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Original scientific paper

Synthesis and structural analysis of polynuclear silver(I) complexes with 4,7-phenanthroline

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Abstract: New polynuclear silver(I) complexes, $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$ (**1**) and $[Ag(PO_2F_2)(4,7\text{-phen})]_n$ (**2**), were synthesized by the reaction of 4,7-phenanthroline (4,7-phen) and the corresponding AgX salt (X = $CF_3SO_3^-$ and PF_6^-) in 1:2 mole ratio, respectively, in methanol/acetone (1:1 volume ratio) at room temperature. The characterization of the complexes was established on the basis of elemental microanalysis, IR and NMR (^1H and ^{13}C) spectroscopic techniques, while their crystal structures were determined by single-crystal X-ray diffraction analysis. The results of spectroscopic and crystallographic analyses revealed that in these complexes, 4,7-phen behaves as a bridging ligand between two metal ions, while the remaining coordination sites of the Ag(I) ions are occupied by the oxygen atom of $CF_3SO_3^-$ and an acetonitrile nitrogen atom in **1** or by two oxygen atoms from two $PO_2F_2^-$, formed after hydrolysis of PF_6^-, in **2**. In the solid state, both complexes are coordination polymers in which the geometry around the Ag(I) ions is distorted tetrahedral.

Keywords: silver(I) complexes; 4,7-phenanthroline; polynuclear complexes; spectroscopy; X-ray crystallography.

INTRODUCTION

Silver(I) complexes with aromatic nitrogen-containing heterocycles (*N*-heterocycles) are of great importance in the field of medicinal chemistry and the coordination polymer design.[1,2] Generally, silver(I) complexes with these ligands are known to possess significant antibacterial activity against a wide range of Gram-positive and Gram-negative bacteria and have shown remarkable activity against different *Candida* species.[3–14] Moreover, they have manifested cytotoxic

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activity against different human tumor cell line, being more active and less toxic to humans than the clinically used platinum(II) complexes.[15] Their effectiveness is thought to be the consequence of the presence of a weak Ag–N bond, which can be easily cleaved in the interaction with thiol-containing proteins and DNA, the process that is a prerequisite for their action.[3]

Besides the significant antimicrobial and antiproliferative activities of silver(I) complexes with aromatic *N*-heterocycles, the Ag(I) ions coordinated by this type of ligands are favorable building blocks for coordination polymers which may find interesting applications for the development of innovative materials, such as liquid crystals.[1,16,17] Coordination polymers based on Ag(I) ions are attracting great attention due to the flexibility of the coordination sphere of this metal ion.[1,16,17] Thus, it can adopt coordination numbers between two and six and form complexes of various geometries such as linear, bent, trigonal, T-shaped, tetrahedral, trigonal pyramidal and octahedral. Besides that, weak contacts such as Ag···Ag, Ag···π and Ag···solvent/counterion interactions significantly affect the geometry and topology of the silver(I)-based coordination polymers in the solid state.[1,18]

In the design of silver(I) coordination polymers having different possible applications, various bridging and chelating *N*-heterocyclic ligands have been used. Among them, phenanthrolines have been investigated due to their coordination diversity which allowed the tuning of the nuclearity and biological activities in a series of silver(I) complexes.[5,13,14] Very recently, five silver(I) complexes with 4,7-phenanthroline ligand (4,7-phen), $[Ag(NO_3)(4,7\text{-phen})]_n$, $[Ag(ClO_4)(4,7\text{-phen})]_n$, $[Ag(CF_3COO)(4,7\text{-phen})]_n$, $[Ag_2(H_2O)_{0.58}(4,7\text{-phen})_3](SbF_6)_2$ and $\{[Ag_2(H_2O)(4,7\text{-phen})_2](BF_4)_2\}_n$, have been synthesized and biologically evaluated, showing higher selectivity towards *Candida* spp. in comparison to bacteria, while being only moderately cytotoxic against healthy human fibroblasts.[14] Moreover, $[Ag(NO_3)(4,7\text{-phen})]_n$ and $[Ag(CF_3COO)(4,7\text{-phen})]_n$ complexes were effective *in vivo* rescuing zebrafish embryos from lethal *C. albicans* infection and reducing the fungal burden by preventing fungal filamentation.[14]

