

Research paper

Water-soluble Ag(I)-based coordination polymers obtained by anion-directed self-assembly of various AgX salts and a phosphobetaine derived from 1,3,5-triaza-7-phosphaadamantane

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Dedicated to Professor Maurizio Peruzzini in recognition of his numerous outstanding achievements in several branches of modern chemistry.

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ABSTRACT

A new, solvent-free method has been developed for the synthesis of 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (L). It is disclosed here that 1,3,5-triaza-7-phosphaadamantane (PTA) reacted cleanly with acrylic acid in a planetary ball mill resulting in 88% yield of the corresponding *P*-carboxy-ethyl derivative, in striking contrast to the complete failure of the synthesis of the same product from the same reactants in solution. The resulting phosphobetaine, L gave crystalline 1D coordination polymers with Ag⁺-salts bearing PF₆⁻, *p*-toluenesulfonate (tos) and trifluoromethanesulfonate (OTf) anions. According to single-crystal X-ray diffraction studies, the solid state structures of these coordination polymers were decisively influenced by the anion of the Ag⁺-salt used for synthesis. In addition to single-crystal X-ray diffraction, the new Ag-based coordination polymers, namely [Ag(μ₃-L-κ³N:O:O')]_n(PF₆)_n, (1), [Ag(tos)(μ₃-L-κ³N:O:O')]_n·nH₂O, (2), and [Ag(OTf)(μ₃-L-κ³N:O:O')]_n, (3) were characterized also by elemental analysis, ¹H-, ¹³C-, and ³¹P NMR, as well as IR spectroscopies and with ESI mass spectrometry. Determination of the hydrodynamic diameter of the phosphobetaine ligand and its Ag⁺-complexes by diffusion NMR measurements revealed, that upon dissolution in water these compounds did not retain their polymeric nature.

1. Introduction

Coordination polymers exhibit useful properties in several respects, such as, for example, catalysis, storage or separation of gases, luminescence, etc. [1–3]. The self-assembled, solid architectures can be modified relatively easily with the change of the metal ion or the complexing agents, or with the use of ancillary ligands. The resulting structures are influenced by several parameters, such as the temperature, pH, and the coordination ability of the solvent. In several cases, the anion of the applied metal salt also has an effect on the resulting structure [4–6] which is illustrated by the polymers obtained in the reaction of various Ag-salts and 1,3,5-triaza-7-phosphaadamantane (PTA; Scheme 1).

PTA is soluble in water and in polar organic solvents, and by virtue of

its four donor atoms, it is capable of coordinating several (identical or different) metal ions [7–9]. The first PTA-containing water-soluble organometallic polymer was synthesized by Peruzzini, Romerosa and co-workers, in which Ru(II) and Ag(I) ions were held together by a *P,N*-coordinated ligand [10]. Other polymers were obtained by coordination of various metal ions, such as Au, Co, Zn to [(Cp)Ru(PTA)₂Cl] [11–19]. PTA-based polymers, containing exclusively Ag(I)-ions, have also been described [20–29], several of which showed antitumor and antibacterial effects.

The first polymer in which PTA served as a tridentate bridging ligand between Ag(I) ions to form a 2D coordination network, was isolated from an aqueous solution containing PTA and AgNO₃ in equimolar amounts. In the polymer assembled from [(Ag(κOH₂)(μ₃-PTA-κ³P:N:N))]

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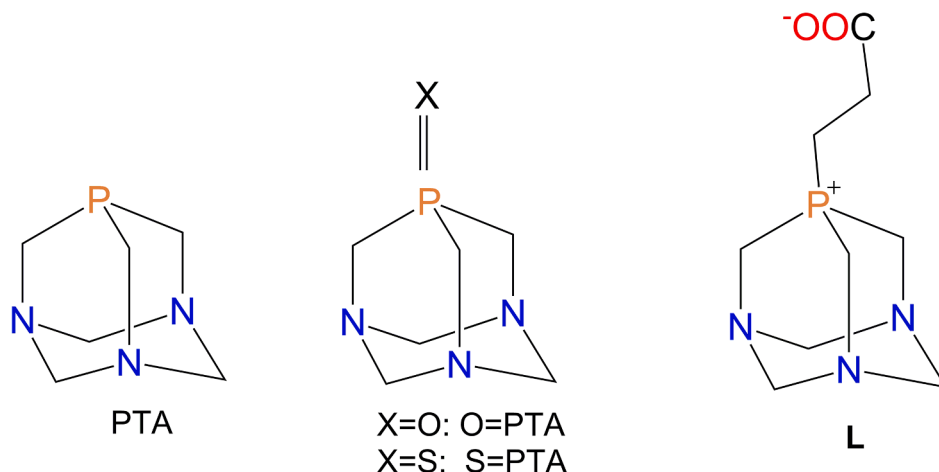
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Scheme 1. PTA (1,3,5-triaza-7-phosphaadamantane), its oxide and sulphide and 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (L).

repeating units, each Ag^+ was coordinated by three PTA and one H_2O molecule in a distorted tetrahedral arrangement, while the anions were placed into the holes of the polymeric network [20]. However, when benzoic acid (or its derivatives) were added to a solution of PTA and AgNO_3 in a solvent mixture of $\text{MeOH}:\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$ (5:5:0.5 mL), coordination polymers of diverse topologies were obtained, as a result of the effects of the carboxylate and other coordinating groups of the ancillary ligands [21]. Similar observations were made with the use of aliphatic dicarboxylic acids [22,24,26], substituted cyclohexanecarboxylic acids [22] and pyromellitic acid, too [28]. The influence of an ancillary reagent on the composition and structure of the products is conspicuously shown by the aqueous reaction of PTA with $\text{Cu}(\text{NO}_3)_2$, which –in the absence of any additive– yields $[\text{Cu}(\text{PTA})_4](\text{NO}_3) \times 6\text{H}_2\text{O}$ but results in formation of the polymeric $[\text{Cu}(\mu\text{-N}_3)(\mu_2\text{-PTA}:\kappa^2\text{P:N})]_n$ in presence of NaN_3 [30]. In fact, the latter compound was the first example of a homometallic 1D coordination polymer with PTA.

While the reaction of PTA with AgNO_3 yielded a polymer in which the nitrate anion did not coordinate to Ag^+ [20], in the polymers obtained with the use of Ag-nitrite, Ag-acetate, and Ag-trifluoroacetate the anions were bonded directly to the metal ion. In the ladder-type polymers $[\text{Ag}(\mu_2\text{-PTA}:\kappa^2\text{P:N})(\mu_2\text{-O}_2\text{N}:\kappa^2\text{O}:\text{O}')]_n$ [27], $[(\text{Ag}(\mu_2\text{-PTA}:\kappa^2\text{P:N})(\mu_2\text{-O}_2\text{CCH}_3:\kappa^2\text{O}:\text{O}')]_n \cdot 2\text{H}_2\text{O}$, and $[(\text{Ag}(\mu_2\text{-PTA}:\kappa^2\text{P:N})(\mu_2\text{-O}_2\text{CCF}_3:\kappa^2\text{O}:\text{O}')]_n \cdot n\text{H}_2\text{O}$ [29], both PTA and the anions behaved as bidentate ligands.

The anions also influence the structure of the Ag(I)-based polymers obtained with PTA-oxide ($\text{O} = \text{PTA}$, Scheme 1). The product of complex formation between PTA-oxide and AgNO_3 was $[\text{Ag}(\text{NO}_3)(\mu_3\text{-}\{\text{O} = \text{PTA}\}:\kappa^3\text{O:N:N})]_n$, however, the reaction of Ag_2SO_4 yielded $[\text{Ag}_2(\mu_2\text{-SO}_4)(\mu_5\text{-}\{\text{O} = \text{PTA}\})(\text{H}_2\text{O})]_n$, in which three nitrogen atoms coordinate to one Ag^+ , each, while the oxygen is bound to two Ag(I) ions [31]. The reaction of the same two Ag-salts with PTA-sulfide ($\text{S} = \text{PTA}$, Scheme 1), resulted in the formation of $[\text{Ag}(\mu_3\text{-}\{\text{S} = \text{PTA}\}:\kappa^3\text{S:N:N})]_n(\text{NO}_3)_n \cdot n\text{H}_2\text{O}$ and $[\text{Ag}_4(\mu_2\text{-SO}_4)_2(\mu_4\text{-}\{\text{S} = \text{PTA}\})(\mu_5\text{-}\{\text{S} = \text{PTA}\})(\text{H}_2\text{O})_2]_n \times 2n\text{H}_2\text{O}$ polymers [32–33]. In addition, in the coordination polymer $[\text{Cu}_6(\mu_3\text{-I})_6(\mu_3\text{-}\{\text{O} = \text{PTA}\}:\kappa^3\text{N:N:N})_2]_n$ (obtained in the reaction of Cu(I)-iodide and $\text{PTA} = \text{O}$), exclusive N-coordination of PTA-oxide was determined [34].

