

Synthesis, Characterization, and Photoluminescence Properties of Silver(I) Metal-Organic Polymers with Nanochannels Based on 2-Sulfoterephthalic Acid and Di(pyridin-2-yl)amine Ligands

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Two new silver(I) 3D coordination polymers, namely $[\text{Ag}_3(2\text{-stp})(\text{dpa})]_n$ (**1**) and $\{[\text{Ag}_2(2\text{-stp})(\text{H}_2\text{O})] \cdot \text{Hdpa}\}_n$ (**2**) (2-NaH₂stp = sodium 2,5-dicarboxysulfonate, dpa = di(pyridine-2-yl)amine) were synthesized. The complexes were characterized by elemental analysis, FT-IR spectra, thermogravimetric analyses (TGA), and single-crystal X-ray diffraction. In complex **1**, three neighboring Ag ions are bridged by N- and O-atom, forming a 3D coordination network. The molecular structure of **2** is cation–anion species, forming 3D host–guest supramolecular network with the $[\text{Hdpa}]^+$ cations encapsulated in the nanochannels. The photoluminescence properties of the complexes were also investigated in the solid state at room temperature.

Introduction. – Supramolecular architectures are aesthetically appealing and exhibit potential applications as molecular wires, electrical conductors, and molecular magnets, in host–guest chemistry and in catalysis [1–6]. The range and variety of self-assembly of inorganic structures that can be constructed relies on the presence of suitable metal–ligand interactions and supramolecular contacts, H-bonds, and other weak interactions [7]. In contrast to other transition-metal ions, the Ag^I ion, with a d¹⁰ closed-shell electronic configuration, gives rise to a dynamic range of coordinative geometries including linear, trigonal-planar, tetrahedral, and trigonal-pyramidal [8–10], which may lead to the formation of novel structural motifs. The bifunctional sulfonate–carboxylate ligands have been widely used to construct various coordination complexes, owing to their fascinating characteristics, including strong coordination ability, diverse coordination modes, and abundant H-bonding interactions [11–13]. The design of polymeric coinage d¹⁰ metal complexes with fascinating structures has received much attention [14], among these metals, Ag has received much attention because Ag^I shows a tendency to form coordination polymers and unique Ag–Ag bonds [15]. In this article, we report the syntheses, crystal structures, and properties of two new mixed-ligand coordination complexes, namely $[\text{Ag}_3(2\text{-stp})(\text{dpa})]_n$ (**1**) and $\{[\text{Ag}_2(2\text{-stp})(\text{H}_2\text{O})] \cdot \text{Hdpa}\}_n$ (**2**) (H₂(2-stp) = 2-sulfoterephthalic acid; dpa = di(pyridin-2-yl)amine).

Results and Discussion. – *Structure of $[\text{Ag}_3(2\text{-stp})(\text{dpa})]_n$ (**1**).* The single-crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the $P2_1/c$ space group and

possesses a 3D coordination polymer framework. There are three Ag^{I} ions, one 2-stp ligand, and one dpa ligand in the asymmetric unit. As illustrated in *Fig. 1*, both $\text{Ag}(1)$ and $\text{Ag}(3)$ are three-coordinated by N- and O-atoms: two N-atoms from two dpa ligands, one O-atom from 2-stp ligand for $\text{Ag}(1)$ ($\text{Ag}(1)\text{--O}(1) = 2.272(3)$, $\text{Ag}(1)\text{--N}(1) = 2.387(4)$, $\text{Ag}(1)\text{--N}(3)\#1 = 2.278(4)$ Å), and three O-atoms of another three 2-stp ligands for $\text{Ag}(3)$ ($\text{Ag}(3)\text{--O}(3) = 2.278(4)$, $\text{Ag}(3)\text{--O}(7)\#2 = 2.205(3)$, $\text{Ag}(3)\text{--O}(3)\#4 = 2.556(4)$ Å). $\text{Ag}(2)$ is four-coordinated by four O-atoms from three different 2-stp ligands ($\text{Ag}(2)\text{--O}(2) = 2.209(3)$, $\text{Ag}(2)\text{--O}(2)\#3 = 2.554(3)$, $\text{Ag}(2)\text{--O}(6)\#2 = 2.173(3)$, and $\text{Ag}(2)\text{--O}(4)\#2 = 2.452(4)$ Å).