In the present study, 4,7-phen reacted with two AgX salts (X = $CF_3SO_3^-$ and PF_6^-), yielding new polynuclear silver(I) complexes, $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$ (**1**) and $[Ag(PO_2F_2)(4,7\text{-phen})]_n$ (**2**). These complexes were fully characterized by spectroscopy (IR, ^{1}H- and ^{13}C-NMR) and single-crystal X-ray crystallography.

EXPERIMENTAL

Reagents

Silver(I) salts ($AgCF_3SO_3$ and $AgPF_6$), 4,7-phenanthroline (4,7-phen), methanol, acetone, acetonitrile, dimethyl sulfoxide (DMSO) and deuterated dimethyl sulfoxide (DMSO-d_6)

were purchased from the Sigma–Aldrich Chemical Co. All the employed chemicals were of analytical reagent grade and used without further purification.

Measurements

Elemental microanalysis of the silver(I) complexes for carbon, hydrogen and nitrogen was performed at the Adolphe Merkle Institute of the University of Fribourg. The NMR spectra were recorded at 25 °C on a Varian Gemini 2000 spectrometer (^{1}H at 200 MHz, ^{13}C at 50 MHz). 5.0 mg of 4,7-phen and the corresponding silver(I) complex was dissolved in 0.6 mL of DMSO-d_6 and transferred into a 5 mm NMR tube. Chemical shifts are expressed in ppm (δ / ppm) and scalar couplings are reported in Hertz (J / Hz). Chemical shifts were calibrated relative to those of the solvent. The IR spectra were recorded as KBr pellets on a Perkin–Elmer Spectrum One FT-IR spectrometer over the wavenumber range of 4000–450 cm^{-1}. Analytical and spectral data of the compounds are given in Supplementary material to this paper.

*Synthesis of complexes **1** and **2***

10.0 mL of methanolic solution of the corresponding silver(I) salt (0.50 mmol, 128.4 mg of $AgCF_3SO_3$ for **1** and 126.4 mg of $AgPF_6$ for **2**) was added dropwise to a solution of 4,7-phen (0.25 mmol, 45.0 mg) in 10.0 mL of warm acetone with stirring at room temperature. The stirring was continued for 3 h in the dark at room temperature, the white precipitate was filtered off and dissolved in acetonitrile. The obtained solution was left to evaporate slowly at room temperature. After 3–5 days, colorless crystals of **1** and **2** suitable for single crystal X-ray analysis were formed. These crystals were filtered off and dried in the dark at room temperature. Yield (calculated on the basis of the *N*-heterocyclic ligand): 73 % (87.3 mg) for **1** and 66 % (64.2 mg) for **2**.

Crystallographic data collection and refinement of the structure

Crystal data and details of the structure determinations are listed in Table I. A suitable crystal was mounted on a mylar loop in oil on a STOE IPDS 2 diffractometer. The crystals were kept at 250(2) K for **1** and 293(2) K for **2** during data collection. Using Olex2,[19] the structures were solved with the ShelXT[20] structure solution program using Intrinsic Phasing and refined with the ShelXL[21] refinement package using Least Squares minimization. Drawings were prepared with Mercury computer graphics program.[22]

TABLE I. Details of the crystal structure determination of $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$ (**1**) and $[Ag(PO_2F_2)(4,7\text{-phen})]_n$ (**2**) complexes

Property	**1**	**2**
Empirical formula	$C_{15}H_{11}AgF_3N_3O_3S$	$C_{12}H_8AgF_2N_2O_2P$
Formula weight	478.20	389.04
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a / Å	13.6834(11)	10.3939(4)
b / Å	8.0480(5)	14.7587(5)
c / Å	15.5345(13)	8.0940(5)
α / °	–	–
β / °	103.199(6)	97.683(4)
γ / °	–	–
V / Å^3	1665.5(2)	1230.48(10)
F_{000}	944	760
Z	4	4