In the Morita-Baylis-Hillman type reaction of aldehydes with ethylacrylate, catalyzed by PTA, a P-substituted PTA derivative, 7-(2-carboxy-ethyl)-1,3,5-triaza-7-phosphonia-tricyclo[3.3.1.1^{3,7}]decane (L, Scheme 1) was isolated as a reaction intermediate [35,36].

In this paper, we report a new, mechanochemical synthesis of the above phosphobetaine, L. Furthermore, coordination chemical properties of L were investigated the first time. In aqueous solutions, reactions of L with three AgX salts ($\text{X} = \text{PF}_6$, CF_3SO_3 , $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$) resulted in formation of coordination polymers. The solid state structure of the polymers was determined by single crystal X-ray diffraction, while the

molecular state of the polymers after dissolution in water was studied by diffusion NMR experiments. The results of these studies are also reported here.

2. Experimental part

2.1. Materials and methods

PTA was synthesized as described in the literature [37]. All other chemicals were commercial products of high purity and were used without further purification.

Elemental analyses were done on an Elementar Vario Micro (CHNS) equipment. High-resolution electrospray ionization mass spectra (HR ESI-MS) measurements were carried out on a Bruker maXis II MicroTOF-Q type Qq-TOF-MS instrument, controlled by Compass Data Analysis 4.4 software. Mass spectra were evaluated by the IsoPro 3.1 program. A Perkin Elmer Instruments Spectrum One FT-IR spectrometer equipped with a Universal ATR Sampling Accessory was used to record the IR spectra. Peak labelling: *w* (weak), *m* (medium), *s* (strong), *vs* (very strong).

NMR measurements were carried out with the use of BRUKER DRX 360 or Bruker Avance I 400 MHz spectrometers equipped with z-gradient BBI probe head. Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS (¹H), (¹³C) and to 85% H_3PO_4 (³¹P). Spectra were evaluated with the use of the Bruker TopSpin 3.6.2 program. Multiplicities: *s* (singlet), *d* (doublet), *t* (triplet), *dt* (doublet of triplets), *h* (heptet), *m* (multiplet).

Diffusion NMR measurements [38–43] were carried out at 298 ± 0.2 K (Bruker BSCU 05 cooling unit) with the use of a stimulated spin echo pulse sequence together with a bipolar gradient (LEDBPGP2S) to minimize the effects of eddy currents. Diffusion of D_2O and the Ag(I)-based coordination polymers could be investigated with the same parameter set. Diffusion time $\Delta = 30$ ms, and gradient pulse length $\delta = 6$ ms were applied throughout. Gradient field strength (*G*) was varied in the 2–95% range in 32 quadratic steps. The maximum pulsed gradient strength was approximately 50 G cm^{-1} . Experimentally determined echo intensities were evaluated by the following equation:

$$I = I_{(0)} \times \exp(-G^2 \gamma^2 \delta^2 D(\Delta - \delta/3))$$

where *I* and *I*₍₀₎ are the echo intensities at a given and at the initial gradient strength, respectively; *G*: pulsed gradient strength (T m^{-1}); γ : gyromagnetic ratio (MHz T^{-1}); Δ : diffusion time (s); *D*: diffusion coefficient ($\text{m}^2 \text{s}^{-1}$); δ : gradient pulse length (s). All experiments involved 32 measurement points and the series of resulting spectra were evaluated by the MestreNova © 8.1 software. The calibration constant of the

gradient field was left unchanged during the evaluation. The diffusion coefficient D_2O , determined with the use of the same constant, was equal to that known from the literature ($1.902 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [44]). From the experimentally determined diffusion constants (D) of the silver complexes, the hydrodynamic radii (R_D) of the diffusing species were obtained with the use of the Einstein–Stokes equation: $D_{\text{exp}} = k_B T (6\pi\eta R_D)^{-1}$ (k_B = Boltzmann constant, η = viscosity of the solution).

Single crystal X-ray diffraction measurements were made on a Bruker-Nonius MACH3 four-circle diffractometer [45] or on a SuperNova CCD diffractometer [46] with Mo K α ($\lambda = 0.71073$) radiation in both cases. The structures were solved and refined with the use of SHELX [47,48] software packages, and managed by the OLEX² [49], and WINGX [50] crystallographic suites. The optimized structures of the molecules were analyzed with the use of PLATON [51], graphics were prepared with the Mercury [52] and OLEX² software.

The crystallographic data for all coordination polymers (including structure factors) were deposited in the Cambridge Crystallographic Data Centre (CCDC) with No 2046048, 2046052–2046053.

2.2. Synthesis of **L** and its Ag-based coordination polymers

2.2.1. 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (**L**)

A. In solution, ligand **L** was prepared by a modified literature procedure [35]. Under a well ventilated hood, in a 100 mL Schlenk flask, 500 mg (3.18 mmol) PTA was dissolved in 5 mL deoxygenated water, followed by the addition of 310 μL (3.4 mmol, $\rho = 0.95 \text{ g/mL}$) methyl acrylate. To this reaction mixture, the minimum amount of acetone was added dropwise to obtain a homogeneous solution, which was then stirred at 70 °C for 7 h. The volatiles were removed under reduced pressure, the off-white residue was dissolved in 5 mL methanol, and filtered through a Hyflo Super Cel pad. The solvent was evaporated, the white residue was washed with $3 \times 10 \text{ mL}$ acetone followed by $2 \times 10 \text{ mL}$ diethyl ether. Yield: 752 mg (89%).

B. The mechanochemical procedure. Into a 12 mL RETSCH-type stainless steel jar were added 157 mg (1 mmol) PTA and 69 μL (1 mmol) acrylic acid together with 5 pieces of stainless steel milling balls ($\varnothing 5 \text{ mm}$). The mixture was milled at 550 rpm for 2 h (in cycles of 2 min milling + 1 min cooling). The product was washed out from the jar with the minimum amount of water which was subsequently evaporated. The white residue was washed with 5 mL acetone followed by 5 mL diethyl ether. Yield 200 mg (88%).

The products of both procedures displayed spectroscopic characteristics identical to those published in the literature [35,36] (Fig. S1A, S1B).

Safety Warnings! Methyl acrylate is a colourless liquid with a burning smell. It is toxic and flammable, and its use requires a well-ventilated hood. Please, consult the MSDS sheet.

2.2.2. Reactions of 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (**L**) with AgX salts

To a solution of 100 mg (0.44 mmol) 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (**L**) in 4 mL water, was added with exclusion of light 1 mmol AgX (253 mg AgPF₆, or 257 mg AgCF₃SO₃ or 297 mg Ag-tosylate) dissolved in 3 mL water. 2-Propanol was layered on the top of the aqueous reaction mixtures which were then stored in the refrigerator. In about 2 weeks the products separated as colourless crystals which were isolated by filtration and washed with cold 2-propanol and finally dried.

$[\text{Ag}(\mu_3\text{-L-}\kappa^3\text{N:O:O'})_n(\text{PF}_6)_n$ (**1**)

Yield (based on **L**): 109 mg (51%)

¹H NMR (360 MHz, D₂O, 25 °C): δ 4.65 (d, $J_{\text{AB}} = 13.5 \text{ Hz}$, 3H, $N\text{-CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}$), 4.60 (d, $^2J_{\text{PH}} = 6.8 \text{ Hz}$, 6H, $^+\text{P-CH}_2\text{-N}$), 4.53 (d, $J_{\text{AB}} = 13.2 \text{ Hz}$, 3H, $N\text{-CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}$), 2.59 (dt, $^2J_{\text{PH}} = 23.8$, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 2H, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$), 2.35 (dt, $^3J_{\text{PH}} = 13.5$, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 2H, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$) ppm (Fig. S2A).

¹³C{¹H} NMR (90 MHz, D₂O, 25 °C): δ 179.4 (d, $^3J_{\text{PC}} = 4 \text{ Hz}$, COO^-), 71.6 (d, $^3J_{\text{PC}} = 9 \text{ Hz}$, $N\text{-CH}_2\text{-N}$), 49.0 (d, $^1J_{\text{PC}} = 38 \text{ Hz}$, $^+\text{P-CH}_2\text{-N}$), 29.0 (d, $^2J_{\text{PC}} = 7 \text{ Hz}$, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$), 18.6 (d, $^1J_{\text{PC}} = 36 \text{ Hz}$, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$) ppm (Fig. S2B).

³¹P{¹H} NMR (145 MHz, D₂O, 25 °C): δ -37.5 (s), -145.0 (h) ppm (Fig. S2C).

Analysis: C₉H₁₆AgF₆N₃O₂P₂ (482.05): calcd. C 22.42, H 3.35, N 8.72; found C 22.42, H 3.50, N 8.78.

IR (ATR): ν/cm^{-1} : 505 (m), 556 (vs), 609 (s), 649 (m), 826 (vs), 944 (vs), 955 (s), 963 (m), 1109 (m), 1197 (m), 1238 (s), 1280 (s), 1291 (s), 1417 (s), 1538 (s), 1563 (vs), 1597 (s).