Moreover, there are two kinds of $\text{Ag} \cdots \text{Ag}$ interactions in the coordination environments of the Ag^{I} ions, one is between $\text{Ag}(1)$ and $\text{Ag}(2)$ with distance of $2.9363(5)$ Å, and the other is between $\text{Ag}(2)$ and $\text{Ag}(3)$ with a distance of $2.9039(6)$ Å. Both are slightly longer than the $\text{Ag}\text{--Ag}$ separation in metallic state (2.889 Å) and significantly shorter than the sum of the *Van der Waals* radii (3.44 Å) [16].

Complex **1** exhibits a 3D supramolecular structure, which can be rationalized in the following manner. First, the two Ag^{I} ions are linked by the carboxylate and sulfonate groups of 2-stp anions in a μ_7 -bridging mode (*Fig. 2*) to form 2D layers containing $\text{Ag}(2) \cdots \text{Ag}(3)$ interactions (*Fig. 3*). Subsequently, with Ag as node, two pairs of reverse-direction bidentate dpa ligands link adjacent carboxylate O-atom (O(1)) from 2-stp to form a 3D framework (*Fig. 4*). Additionally, the NH_2 group of dpa ligands form H-bonds ($\text{N}(2)\text{--H}(2) \cdots \text{O}(1)$ $3.013(5)$ Å) with the coordinated O(1)-atom of the COO groups, which further enhances the stability of the 3D framework.

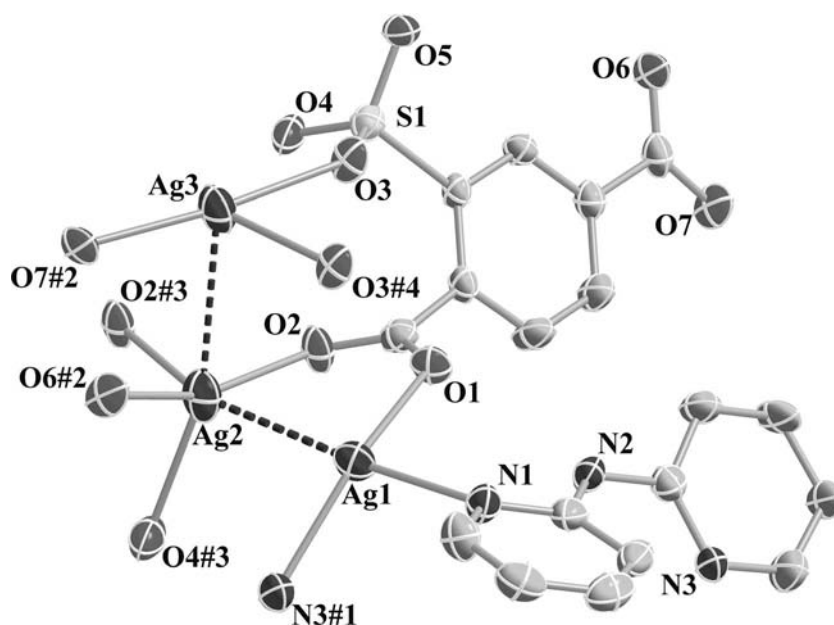
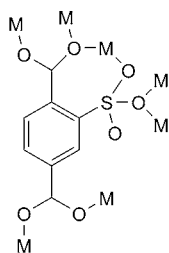
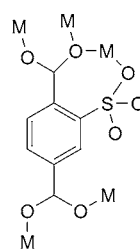
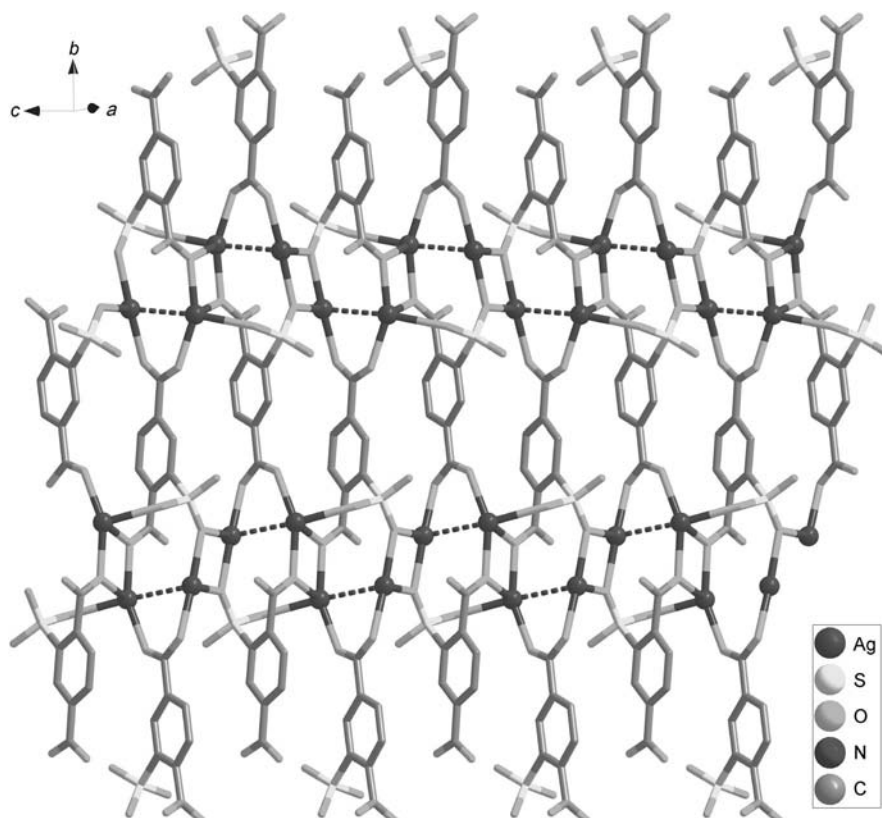