TABLE I. Continued

Property	**1**	**2**
X-radiation, λ / Å	Mo-K_α 0.71073	Mo-K_α 0.71073
Data collect. temperature, K	250(2)	293(2)
Calculated density, Mg m^{-3}	1.907	2.100
Absorption coefficient, mm^{-1}	1.389	1.794
Crystal size, mm^3	0.270 × 0.190 × 0.110	0.260 × 0.153 × 0.040
2θ range, °	5.3 to 50.3	3.9 to 50.3
index ranges h, k, l	-16 ... 16, -9 ... 9, -18 ... 18	-12 ... 12, -17 ... 17, -9 ... 9
No. of collected & indep. reflections	20622, 2962	15604, 2192
R_{int}	0.0842	0.0315
Data / restraints / parameters	2962 / 34 / 237	2192 / 0 / 181
Goodness-on-fit on F^2	1.066	1.047
Final R indices [$I \geq 2\sigma(I)$]	0.0597, 0.1595	0.0269, 0.0687
Final R indices (all data)	0.0679, 0.1660	0.0325, 0.0711
Difference density: max, min / e Å^{-3}	0.94, –1.86	0.67, –0.49
CCDC number	1899714	1899713

RESULTS AND DISCUSSION

*Synthesis and structural features of complexes **1** and **2***

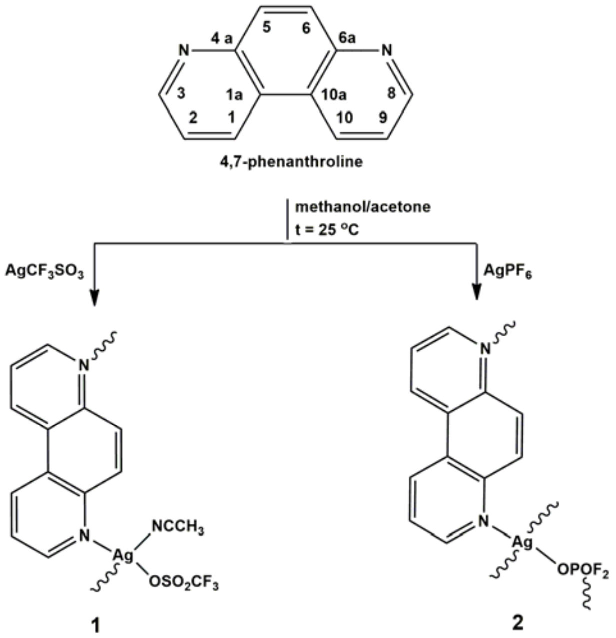
The silver(I) complexes with 4,7-phenanthroline (4,7-phen) were synthesized according to the route presented in Scheme 1. The reactions between 4,7-phen and AgX (X = $CF_3SO_3^-$ and PF_6^-) in 1:2 mole ratio were performed in methanol/acetone (1:1 volume ratio) at room temperature yielding the polynuclear $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$ (**1**) and $[Ag(PO_2F_2)(4,7\text{-phen})]_n$ (**2**) complexes. The composition and structural formula of both silver(I) complexes were consistent with the elemental analysis, IR and solution NMR (^{1}H and ^{13}C) spectroscopic results and were also supported by single-crystal X-ray diffraction analyses. In these complexes, 4,7-phen acts as a bridging ligand between two metal ions, being in accordance with its coordination mode in the previously synthesized silver(I) complexes with this *N*-heterocycle.[14] In complex **1**, the $CF_3SO_3^-$ is monodentately coordinated to the Ag(I) ion, while the fouth coordination site is occupied by the acetonitile nitrogen atom. Instead of the expected PF_6^- in **2**, this complex contains two bridging $PO_2F_2^-$ that are monodentately coordinated to Ag(I) ion *via* oxygen atoms. It can be assumed that $PO_2F_2^-$ was formed by the hydrolysis of PF_6^-, a process previously described in the literature:[23,24]