ESI-MS (positive ion mode; aqueous solution) most intense signals, m/z : [**L** + Na]⁺, C₉H₁₆N₃NaO₂P, calcd. 252.0872, found 252.0878; and [**2L** + Na]⁺, C₁₈H₃₂N₆NaO₄P₂, calcd. 481.1852, found 481.1854.

$[\text{Ag}(\text{tos})(\mu_3\text{-L-}\kappa^3\text{N:O:O'})_n\cdot n\text{H}_2\text{O}$ (**2**)

Yield (based on **L**): 201 mg (90%)

¹H NMR (360 MHz, D₂O, 25 °C): δ 7.72 (d, $^3J_{\text{HH}} = 8.2 \text{ Hz}$, Ph, 2H), 7.40 (d, $^3J_{\text{HH}} = 8.2 \text{ Hz}$, Ph, 2H), 4.63 (d, $J_{\text{AB}} = 13.6 \text{ Hz}$, 3H, $N\text{-CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}$), 4.59 (d, $^2J_{\text{PH}} = 6.8 \text{ Hz}$, 6H, $^+\text{P-CH}_2\text{-N}$), 4.52 (d, $J_{\text{AB}} = 13.2 \text{ Hz}$, 3H, $N\text{-CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}$), 2.58 (dt, $^2J_{\text{PH}} = 23.7$, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 2H, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$), 2.42 (s, 3H, CCH₃), 2.34 (dt, $^3J_{\text{PH}} = 13.5$, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 2H, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$) ppm (Fig. S3A).

¹³C{¹H} NMR (90 MHz, D₂O, 25 °C): δ 179.4 (d, $^3J_{\text{PC}} = 4 \text{ Hz}$, COO^-), 143.4 (s, Ph), 140.4 (s, Ph), 130.3 (s, Ph), 126.2 (s, Ph), 71.7 (d, $^3J_{\text{PC}} = 9 \text{ Hz}$, $N\text{-CH}_2\text{-N}$), 49.1 (d, $^1J_{\text{PC}} = 38 \text{ Hz}$, $^+\text{P-CH}_2\text{-N}$), 29.1 (d, $^2J_{\text{PC}} = 7 \text{ Hz}$, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$), 21.3 (s, -CH₃), 18.8 (d, $^1J_{\text{PC}} = 37 \text{ Hz}$, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$) ppm (Fig. S3B).

³¹P{¹H} NMR (145 MHz, D₂O, 25 °C): δ -37.6 (s) ppm (Fig. S3C).

Analysis: C₁₆H₂₃AgN₃O₅PS·H₂O (526.29): calcd. C 36.51, H 4.79, N 7.98, S 6.09; found C 36.20, H 4.73, N 7.29, S 6.07.

IR (ATR): ν/cm^{-1} : 559 (vs), 569 (vs), 680 (vs), 705 (w), 755 (s), 779 (s), 813 (s), 911 (m), 944 (vs), 968 (s), 975 (s), 1009 (vs), 1031 (vs), 1118 (vs), 1174 (vs), 1204 (vs), 1302 (m), 1415 (s), 1557 (s), 1569 (s).

ESI-MS (positive ion mode; aqueous solution) most intense signals, m/z : [**L** + Na]⁺, C₉H₁₆N₃NaO₂P, calcd. 252.0872, found 252.0880; [**L** + Ag]⁺, C₉H₁₆N₃AgO₂P, calcd. 336.0026, found 336.0026; [**2L** + Na]⁺, C₁₈H₃₂N₆NaO₄P₂, calcd. 481.1852, found 481.1854; and [**2L** + Ag]⁺, C₁₈H₃₂N₆AgO₄P₂, calcd. 565.1005, found 565.1008.

$[\text{Ag}(\text{OTf})(\mu_3\text{-L-}\kappa^3\text{N:O:O'})_n$ (**3**)

Yield (based on **L**): 106 mg (50%)

¹H NMR (360 MHz, D₂O, 25 °C): δ 4.65 (d, $J_{\text{AB}} = 13.2 \text{ Hz}$, 3H, $N\text{-CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}$), 4.60 (d, $^2J_{\text{PH}} = 6.8 \text{ Hz}$, 6H, $^+\text{P-CH}_2\text{-N}$), 4.52 (d, $J_{\text{AB}} = 13.5 \text{ Hz}$, 3H, $N\text{-CH}^{\text{A}}\text{H}^{\text{B}}\text{-N}$), 2.59 (dt, $^2J_{\text{PH}} = 23.8$, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 2H, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$), 2.35 (dt, $^3J_{\text{PH}} = 13.7$, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 2H, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$) ppm (Fig. S4A).

¹³C{¹H} NMR (90 MHz, D₂O, 25 °C): δ 179.4 (d, $^3J_{\text{PC}} = 4 \text{ Hz}$, COO^-), 122.3 (s, CF₃), 118.8 (s, CF₃), 71.9 (d, $^3J_{\text{PC}} = 9 \text{ Hz}$, $N\text{-CH}_2\text{-N}$), 49.4 (d, $^1J_{\text{PC}} = 37 \text{ Hz}$, $^+\text{P-CH}_2\text{-N}$), 29.2 (d, $^2J_{\text{PC}} = 7 \text{ Hz}$, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$), 18.8 (d, $^1J_{\text{PC}} = 37 \text{ Hz}$, $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$) ppm (Fig. S4B).

³¹P{¹H} NMR (145 MHz, D₂O, 25 °C): δ -37.6 (s) ppm (Fig. S4C).

Analysis: C₁₀H₁₆AgF₃N₃O₅PS (486.15): calcd. C 24.71, H 3.32, N 8.64, S 6.60; found C 24.86, H 3.43, N 8.71, S 6.62

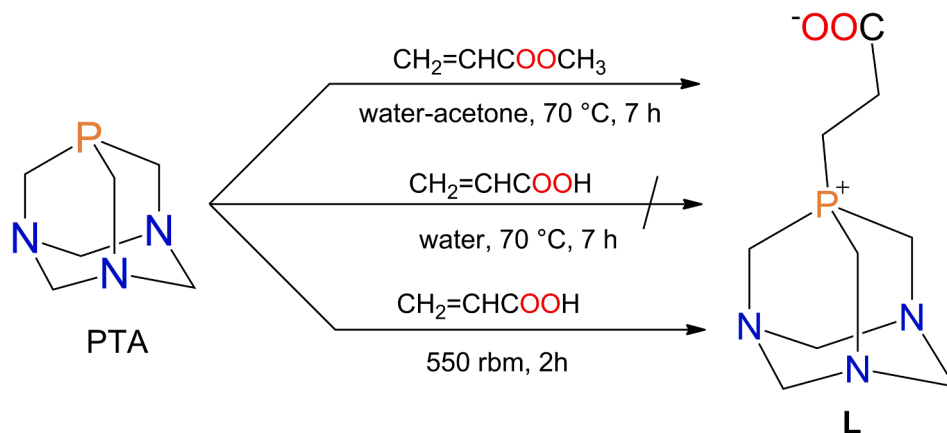
IR (ATR): ν/cm^{-1} : 516 (vs), 573 (vs), 604 (vs), 633 (vs), 749 (vs), 902 (s), 945 (vs), 973 (vs), 1008 (vs), 1028 (vs), 1152 (vs), 1169 (vs), 1225 (vs), 1256 (vs), 1290 (vs), 1411 (s), 1560 (vs), 1594 (s).

ESI-MS (positive ion mode; aqueous solution) most intense signals, m/z : [**L** + Ag]⁺, C₉H₁₆N₃AgO₂P, calcd. 336.0026, found 336.0026; and [**2L** + Ag]⁺, C₁₈H₃₂N₆AgO₄P₂, calcd. 565.1005, found 565.1008.

3. Results and discussion

3.1. Synthesis of 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (**L**)

The literature method of the synthesis of **L** involved stirring of PTA and six equivalents of ethyl acrylate at room temperature for 6 h in a



Scheme 2. Synthesis of 7-(2-carboxy-ethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1^{3,7}]decane (L).