Fig. 1. Perspective view of the coordination environment of the Ag^{I} ion in **1**. The H-atoms were omitted for clarity. Symmetry codes: #1 ($-x, -y + 1, -z + 2$); #2 ($-x + 1, y - 1/2, -z + 5/2$); #3 ($-x + 1, -y + 1, -z + 3$); #4 ($-x + 1, -y + 1, -z + 2$)

a) $\mu_7\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$

 b) $\mu_5\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$

 Fig. 2. The coordination modes of 2-stp ligand in complexes **1** and **2**

 Fig. 3. Perspective views of the 2D layer through μ_7 -bridging 2-stp ligand

Structure of $\{[Ag_2(2\text{-stp})(H_2O)] \cdot Hdpa\}_n$ (**2**). Complex **2** crystallizes also in the space group $P2_1/c$ and adopts a novel 3D supramolecular structure. It contains a $[Ag_2(2\text{-stp})(H_2O)]$ anion and a $[Hdpa]^+$ cation. As shown in Fig. 5, Ag(1) adopts a *T*-shaped geometry completed by three O-atoms from two 2-stp ligands and coordinated H_2O molecule ($Ag(1)\text{--}O(6) = 2.165(5)$, $Ag(1)\text{--}O(9) = 2.546(7)$, $Ag(1)\text{--}O(2)\#1 =$