$$PF_6^- + H_2O \rightarrow POF_4^- + 2HF \tag{1}$$

$$POF_4^- + H_2O \rightarrow PO_2F_2^- + 2HF \tag{2}$$

Description of the single crystal structure

The molecular structures of silver(I) complexes **1** and **2** with the anisotropic displacement ellipsoids and the atom numbering scheme are shown in Fig. 1, while the selected bond distances, Å and angles, °, with the estimated standard deviations are given in Table II.



Scheme 1. Schematic presentation of the synthesis of $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$ (**1**) and $[Ag(PO_2F_2)(4,7\text{-phen})]_n$ (**2**) complexes.The solid products of these reactions were recrystallized in acetonitrile. The numbering scheme of carbon atoms in 4,7-phen is in agreement with IUPAC recommendations for fused ring systems and does not match the one applied in the X-ray analysis of silver(I) complexes.

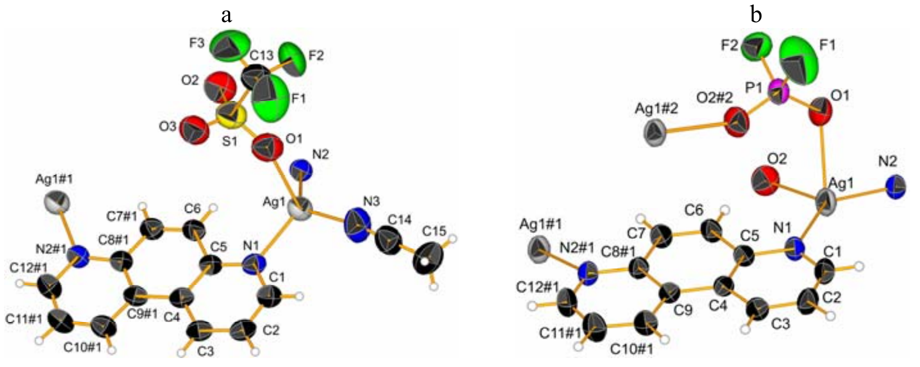


Fig. 1. Molecular structures of: a) $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$ (**1**) and b) $[Ag(PO_2F_2)(4,7\text{-phen})]_n$ (**2**) complexes. Displacement ellipsoids are drawn at 50 % probability level and H atoms are represented by spheres of arbitrary size. Symmetry codes for complex **1**: #1: 1–*x*, 1/2+*y*, 3/2–*z* and for **2**: #1: 1–*x*, -1/2+*y*, 1/2–*z*, #2: x, 3/2–*y*, 1/2+*z*.

TABLE II. Selected bond distances and valence angles (°) in silver(I) complexes **1** and **2**; Symmetry code: (#2) *x*, –*y*+3/2, *z*–1/2