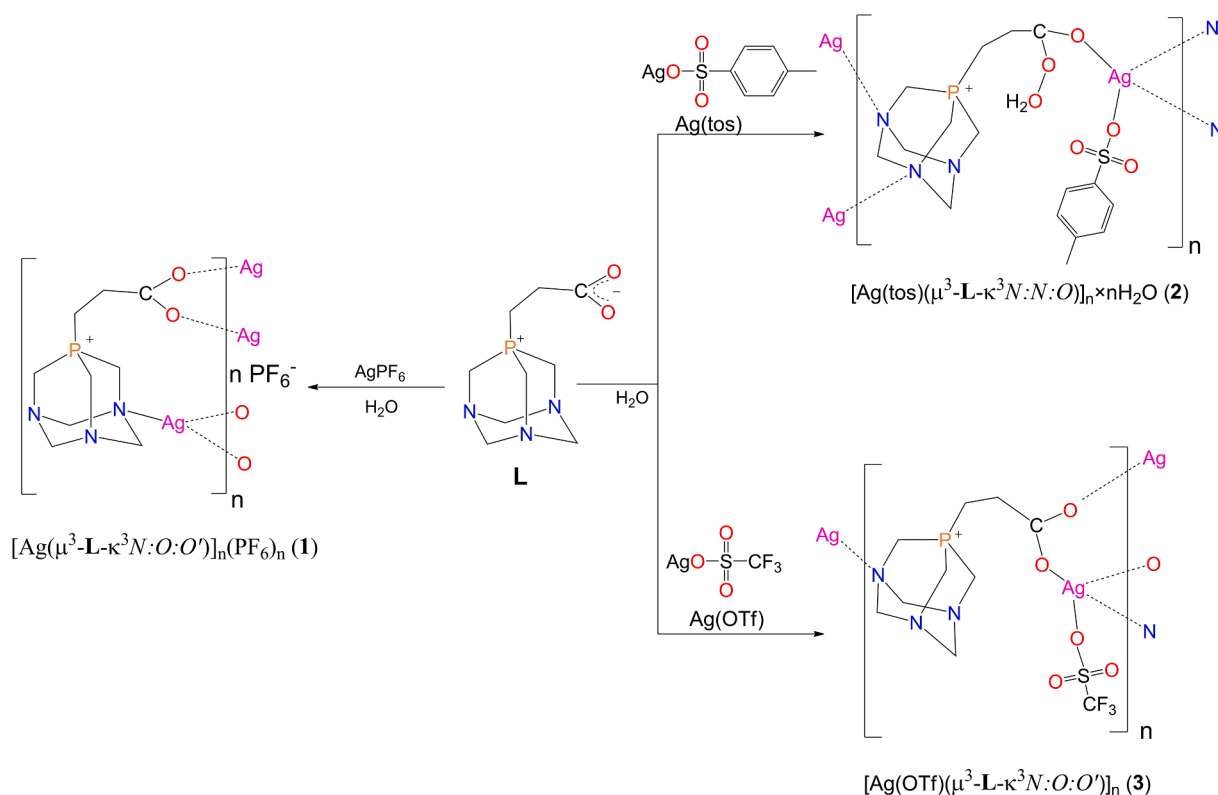


Fig. 1. Different coordination modes of L with various Ag-salts.

solvent mixture of THF-water (4:1, v/v) [35]. We have shown, that no excess of the acrylate is required since reaction of an equimolar mixture of PTA and methyl-acrylate in acetone–water at 70 °C results in the formation of the phosphobetaine L with 89% yield in 7 h (Scheme 2).

We have reported earlier, that reaction of PTA with unsaturated dicarboxylic acids in aqueous solution also led to the formation of phosphobetaines [53]. In contrast, in the reaction between acrylic acid and PTA, no P-substituted product was detected in aqueous solution even at 70 °C in 7 h. Conversely, when the same reaction was attempted under solvent-free conditions, after milling of PTA and acrylic acid in a planetary ball mill at 550 rpm for 2 h, L was isolated in 88% yield (Scheme 2). This is another excellent example, when mechanochemical procedures offer synthetic possibilities unavailable in solution synthesis or result in better yields and product qualities.

3.2. Synthesis and solid state structure of Ag-based coordination polymers of L

AgX salts ($X = \text{PF}_6^-$, CF_3SO_3^- , $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$) were dissolved in water with exclusion of light, and added to the aqueous solutions of L ($n_{\text{Ag}}:n_{\text{L}} = 2.27$) also in the dark. The resulting solutions were layered with 2-propanol and were stored in a refrigerator. Colourless crystals were isolated (with 50–90% yield, depending on the AgX salt) which were not sensitive to oxygen or visible light. Microanalysis of the compounds showed that these crystals were 1:1 adducts of AgX and L. In the case of $X = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (tosylate = tos) the product contained one molecule of water per one Ag^+ , too.

The products were also obtained as single crystals and their structures were determined by X-ray diffraction. Fig. 1 shows the coordination modes determined by the anions.

Relevant crystal data and crystallographic measurement parameters

Table 1

Crystal data and structure refinement of the coordination polymers.

	1	2	3
Empirical formula	[AgC ₉ H ₁₆ N ₃ O ₂ P]	[AgC ₉ H ₁₆ N ₃ O ₂ P]	[AgC ₉ H ₁₆ N ₃ O ₂ P]
Formula weight	482.06	526.29	486.16
Crystal size [mm]	0.24 × 0.3 × 0.35	0.02 × 0.15 × 0.30	0.08 × 0.10 × 0.40
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁
Crystal habit	colourless, block	colourless, plate	colourless, block
a [Å]	9.267(4)	17.6574(6)	9.3209(1)
b [Å]	11.818(2)	6.4618(2)	12.2181(2)
c [Å]	13.543(3)	17.1100(5)	13.9406(2)
α [°]	90	90	90
β [°]		92.250(2)	
γ [°]		90	
V [Å ³]	1483.2(8)	1950.72(11)	1587.61(4)
Z	4	4	4
Density (calc.) [g cm ⁻³]	2.159	1.792	2.034
Absorption coefficient (μ) [mm ⁻¹]	1.652	1.262	1.563
F(000)	952	1072	968
2θ range [°]	5.326 – 52.046	6.506 – 59.294	5.498 to 59.35
Index ranges	0 ≤ h ≤ 11 –14 ≤ k ≤ 3 –16 ≤ l ≤ 16	–22 ≤ h ≤ 22, –8 ≤ k ≤ 8, –22 ≤ l ≤ 18	–12 ≤ h ≤ 12, –16 ≤ k ≤ 16, –17 ≤ l ≤ 19
Total refls.	3281	16,340	55,412
Unique refls.	2904 [R _{int} = 0.0276]	4847 [R _{int} = 0.0357]	4324 [R _{int} = 0.0540]
Data/restraints/parameters	2904/0/208	4847/0/257	4324/0/217
Final R ₁ , wR ₂ (Obs. data)	0.0620, 0.1721	0.0374, 0.0732	0.0495, 0.1355
Final R ₁ , wR ₂ (All. data)	0.0714, 0.2010	0.0553, 0.0827	0.0626, 0.1493
Goodness of fit (GOF) on F ² (S)	1.153	1.064	1.012
Δρ _{max} /Δρ _{min} [e. Å ⁻³]	1.79/–3.18	0.68/–0.75	1.52/–1.04
CCDC	2,046,048	2,046,052	2,046,053

are collected in Table 1.

The polymer formed in the reaction of **L** and AgPF₆, [(Ag(μ₃-L-κ³N:O:O'))_n(PF₆)_n] (**1**), crystallizes in the orthorhombic P2₁2₁2₁ space group. In addition to the N,O,O'-coordinated Ag(I), there is a zwitterionic **L** and a discrete PF₆-ion in the asymmetric unit (Fig. S5A). Although crystallization was performed from water, neither Ag-coordinated H₂O nor water of crystallinity were found in the crystal (Fig. 1).

The bond lengths and angles of the Ag-coordinated phosphobetaine agree within the limits of accuracy with the same parameters in the free **L** described before [36]. A notable exception is the P1–O11 distance (2.639(10) Å) which is shorter in **1** than in **L** (2.661 Å). In **1**, each Ag(I) atom is surrounded by three phosphobetaine molecules (Fig. 1, Fig. S5B). Two of these phosphobetaines coordinate to the Ag(I) atom with one of their carboxylate oxygens, while the third **L** binds to the same Ag(I) with one nitrogen atom of the phosphadamantane moiety, altogether resulting in a slightly distorted trigonal, Y-shape coordination geometry (Fig. 1). There are 17 structures reported in the literature in which PTA is coordinated with its nitrogen to an Ag(I)-ion. In those complexes, the characteristic Ag–N_(PTA) distance is in the range of a 2.302–2.541 Å [54], i.e. the Ag–N_(PTA) distance in **1** (2.232(11) Å) is shorter.

The bridging coordination of the **L** ligands to two silver ions results in formation of chain polymers (Fig. 2, Fig. S5C). The packing diagram (Fig. 1) shows that with the involvement of two Ag⁺ ions and two **L** ligands, 12-membered macrocycles are formed, in which the Ag(1)...Ag(1) distance is 5.085 Å, indicating no interaction between the metal ions.

The crystal lattice is held together by weak C–H...O and C–H...F hydrogen bonds (Figs. S5D–S5F) and the PF₆-ions occupy the voids between the polymer backbones. The bond length data indicating weak interactions are contained in Table S1.

Formation of the coordination polymer, [Ag(tos)(μ₃-L-κ³N:O:O'))_n·nH₂O (**2**), obtained in the aqueous reaction of Ag(tos) and **L**, is assisted by the O-donor atom of the anion (Fig. 3). The compound crystallizes in the centrosymmetric monoclinic P2₁/c space group. In the asymmetric unit, in addition to the Ag(I)-ion, **L** and the tosylate anion, a water molecule is found, too (Z = 4) (Fig. S6A).