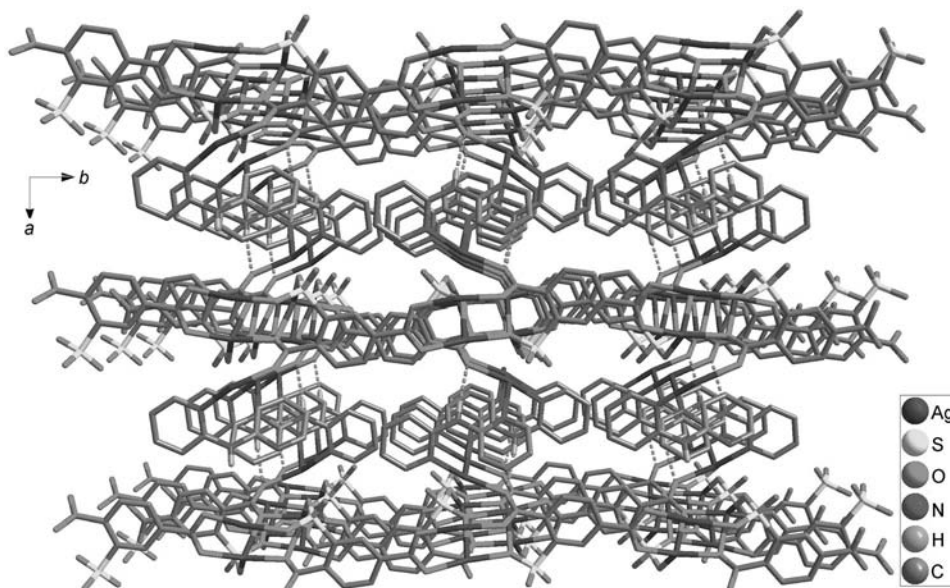


Fig. 4. Perspective views of the 3D network

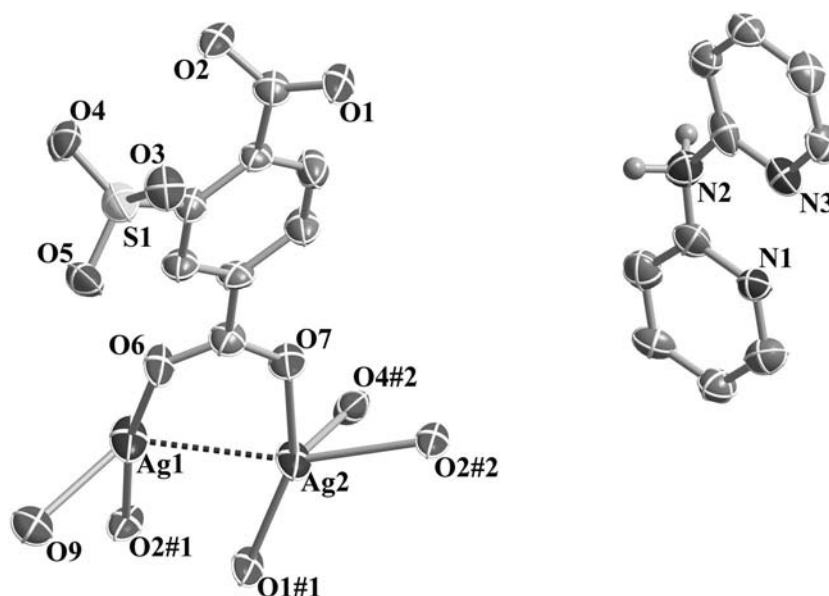


Fig. 5. Perspective view of the coordination environment of the Ag^+ ion in **2**. The H-atoms were omitted for clarity. Symmetry codes: #1 ($x+1, y, z+1$); #2 ($x+1, -y+1/2, z+1/2$)

2.169(4) Å). Ag(2) has a four-coordinated distorted tetrahedral geometry completed by four O-atoms from three different 2-stp ligands (Ag(2)–O(7) = 2.266(5), Ag(2)–O(1)#1 = 2.243(4), Ag(2)–O(2)#2 = 2.447(4), Ag(2)–O(4)#2 = 2.558(5) Å).

Along the *b* axis, the 2-stp anions play the role of an organic pillar, adopt $\mu 5-\eta 2:\eta 1:\eta 1:\eta 1:\eta 1$ coordination modes (Fig. 2, *a*) to interconnect Ag centers, forming 2D $[\text{Ag}_2(2\text{-stp})\text{H}_2\text{O}]_n$ -layers, including $\text{Ag} \cdots \text{Ag}$ interactions with a distance of 2.833(1) Å (Fig. 6). The 2D layers are further interconnected *via* H-bonds to afford an unusual 3D supramolecular architecture existing in continuous channels occupied by $[\text{Hdpa}]^+$ cations, thus giving rise to the 3D host–guest supramolecular network with the $[\text{Hdpa}]^+$ cations encapsulated in the channels (Fig. 7).

FT-IR Spectra and Thermogravimetric (TG) Analyses. The IR spectra of compounds **1** and **2** showed peaks attributable to the carboxy- and sulfo-group stretching vibrations. The characteristic bands of the carboxy groups appeared in the range of 1655–1524 cm^{-1} for asymmetric stretching and of 1382–1226 cm^{-1} for symmetric stretching. The absorption band in the ranges of 1190–1136 and 1070–1016 cm^{-1} were assigned to asymmetric and symmetric stretching, respectively, of the sulfo group.

The thermogravimetric (TG) analysis was performed under N_2 on polycrystalline samples of compounds **1** and **2** (Fig. 8). The TG curve of **1** shows the first weight loss of 22.85% in the temperature range of 200–300°, indicating the exclusion of dpa ligands (calc. 23.20%). Then, from 300 to 500° release of 2-stp begins without a clear inflection with the residue of Ag_2O (obs. 25.50%; calc. 26.50%). Complex **2** starts to lose one lattice H_2O molecule in the temperature range of 100–200° (obs. 2.77%; calc. 2.61%), then from 250 to 700° release of 2-stp ligand and $[\text{Hdpa}]^+$ begins without a clear inflection with the residue of Ag (obs. 52.29%; calc. 52.70%).