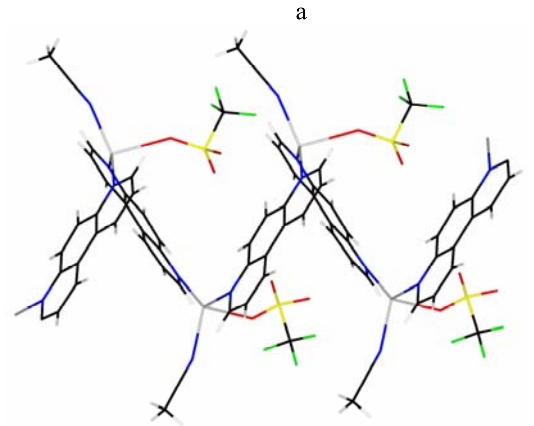
1		**2**	
Bond	Bond distance, Å	Bond	Bond distance, Å
Ag1—N1	2.305(5)	Ag1—N1	2.240(3)
Ag1—N2	2.251(5)	Ag1—N2	2.252(3)
Ag1—N3	2.284(7)	Ag1—O1	2.500(3)
Ag1—O1	2.505(6)	Ag1—O2	2.499(3)
	Valence angles, °		Valence angles, °
N1—Ag1—N2	130.94(17)	N1—Ag1—N2	143.77(10)
N2—Ag1—N3	128.3(2)	N1—Ag1—O1	108.67(10)
N1—Ag1—N3	96.5(2)	N1—Ag1—O2	115.62(9)
N1—Ag1—O1	98.1(2)	N2—Ag1—O1	90.84(10)
N2—Ag1—O1	94.7(2)	N2—Ag1—O2	95.47(10)
N3—Ag1—O1	97.8(3)	O1—Ag1—O2	85.80(11)
C1—N1—Ag1	120.9(4)	C1—N1—Ag1	121.2(2)
C5—N1—Ag1	121.6(4)	C5—N1—Ag1	121.2(2)
C12—N2—Ag1	121.2(4)	C12—N2—Ag1	117.0(2)
C8—N2—Ag1	121.8(4)	C8—N2—Ag1	123.7(2)
C14—N3—Ag1	162.2(9)	P1—O1—Ag1	122.28(16)
S1—O1—Ag1	145.9(4)	P1#2—O2—Ag1	151.58(19)

In the solid state, both complexes **1** and **2** are coordination polymers. In **1**, each Ag(I) ion is surrounded by two 4,7-phen, one acetonitrile and one monodentately coordinated trifluoromethanesulfonate (triflate) anion (Fig. 1a).

An extended view of polynuclear silver(I) complex **1** is shown in Fig. 2a. This complex has a distorted tetrahedral geometry, what can be concluded from the value of τ_4 parameter[25] of 0.71, $\tau_4 = [360° – (\beta + \alpha)]/141°$, where β and α are the largest angles around the Ag(I) ion (β = N1—Ag1—N2 = 130.9(2)° and α = N2—Ag1—N3 = 128.3(2)°). The Ag1–N1/N2(4,7-phen) bond distances in **1** (Table I) adopt values of 2.305(5) and 2.251(5) Å, respectively, and are comparable with those observed in the other pseudo tetrahedral silver(I) complexes with aromatic *N*-heterocycles.[8–14] The Ag1–N3 (acetonitrile) bond distance of 2.284(7) Å falls in the normal range of 2.18–2.33 Å.[26] On the other hand, the Ag1–O1 bond distance of 2.505(6) Å is much longer than usual covalent silver(I)–oxygen bonds of approximately 2.3 Å.[8] In complex **1**, two Ag(I) ions are connected by one 4,7-phen, which behaves as a bridging ligand. The intramolecular Ag···Ag interaction is not observed in this complex, considering the fact that Ag···Ag distance of 7.689 Å is much longer than the commonly Ag···Ag bond range of 2.853–3.290 Å.[27]

Similar to **1**, complex **2** has a distorted tetrahedral geometry (τ_4 = 0,71; Fig. 1b and Table II). In this coordination polymer, each Ag(I) ion is coordinated by two 4,7-phen and two $PO_2F_2^-$ (Fig. 1). Two Ag(I) ions are bridged by one 4,7-phen and one $PO_2F_2^-$, with *d*(Ag–N) = 2.240(3) and 2.252(3) Å and *d*(Ag–O) =

2.500(3) and 2.499(3) Å (an extended view of **2** is presented in Fig. 2b). The Ag–N(4,7-phen) bond lengths in **2** are slightly shorter than in **1**, while the Ag–O bond distances are comparable in these two silver(I) complexes (Table II).