In contrast to the {[Ag₃(tos)₃(hmt)₃(H₂O)] × 3H₂O} polymer [55] obtained in the reaction of Ag(tos) and hexamethylenetetramine (hmt, urotropine), in **2**, nitrogen donor atoms of only two (and not all three) **L** phosphobetaines are coordinated to Ag(I) (Fig. 3). The Ag1–N1⁽ⁱ⁾ bond lengths (2.363(2) Å) agree well with the average values determined for

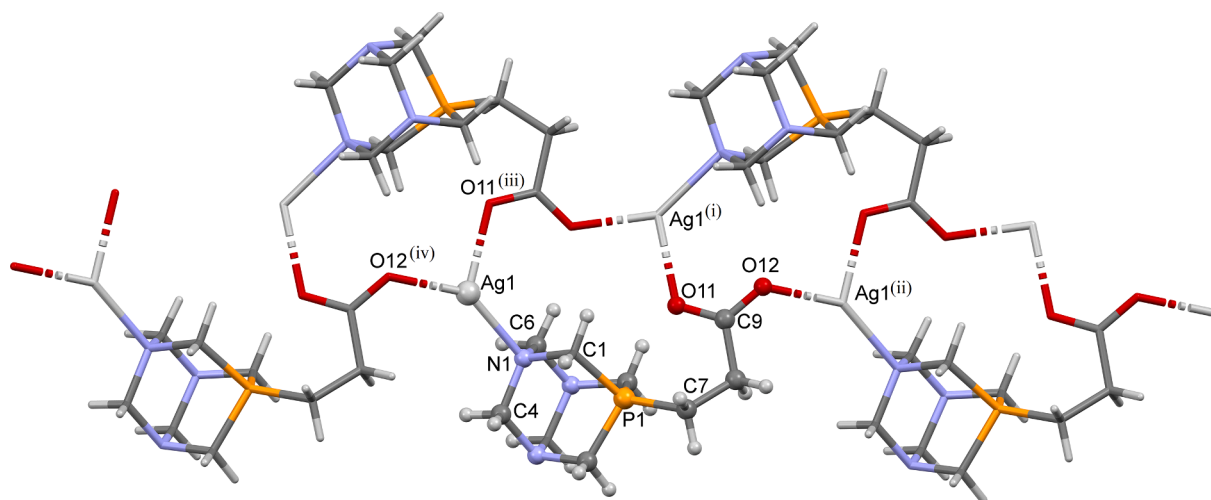


Fig. 2. Coordination environment of Ag(I) in [(Ag(μ₃-L-κ³N:O:O'))_n(PF₆)_n] (**1**). The asymmetric unit of **1** is given in ball and sticks, and the symmetry-generated part of the polymer is given in capped sticks representation. PF₆-ions are omitted for clarity. Selected bond lengths (Å) and angles (°) Ag1–N1 = 2.232(11), Ag1–O11⁽ⁱⁱⁱ⁾ = 2.291(9), Ag1–O12^(iv) = 2.210(10), O11–Ag1⁽ⁱ⁾ = 2.291(9), O12–Ag1⁽ⁱⁱⁱ⁾ = 2.210(10), O11–P1 = 2.639(10), C1–N1–Ag1 = 104.5(7), C4–N1–Ag1 = 115.4(8), C6–N1–Ag1 = 106.7(8), C9–O11–Ag1 = 117.8(8), C9–O12–Ag1 = 122.1(8), N1–Ag1–O11⁽ⁱⁱⁱ⁾ = 120.8(3)°, O12^(iv)–Ag1–N1 = 144.3(4) and O11⁽ⁱⁱⁱ⁾–Ag1–O12^(iv) = 94.8(3)°; [Symmetry codes: (i) 1/2 + x, 3/2–y, 2–z; (ii) 1 + x, +y, +z; (iii) –1/2 + x, 3/2–y, 2–z; (iv) –1 + x, +y, +z].

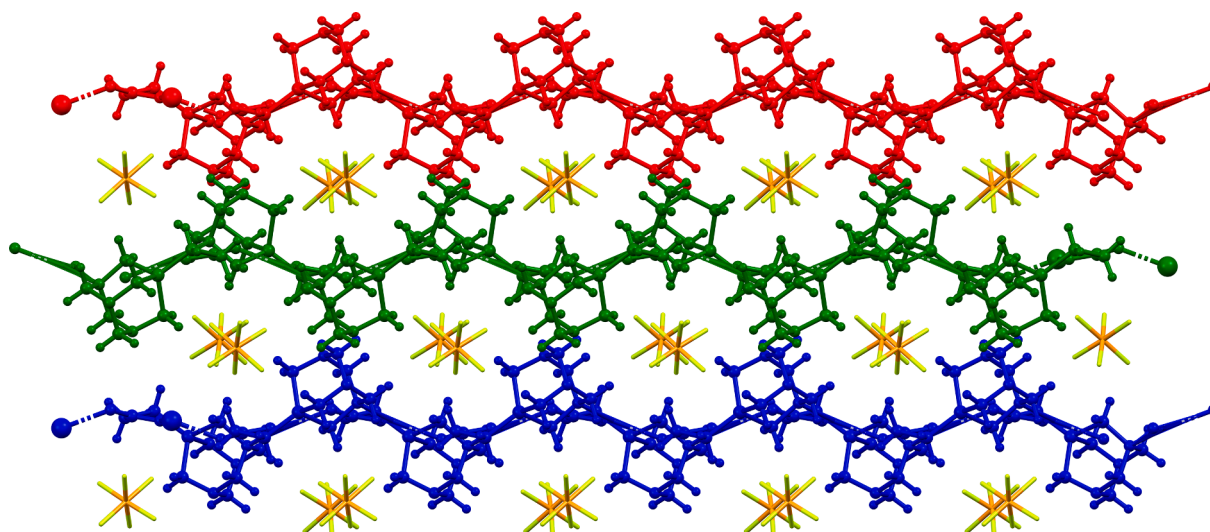


Fig. 3. Ag-based polymer chains in the lattice of $[(\text{Ag}(\mu_3\text{-L-}\kappa^3\text{N:O'O}'))_n(\text{PF}_6)_n]$ (1). (Each chain is drawn in a different color).