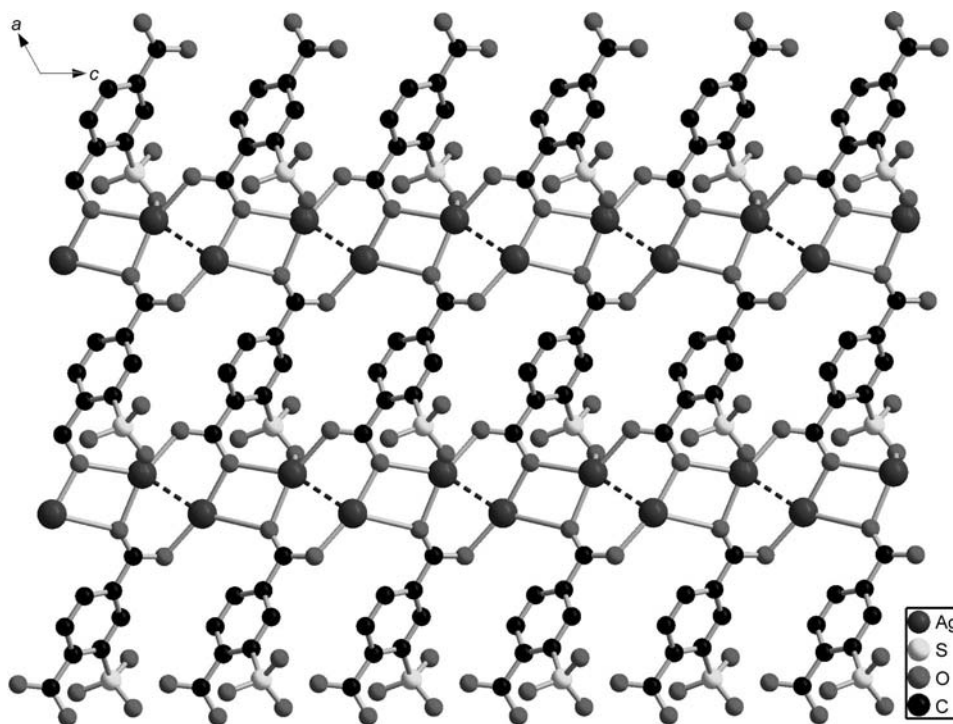


Fig. 6. View of the 2D $[\text{Ag}_2(2\text{-stp})]_n$ layer structure, including $\text{Ag} \cdots \text{Ag}$ interactions