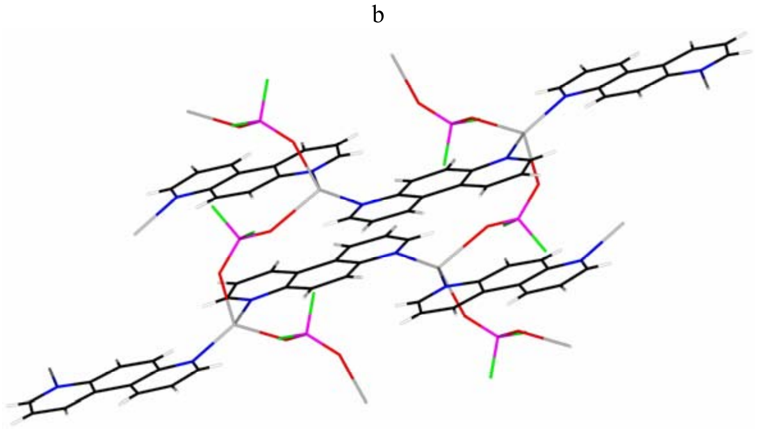


Fig. 2. An extended view of polynuclear silver(I) complexes: a) **1** and b) **2**.

The coordination mode of 4,7-phenanthroline in silver(I) complexes **1** and **2** is the same as in the previously characterized silver(I) complexes with this aromatic *N*-heterocycle.[14] Almost all of the synthesized silver(I) complexes with 4,7-phen are polynuclear species, with the exception of $[Ag_2(H_2O)_{0.58}(4,7\text{-phen})_3](SbF_6)_2$ complex, which is obtained in the reaction of $AgSbF_6$ with an equimolar amount of 4,7-phen in the ethanolic solution.[14] Contrary to 4,7-phen, its structural isomer 1,7-phenanthroline affords mononuclear silver(I) complexes, namely $[Ag(NO_3)(1,7\text{-phen})_2]$ and $[Ag(1,7\text{-phen})_2]X$ ($X = ClO_4^-$, $CF_3SO_3^-$, BF_4^- and SbF_6^-), in which it is monodentately coordinated *via* the less sterically hindered N7 nitrogen atom.[12]

Spectroscopic characterization

The IR and NMR (^{1}H and ^{13}C) spectroscopic data for silver(I) complexes **1** and **2** are given in Supplementary material. The IR spectra of the complexes show the bands which can be attributed to the coordinated 4,7-phen, $CF_3SO_3^-$ and $PO_2F_2^-$ ligands. Thus, in the IR spectrum of **1** with coordinated triflate, a number of strong absorptions in the 1300–1000 cm^{-1} region can be observed. The bands at 1263, 1255 and 1031 cm^{-1} can be assigned to the asymmetric and symmetric stretching modes of the $-SO_3$ group of the triflate anion.[28,29] The splitting of the band corresponding to asymmetric stretching vibration of $-SO_3$ group is an indication of the monodentate coordination of the triflate in **1**.[29] The two bands at 1247 and 1168 cm^{-1} are due to the symmetric and asymmetric stretching modes of $-CF_3$ group, respectively. Additionally, the medium intensity bands at 635 and 517 cm^{-1}, and at 754 and 594 cm^{-1} can be ascribed to the symmetric and asymmetric deformations of $-SO_3$ and $-CF_3$ groups in $CF_3SO_3^-$, respectively.[29] The hydrolysis of PF_6^- and the coordination of $PO_2F_2^-$ to Ag(I) in **2** can be also confirmed from the IR spectrum of this complex. Beside the very strong band at 838 cm^{-1} which is attributed to the ν(PF) mode, two bands at 1305 and 1149 cm^{-1} due to the ν(PO) indicate that the hydrolysis of PF_6^- to $PO_2F_2^-$ occurred in the investigated reaction.[23]