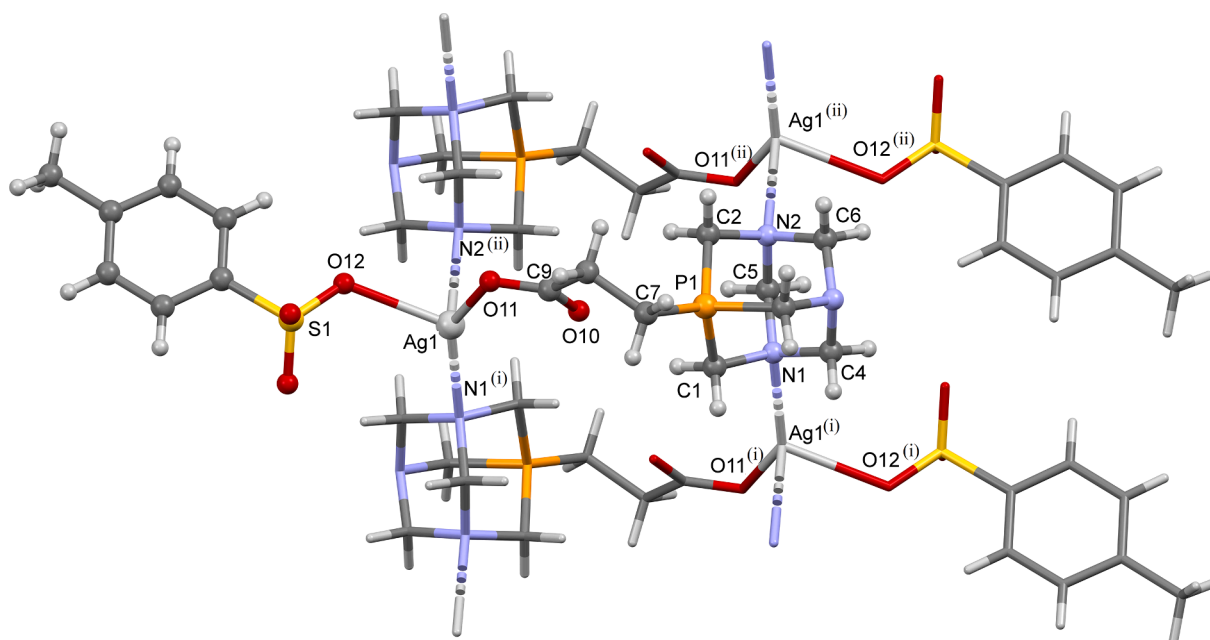


Fig. 4. Coordination environment of Ag(I) in $[\text{Ag}(\text{tos})(\mu_3\text{-L-}\kappa^3\text{N:N:O})]_n \cdot n\text{H}_2\text{O}$, 2. The asymmetric unit of 2 is given in ball and sticks, and the symmetry-generated part of the polymer is given in capped sticks representation. Water molecules are omitted for clarity. Selected bond length (Å) and angles (°): $\text{Ag1-O11} = 2.284(2)$, $\text{Ag1-N1}^{(i)} = 2.363(2)$, $\text{Ag1-O12} = 2.417(2)$, $\text{Ag1-N2}^{(ii)} = 2.577(2)$, $\text{N1-Ag}^{(i)} = 2.363(2)$, $\text{N2-Ag}^{(ii)} = 2.363(2)$, $\text{P1-C7} = 1.796(3)$, $\text{O11-Ag1-N1}^{(i)} = 140.56(8)$, $\text{O11-Ag1-O12} = 95.78(9)$, $\text{O11-Ag1-N2} = 99.36(8)$, $\text{N1}^{(i)}\text{-Ag1-O12} = 115.64(9)$, $\text{N1}^{(i)}\text{-Ag1-N2}^{(ii)} = 108.18(8)$, $\text{O12-Ag1-N2}^{(ii)} = 81.05(7)$, $\text{C9-O11-Ag1} = 106.12(19)$, $\text{C5-N1-Ag1}^{(i)} = 119.37(17)$, $\text{C1-N1-Ag1}^{(i)} = 101.40(16)$, $\text{C4-N1-Ag1}^{(i)} = 105.67(16)$, $\text{S1-O12-Ag1} = 124.42(14)$, $\text{C2-N2-Ag1}^{(ii)} = 111.76(16)$, $\text{C5-N2-Ag1}^{(ii)} = 103.42(15)$, $\text{C6-N2-Ag1}^{(ii)} = 109.17(16)$; [Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$].

Ag-PTA complexes (2.302–2.541 Å [54]). However, the $\text{Ag1-N2}^{(ii)}$ distance (2.577(2) Å) is larger than the longest Ag-N distance determined for an Ag-PTA complex, namely (2.541 Å) found in $[\text{Ag}_2(\mu_4\text{-PTA})(\mu_4\text{-mal})]_n$ (mal: malonato) [26].

In 2, the Ag(I)-ion is found in a distorted tetrahedral (AgN_2O_2) coordination geometry. Two ligands are N-bonded, while the tosylate anion and the third L coordinate through one of their oxygen donor atoms, (Fig. 3, Fig. S6A–S6B). There is no interaction between the metal ion and the other carboxylate oxygen atom of L ($\text{Ag1-O10} = 2.859(2)$ Å).

With the participation of one silver ion, two phosphabetaïne ligands and two tosylate anions, 16-membered macrocycles are formed, which overlap and form a tube-like array (Fig.s S6B–S6C). The structure is held

together by strong hydrogen bonds between the neighbouring stacked macrocycles. Network of hydrogen-bonds are formed with participation of carboxylate oxygen atoms (O10 and O11) of coordinated L, and water molecules of the crystal structure. The outcome is a 1D polymer network (Fig. 4, Figs. S6D–S6F).

There are also weak C–H...O interactions between the polymer chains (Table S2). Surprisingly, no π - π stacking interactions can be observed between the aromatic units of tosylate anion.

In the coordination polymer $[\text{Ag}(\text{OTf})(\mu_3\text{-L-}\kappa^3\text{N:O'O}')]_n$ (3) (for unit cell see Fig. S7A–S7B), a different coordination mode can be observed than in 2, although this polymer contains a similar sulfonate-bearing anion, triflate (OTf). 3 crystallizes in the common orthorhombic $P2_12_12_1$ space group. The molecular structures of the free and

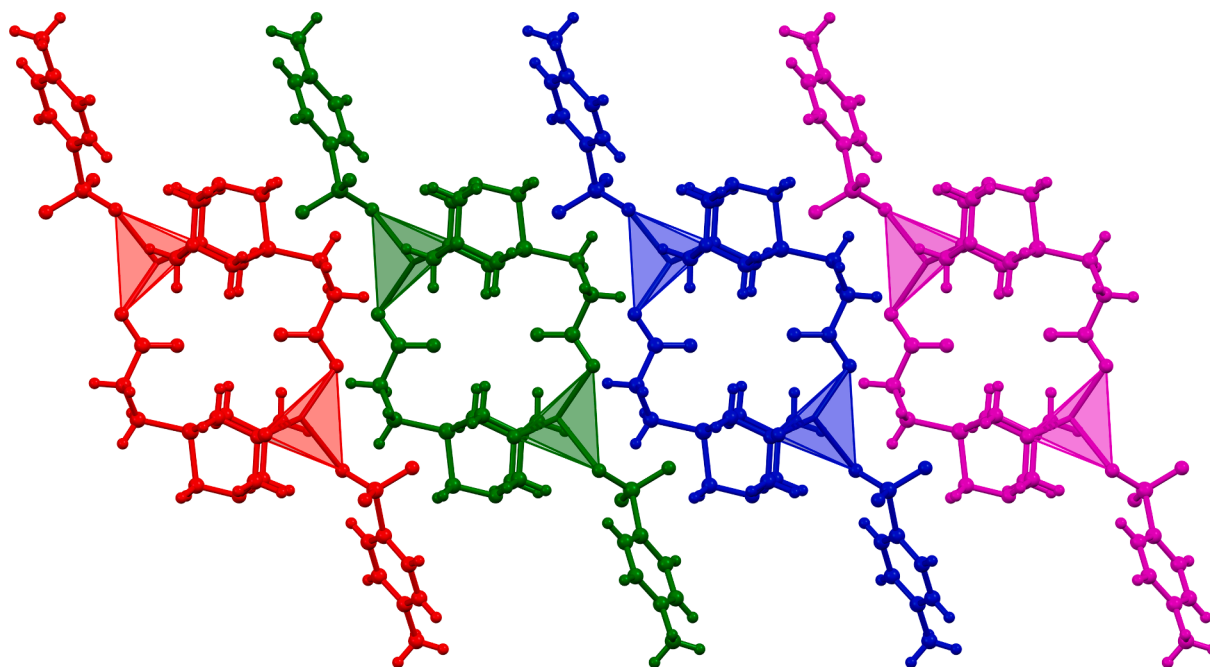


Fig. 5. Tube-like arrays in the lattice of $[\text{Ag}(\text{tos})(\mu_3\text{-L-}\kappa^3\text{N:N:O})]_n \cdot n\text{H}_2\text{O}$, **2**. (Each tube with polyhedrons of silver atoms is drawn in a different color.)