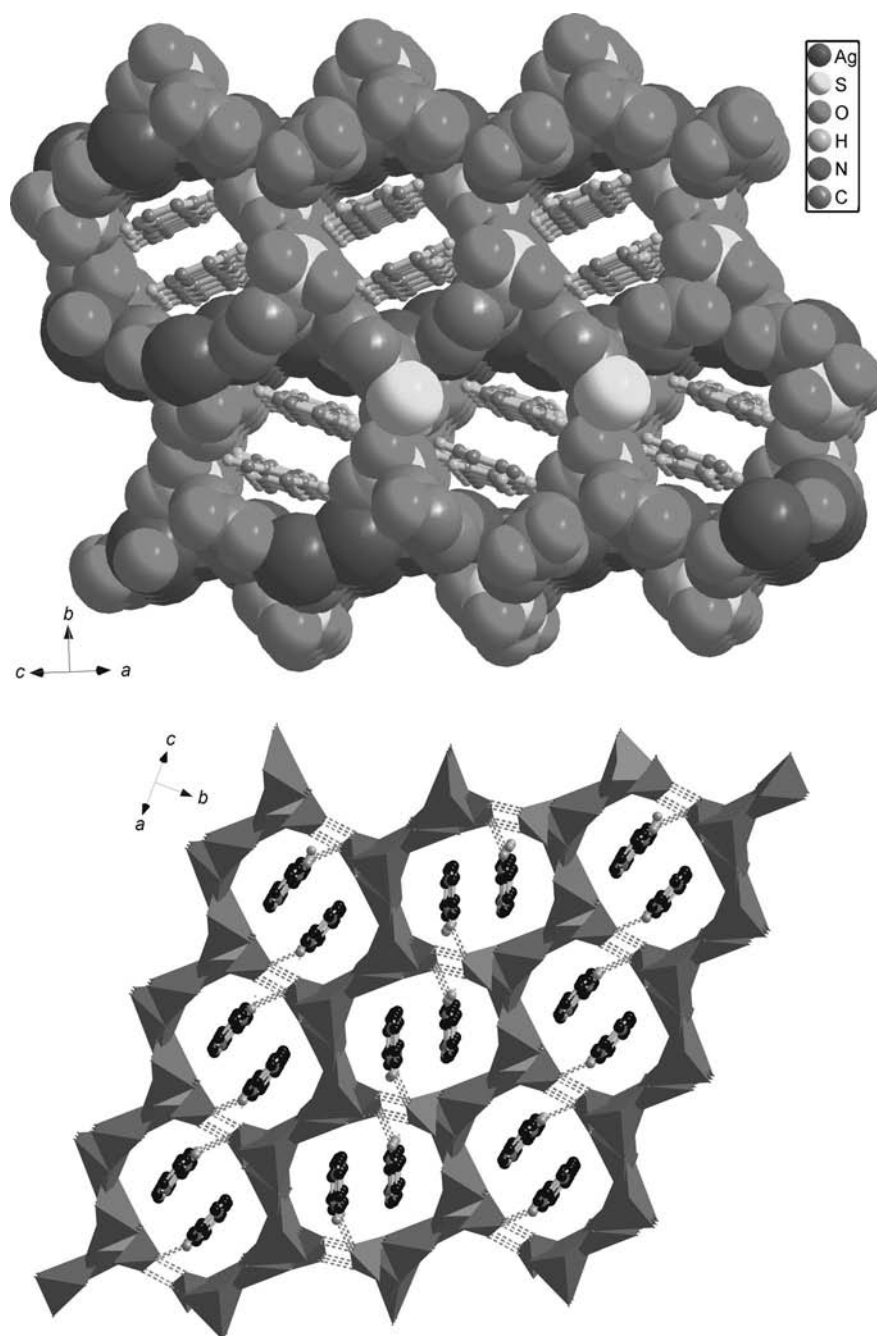


Fig. 7. 3D Host-guest supramolecular network with the $[Hdpa]^+$ cations encapsulated in the nano-channels

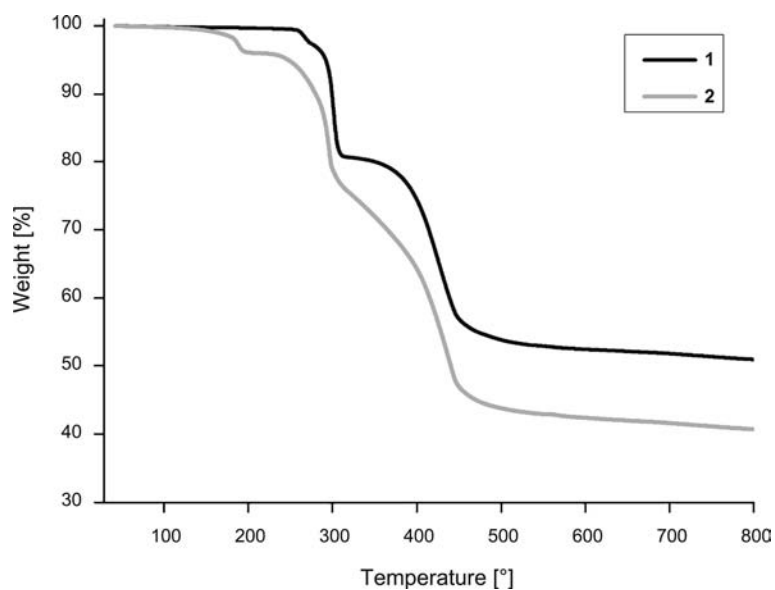


Fig. 8. Thermal gravimetric analysis (TGA) curves for complexes **1** and **2**

The photoluminescence properties of **1** and **2** were examined in the solid state at room temperature (Fig. 9). Complexes **1** and **2** exhibit the maximum broad emission peaks at 418 (λ_{ex} 358 nm) and 405 nm (λ_{ex} 363 nm), respectively, which can be assigned

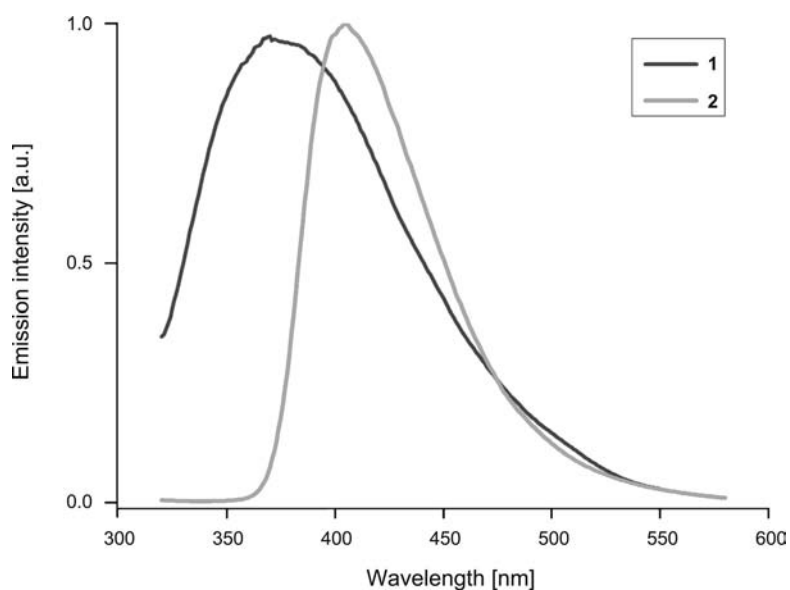


Fig. 9. The solid-state emission photoluminescent spectra of **1** (λ_{ex} 358 nm) and **2** (λ_{ex} 363 nm) at room temperature