Solution state ^{1}H- and ^{13}C-NMR spectra were recorded in deuterated DMSO with the aim to confirm the coordination of 4,7-phen to the Ag(I) ion. The spectra of the complexes **1** and **2** were compared with those for the free ligand. In the aromatic region, ^{1}H-NMR spectra of the complexes contain the same number of signals as that of the 4,7-phen, indicating that symmetric species are present in solution and that the ligand is coordinated to the Ag(I) ion *via* both donor nitrogen atoms (N4 and N7). However, the resonances for these protons are only slightly shifted downfield compared to those of the free 4,7-phen (up to +0.05 for H5/H6 in **2**). Only small shifts of the resonances of the silver(I) complexes with respect to those for the corresponding ligand seem to be characteristic spectroscopic feature of the silver(I) complexes in solution and was assumed to be the consequence of the fast ligand exchange on the NMR timescale.[6] In addition, a singlet at 2.07 ppm, attributed to the acetonitrile protons, is observed in the spectrum of **1.**

The ^{13}C-NMR spectra were found to be almost identical for the both silver(I) complexes, excluding resonances assigned to the carbon atoms of the coordinated acetonitrile in **1**. Similar to the proton resonances, upon 4,7-phen coordination to Ag(I) ion, the signals of its carbon atoms remain almost unaffected.

CONCLUSION

We have shown that the reactions between 4,7-phen and AgX salts (X = $CF_3SO_3^-$ and PF_6^-) in 1:2 mole ratio, respectively, in methanol/acetone lead to the formation of polynuclear silver(I) complexes, $[Ag(CF_3SO_3)(4,7\text{-phen})(CH_3CN)]_n$

and [Ag(PO_2F_2)(4,7-phen)]$_n$. The crystallographic results revealed that these complexes have a distorted tetrahedral geometry with 4,7-phen being bridging ligand between two Ag(I) ions. The present results are in accordance with those previously reported for the reactions of the same *N*-heterocyclic ligand with different AgX salts (X = NO_3^-, CF_3COO^-, BF_4^-, ClO_4^- and SbF_6^-), most of them leading to the formation of polynuclear silver(I) species with different geometry of Ag(I) metal ion.[14] The only exception was a dinuclear [$Ag_2(H_2O)_{0.58}$(4,7-phen)$_3$](SbF_6)$_2$ complex, obtained in the reaction of $AgSbF_6$ with 4,7-phen in ethanol.[14] This study confirms that the nuclearity and geometry of the silver(I) complexes with aromatic *N*-heterocyclic ligands strongly depend on the reaction conditions, such as starting silver(I) compound, the nature of *N*-heterocyclic ligand and reaction solvent. All these together should be carefully considered during preparation of new silver(I) complexes for different applications in medicinal and supramolecular chemistry.

SUPPLEMENTARY MATERIAL

Analytical and spectral data are available electronically from http://www.shd.org.rs//JSCS/, or from the corresponding author upon request.

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ИЗВОД

СИНТЕЗА И СТРУКТУРНА АНАЛИЗА ПОЛИНУКЛЕАРНИХ КОМПЛЕКСА СРЕБРА(I) СА 4,7-ФЕНАНТРОЛИНОМ

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Полинуклеарни комплекси сребра(I), [Ag(CF_3SO_3)(4,7-phen)(CH_3CN)]$_n$ (**1**) и [Ag(PO_2F_2)(4,7-phen)]$_n$ (**2**), синтетисани су у реакцијама између 4,7-фенантролина (4,7-phen) и одговарајућих AgX соли (X = $CF_3SO_3^-$ и PF_6^-) у молском односу 1:2 у смеши метанол/ацетон (запремински однос 1:1) на собној температури. Ови комплекси су окарактерисани применом елементалне микроанализе, IR и NMR (^1H и ^{13}C) спектроскопије, док је њихова кристална структура одређена применом методе дифракције X-зрака са монокристала. Резултати спектроскопских и кристалографских испитивања показују да је у овим комплексима, 4,7-phen мостни лиганд између два јона метала, док се за преостала два координациона места координује атом кисеоника из $CF_3SO_3^-$ и атом азота из ацетонитрила у комплексу **1**, односно атоми кисеоника из два $PO_2F_2^-$, добијена хидролизом PF_6^-, у комплексу **2**. У чврстом стању, комплекси сребра(I) су координациони полимери, у којима је геометрија сребро(I) јона дисторгована тетраедарска.

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