(2)
N21–Ag1–O12	97.7(2)	N41–Ag2–O34	94.4(2)
N22–Ag2–N41	160.8(3)	O32–Ag2–O34	71.4(2)

[a] Symmetry operations: i: $3/4+x$, $3/4−y$, z; ii: $3/4+x$, $3/4+y$, $−z$.

A···H–B	A···H (Å)	A···B (Å)	A···H–B (deg)
O12···H26–C26 $(3/4 - x, 3/4 - y, z)$	2.457	3.257(1)	144.44
O32···H210–C210 $(3/4 - x, 3/4 - y, z)$	2.604	3.384(2)	141.87
O32···H46–C46 $(1 - x, -y, -z)$	2.636	3.348(1)	133.98
F111···H41–C41 $(3/4 - x, 3/4 - y, z)$	2.547	3.443(2)	161.49
F313···H46–C46 $(1 - x, -y, -z)$	2.582	3.474(2)	160.72
Cl38···H39–C39 $(1/4 - x, y, 1/4 - z)$	2.810	3.694(2)	159.32
Cl18 ···H29–C29 $(-1/4 + x, 1 - y, -1/4 + z)$	2.879	3.640(3)	139.95
π···π (slipped face-to-face in double chains)	–	3.331(3)	–

Table 3. Intermolecular interactions for **2**.

for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data. The programs used in this work are Stoe's X-AREA [31], including X-RED and X-SHAPE for data reduction and absorption correction [32, 33], and the WINGX suite of programs [34], including SIR-92 [35] and SHELXL-97 [36] for structure solution and refinement, OR-TEP-III [37] for structure drawings, and PLATON [38] for further calculations. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all atoms, anisotropic displacement param-

eters for all non-hydrogen atoms and isotropic displacement parameters for all of the hydrogen atoms. Selected interatomic distances and angles are given in Tables 2 and 3.

CCDC 867846 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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