to the intraligand $\pi-\pi^*$ transition of two ligands stp and dpe, based on the comparison of the location and profile of the emission bands of 2-Na-H₂stp (421 nm) and dpa (459 nm).

Conclusions. – In summary, two new Ag^I coordination polymers with 2-sulfothephthalic acid and di(pyridine-2-yl)amine, [Ag₃(2-stp)(dpa)]_n (**1**) and {[Ag₂(2-stp)(H₂O)]·Hdpa}_n (**2**), have been synthesized and structurally characterized. The photoluminescent properties of the coordination polymers were investigated. The structures of **1** and **2** are 3D network structures.

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Experimental Part

General. All reagent-grade chemicals and solvents were obtained from commercial sources and used without further purification for the syntheses. The fluorescence spectra of powdered samples were recorded in the solid state at r.t. with a *Shimadzu RF-7000* spectrometer. The TG analysis was carried out on a *PerkinElmer TG/DTA 6300* thermal analyzer under flowing N₂, with a heating rate of 10°/min. IR Spectra: *Bruker Equinox 55* FT-IR spectrometer as KBr pellets; $\tilde{\nu}$ in cm⁻¹. Elemental analyses for C, H, and N: *PerkinElmer* analyzer model *1110*. The fluorescence study was carried out on a CHN–O–Rapid Analyzer and an *Elementar Vario Microanalyzer*.

*Synthesis of [Ag₃(2-stp)(dpa)]_n (**1**).* A mixture of AgNO₃ (0.0169 g, 0.10 mmol), sodium 2,5-dicarboxybenzenesulfonate salt (0.0268 g, 0.10 mmol), di(pyridine-2-yl)amine (0.0171 g, 0.010 mmol), and NaOH (0.008 g, 0.20 mmol) were dissolved in dist. H₂O (15 ml) and EtOH (5 ml), and allowed to evaporate in the dark. After 2 weeks, pale-yellow platy crystals were obtained. FT-IR (selected bands): 3294w, 1593s, 1524s, 1382s, 1226s, 1136s, 1059m, 763s, 675w, 615m, 569m, 512m. Anal. calc. for C₁₈H₁₂Ag₃N₃O₇S: C 29.30, H 1.64, N 5.69; found: C 29.18, H 1.56, N 5.58.

*Synthesis of {[Ag₂(2-stp)(H₂O)]·Hdpa}_n (**2**).* A mixture of AgNO₃ (0.0169 g, 0.10 mmol), sodium 2,5-dicarboxybenzenesulfonate salt (0.0268 g, 0.10 mmol), and di(pyridine-2-yl)amine (0.0171 g, 0.010 mmol) were dissolved in dist. H₂O (15 ml) and EtOH (5 ml), and then allowed to evaporate in the dark. After 3 d, colorless block-shaped crystals were obtained. FT-IR (selected bands): 3439w, 2990w, 1655s, 1595s, 1382s, 1190s, 1070m, 1016m, 766s, 677m, 622m, 514m. Anal. calc. for C₁₈H₁₅Ag₂N₃O₈S: C 33.31, H 2.33, N 6.47; found: C 33.26, H 2.22, N 6.34.

Single crystals of the complexes **1** and **2** with appropriate dimensions were mounted on a glass fiber and used for data collection. Data were collected on a *Bruker Smart Apex II CCD* area detector diffractometer with a graphite-monochromated MoK_α radiation source (λ 0.71073 Å). All absorption corrections were performed with the SADABS program [17]. All the structures were solved by direct methods using SHELXS-97 [18] and refined by full-matrix least-square techniques using SHELXL-97 [19]. All the non-H-atoms were treated anisotropically. The positions of the H-atoms were generated geometrically. The crystallographic details of **1** and **2** are collected in *Table 1*¹⁾. Selected bond lengths and bond angles are compiled in *Tables 2* and *3*.