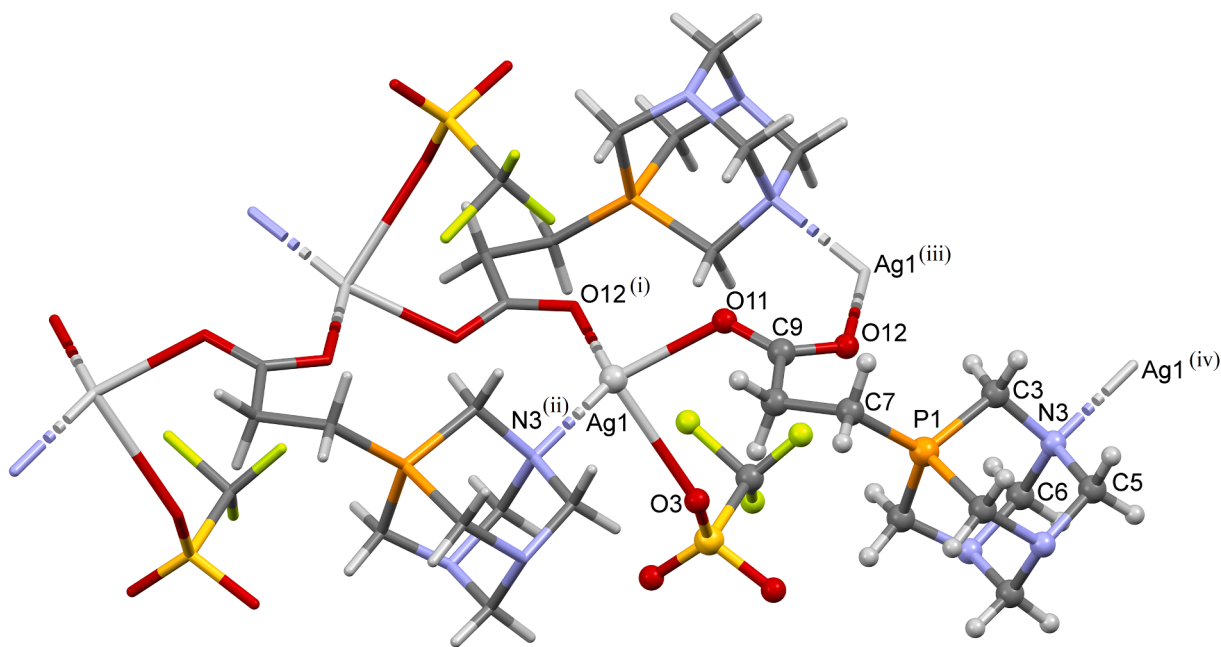


Fig. 6. Coordination environment of Ag(I) in $[\text{Ag}(\text{OTf})(\mu_3\text{-L-}\kappa^3\text{N:O:O}')]_n$, **3**. The asymmetric unit of **3** is given in ball and sticks, and the symmetry-generated part of the polymer is given in capped sticks representation. Selected bond lengths (Å) and angles ($^\circ$): $\text{Ag1-O11} = 2.260(5)$, $\text{Ag1-O12}^{(i)} = 2.290(5)$, $\text{Ag1-N3}^{(ii)} = 2.288(6)$, $\text{P1-C7} = 1.801(7)$, $\text{O12-Ag1}^{(iii)} = 2.290(5)$, $\text{N3-Ag1}^{(iv)} = 2.288(6)$, $\text{Ag1-O3} = 2.692(9)$, $\text{O11-Ag1-O12}^{(i)} = 96.3(2)$, $\text{O11-Ag1-N3}^{(ii)} = 139.6(2)$, $\text{O12}^{(i)}\text{-Ag1-N3}^{(ii)} = 122.0(2)$, $\text{C9-O11-Ag1} = 123.8(5)$, $\text{C9-O12-Ag1}^{(iii)} = 119.1(5)$, $\text{C3-N3-Ag1}^{(iv)} = 105.0(4)$, $\text{C6-N3-Ag1}^{(iv)} = 107.4(5)$, $\text{C5-N3-Ag1}^{(iv)} = 112.9(4)$; [Symmetry codes: (i) $1/2 + x, 1/2 - y, 1 - z$; (ii) $1 + x, y, z$; (iii) $-1/2 + x, 1/2 - y, 1 - z$; (iv) $-1 + x, y, z$].

coordinated **L** are almost identical, except that the P1-O11 distance ($2.747(5)$ Å) in the coordination polymer is much longer than in the free **L** (2.661 Å).

Both oxygen atoms of the phosphobetaine carboxylate group and the N3 nitrogen of the phosphadamantane moiety coordinate to an Ag(I) located in a distorted tetrahedral coordination environment (Fig. 5), and as a result, a chain-polymer is formed.

The backbone of this two-dimensional polymer consists of a linear chain of alternating silver ions and carboxylate groups (Fig. 6).

The $\text{Ag1-N3}^{(i)}$ distance ($2.288(6)$ Å) is one of the shortest known in Ag-PTA complexes; the shortest determined so far, 2.302 Å was found in the $[\text{Ag}(\mu\text{-aba})(\mu\text{-PTA})]_n \times 3n\text{H}_2\text{O}$ (aba = aminobenzoate) complex [21]. The O3 atom of the triflate anion is also coordinated to the Ag(I)-ion, however, this interaction does not contribute to the formation of the chain-polymer (Fig. 7).

Weak C—H...F and C—H...O interactions also help to hold together the polymer chains, however, there are no significant second-order bonds (Fig. 7, Fig. S7C, Table S3).

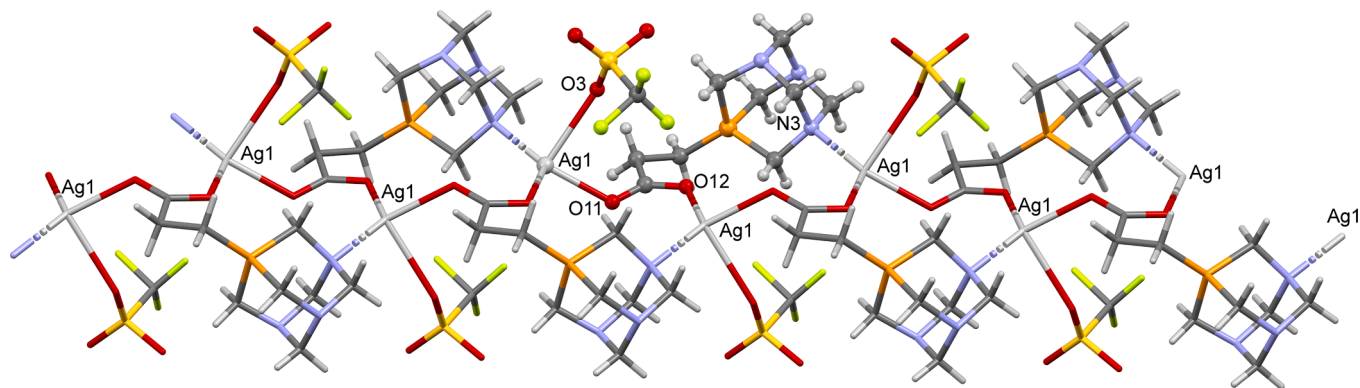


Fig. 7. Partial packing along axis “c” in ribbons of $[\text{Ag}(\text{OTf})(\mu_3\text{-L-}\kappa^3\text{N:O:O'})]_n$, **3**. The asymmetric unit of **3** is given in ball and sticks, and the symmetry-generated part of the polymer is given in capped sticks representation.

Table 2

NMR spectral data for **L** and its silver(I)-based coordination polymers **1–3**.

	^{31}P NMR δ (ppm)	^1H NMR		
		δ (d, 6H, $\text{P}^+\text{-CH}_2\text{-N}$) (ppm)	δ (d, 3H, $\text{N-CH}_2(\text{eq})\text{-N}$) (ppm)	δ (d, 3H, $\text{N-CH}_2(\text{ax})\text{-N}$) (ppm)
L	−37.6	4.57 ($^2J_{\text{P-H}} = 6.6$ Hz)	4.50 ($J_{\text{AB}} = 13.2$ Hz)	4.62 ($J_{\text{BA}} = 13.6$ Hz)
1	−37.5	4.60 ($^2J_{\text{P-H}} = 6.8$ Hz)	4.53 ($J_{\text{AB}} = 13.2$ Hz)	4.65 ($J_{\text{BA}} = 13.5$ Hz)
2	−37.6	4.59 ($^2J_{\text{P-H}} = 6.8$ Hz)	4.52 ($J_{\text{AB}} = 13.2$ Hz)	4.63 ($J_{\text{BA}} = 13.6$ Hz)
3	−37.6	4.60 ($^2J_{\text{P-H}} = 6.7$ Hz)	4.53 ($J_{\text{AB}} = 13.2$ Hz)	4.65 ($J_{\text{BA}} = 13.6$ Hz)

3.3. The molecular state of coordination polymers **1–3** in aqueous solutions

In aqueous solutions, ^{31}P NMR spectra of the coordination polymers **1–3**, obtained in reactions of **L** and AgX -salts, show the characteristic

singlet resonance of free **L** at $\delta = -37.6$ ppm (Table 2). ^1H NMR spectra of the same solutions were also compared to the corresponding spectrum of **L** (Fig. 8). The resonances of the $\text{P}^+\text{-CH}_2\text{-CH}_2\text{-COO}^-$ protons of free and coordinated **L** appear basically the same. However, there are small shifts in the $\text{P}^+\text{-CH}_2\text{-N}$ and $\text{N-CH}_2\text{-N}$ signals (Table 2, Fig. 8) indicating the coordination of Ag(I) to the nitrogen donor atoms of the ligand (see Fig. 9).

The most intense MS signals in the ESI-MS spectrum of $[\text{Ag}(\mu_3\text{-L-}\kappa^3\text{N:O:O'})]_n(\text{PF}_6)_n$ (**1**) recorded with the use of aqueous solutions are $[\text{L} + \text{Na}]^+$, 252.0878 m/z , and $[2\text{L} + \text{Na}]^+$, 481.1854 m/z . In the case of $[\text{Ag}(\text{tos})(\mu_3\text{-L-}\kappa^3\text{N:N:O})]_n \cdot n\text{H}_2\text{O}$ (**2**), the most intense peak also belongs to $[\text{L} + \text{Na}]^+$, however the peaks belonging to $[\text{L} + \text{Ag}]^+$ (336.0026 m/z) and $[2\text{L} + \text{Ag}]^+$ (565.1009 m/z) could be detected, too. Finally, in the ESI-MS spectrum of $[\text{Ag}(\text{OTf})(\mu_3\text{-L-}\kappa^3\text{N:O:O'})]_n$ (**3**), the most intense signals can be attributed to the $[\text{L} + \text{Ag}]^+$ and $[2\text{L} + \text{Ag}]^+$ Ag-containing fragments. Similar observations were published on the spectral characteristics of related PTA-Ag complexes [22–27]. For example, in the spectrum of $[\text{Ag}(\mu_2\text{-PTA:}\kappa^2\text{P:N})(\mu_2\text{-O}_2\text{N:}\kappa^2\text{O:O'})]_n$ recorded with the use of methanol–water solvent mixture the main peak belonged to $[\text{Ag}(\text{PTA})_2]^+$, and higher nuclearity species, such as $[\text{Ag}_2(\text{PTA})_2(\text{NO}_2)]^+$ and