¹⁾ CCDC-903102 and 903103 contain the supplementary crystallographic data for **1** and **2**, resp. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Data for Compounds 1 and 2

	1	2
Empirical formula	C ₁₈ H ₁₂ Ag ₃ N ₃ O ₇ S	C ₁₈ H ₁₅ Ag ₂ N ₃ O ₈ S
<i>M_r</i>	737.98	649.13
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell parameters:		
<i>a</i> [Å]	11.5558(7)	10.7916(6)
<i>b</i> [Å]	22.0004(12)	18.5791(11)
<i>c</i> [Å]	7.8020(5)	11.2595(6)
<i>α</i> [°]	90	90
<i>β</i> [°]	104.389(1)	118.577(1)
<i>γ</i> [°]	90	90
<i>V</i> [Å ³]	1921.3(2)	1982.49(19)
<i>Z</i>	4	4
<i>D_x</i> [g cm ⁻³]	2.551	2.175
<i>μ</i> [mm ⁻¹]	3.188	2.136
<i>θ</i> Range	1.85–25.10	2.19–25.09
Reflections collected	14143	8297
Unique reflections	3395	3502
No. of parameter	290	289
<i>F</i> (000)	1416	1272
<i>R</i> ₁ ^a [<i>I</i> > 2σ], <i>wR</i> ₂ ^b (all data)	0.0313, 0.0956	0.0432, 0.1781
Goodness-of-fit on <i>F</i> ²	1.102	1.081
Largest and hole [e Å ⁻³]	0.806; –1.391	1.088; –1.229

^a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma F_o$. ^b) $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$.

Table 2. Selected Bond Lengths and Angles for Complex 1^a

Lengths [Å]			
Ag(1)–O(1)	2.272(3)	Ag(2)–O(6)#2	2.173(3)
Ag(1)–N(1)	2.387(4)	Ag(2)–O(4)#3	2.452(4)
Ag(1)–N(3)#1	2.278(4)	Ag(3)–O(3)	2.278(4)
Ag(2)–O(2)	2.209(3)	Ag(3)–O(3)#4	2.556(4)
Ag(2)–O(2)#3	2.554(3)	Ag(3)–O(7)#2	2.205(3)
Ag(1)–Ag(2)	2.9363(5)	Ag(2)–Ag(3)	2.9039(6)
Angles [°]			
O(1)–Ag(1)–N(3)#1	152.40(14)	O(6)#2–Ag(2)–O(2)#3	106.82(13)
O(1)–Ag(1)–N(1)	96.73(13)	O(2)–Ag(2)–O(2)#3	78.84(13)
N(3)#1–Ag(1)–N(1)	94.03(14)	O(4)#3–Ag(2)–O(2)#3	82.46(12)
O(6)#2–Ag(2)–O(2)	157.02(14)	O(7)#2–Ag(3)–O(3)	172.38(14)
O(6)#2–Ag(2)–O(4)#3	96.73(14)	O(7)#2–Ag(3)–O(3)#4	108.27(13)
O(2)–Ag(2)–O(4)#3	106.15(13)	O(3)–Ag(3)–O(3)#4	79.26(13)

^a) Symmetry codes: #1 (–*x*, –*y* + 1, –*z* + 2); #2 (–*x* + 1, *y* – 1/2, –*z* + 5/2); #3 (–*x* + 1, –*y* + 1, –*z* + 3); #4 (–*x* + 1, –*y* + 1, –*z* + 2).

Table 3. Selected Bond Lengths and Angles for Complex 2^{a)}

Lengths [Å]			
Ag(1)–O(6)	2.165(5)	Ag(2)–O(1)#1	2.243(4)
Ag(1)–O(2)#1	2.169(4)	Ag(2)–O(7)	2.266(5)
Ag(1)–O(9)	2.546(7)	Ag(2)–O(2)#2	2.447(4)
Ag(1)–Ag(2)	2.8333(7)	Ag(2)–O(4)#2	2.558(5)
Angles [°]			
O(6)–Ag(1)–O(2)#1	166.82(18)	O(7)–Ag(2)–O(2)#2	78.09(16)
O(6)–Ag(1)–O(9)	95.8(2)	O(1)#1–Ag(2)–O(4)#2	90.53(18)
O(2)#1–Ag(1)–O(9)	88.5(2)	O(7)–Ag(2)–O(4)#2	109.22(17)
O(1)#1–Ag(2)–O(7)	154.24(18)	O(2)#2–Ag(2)–O(4)#2	76.72(17)
O(1)#1–Ag(2)–O(2)#2	123.80(15)		

^{a)} Symmetry codes: #1 ($x + 1, y, z + 1$); #2 ($x + 1, -y + 1/2, z + 1/2$).

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