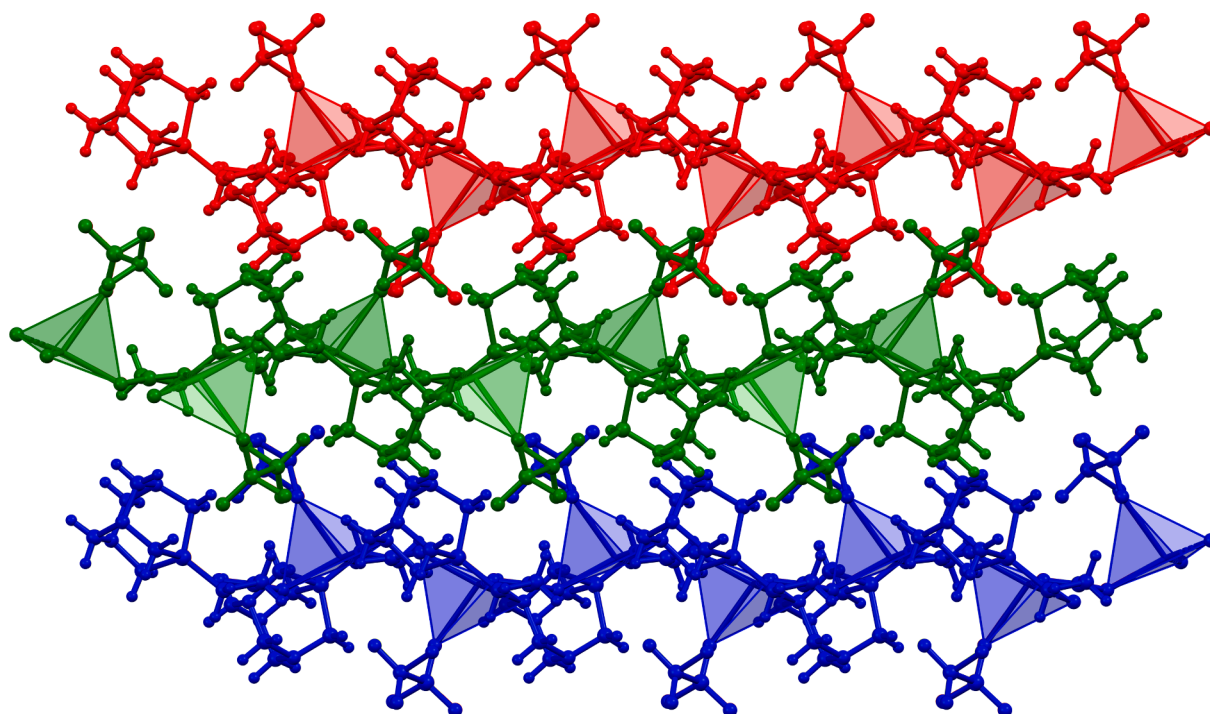


Fig. 8. Polymer chains with silver polyhedra in $[\text{Ag}(\text{OTf})(\mu_3\text{-L-}\kappa^3\text{N:O:O'})]_n$, **3**. (Each chain is drawn in a different color.)

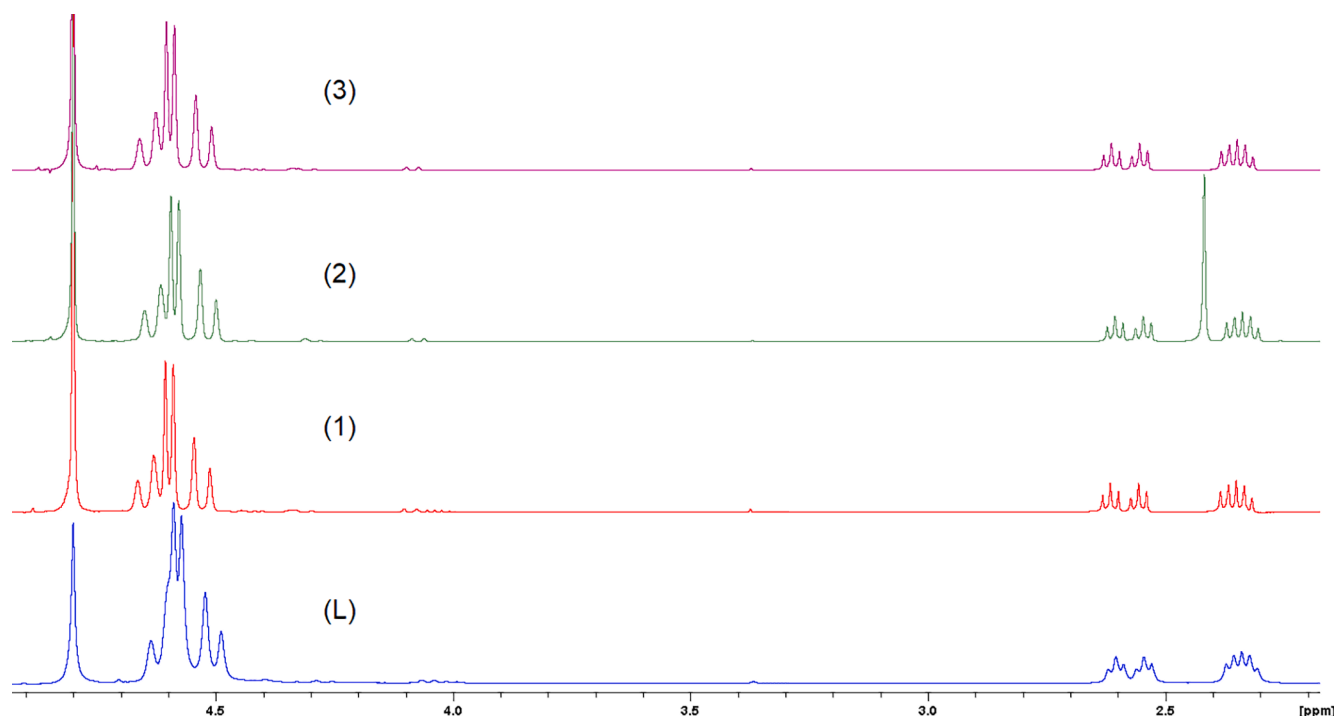


Fig. 9. Overlaid ^1H NMR spectra of aqueous solutions of **L**, **1–3**.

$[\text{Ag}_2(\text{PTA})_3(\text{NO}_2)]^+$ were detected only with low intensity [27].

The ESI-MS data could be rationalized by assuming that the mono- and dinuclear fragments were formed from the polymers during ionization. However, it seems probable, that already the interaction with the (aqueous) solvent leads to the break-up of the polymers into smaller units. To address this question, we carried out diffusion NMR measurements.

Diffusion NMR spectroscopy allows the determination of the diffusion coefficient of a diffusing ion, molecule or particle. The method is briefly outlined in Section 2.1 Materials and methods, and treated excellently in reviews and earlier papers [38–43]. Diffusion coefficients can be used –with certain approximations and limitations– for calculation of the hydrodynamic diameters of the moving species according to the Einstein-Stokes relation. We reasoned that knowledge of the hydrodynamic parameters of **L** and **1–3** in aqueous solutions may help to reveal the molecular state of the species obtained upon dissolution of **1–3** in water. With this aim in mind, diffusion NMR experiments were performed with the use of the Pulsed Field Gradient Spin-Echo (PGSE) NMR method. According to the method, monodimensional NMR spectra were recorded as a function of varying pulsed-field gradient (G) in quadratic steps along the z axis.

Measurements involving **L** were performed on D_2O solutions with $c_{\text{L}} = 0.044$ M concentration at 298.0 ± 0.2 K. The ^1H NMR spectra displayed well-separated resonances of water and **L** (Fig. S8A, S8C). The integral values of the main peak of **L** and peak of water, as the function of the square of the pulsed-gradient field ($\gamma^2 G^2 \delta^2 (\Delta - \delta / 3)$), could be well fitted with a monoexponential function ($I = B \times e^{-G^2 D}$) for both D_2O and **L** (Fig. S8B). From the data shown on Fig. S8B, the values of B were calculated as 17360.6 (D_2O) and 138,707 (**L**).

From these measurements, the diffusion coefficient of D_2O was calculated as $D = 1.62 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which is lower than the value known from the literature ($1.902 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [44]). This difference may arise from the dynamics of water exchange between the hydration sphere of **L** and the bulk water phase. Namely, in the case of a fast exchange, the measurements yield an average diffusion coefficient of bulk and hydration sphere water molecules. For the diffusion coefficient of **L**, $D = 5.22 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ was obtained. As mentioned before,

Table 3

Diffusion coefficients and hydrodynamic diameters of **L** and compounds **1–3** in aqueous solution at $T = 298.0 \pm 0.2$ K, determined by the PGSE NMR method.

	Diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)		Hydrodynamic diameter (nm)
	D_2O	Solute	Solute
L	1.62×10^{-9}	5.22×10^{-10}	0.762 ± 0.002
1	1.88×10^{-9}	5.53×10^{-10}	0.719 ± 0.001
2	1.89×10^{-9}	5.51×10^{-10}	0.722 ± 0.002
3	1.91×10^{-9}	5.57×10^{-10}	0.714 ± 0.001

calculations based on the Einstein–Stokes relation need approximations. In our approach, we regarded the solutions as infinitely dilute, so the actual viscosity of the solutions was taken equal to the viscosity of the solvent (water). Furthermore, the diffusing species were approximated spherical, moving randomly out from their given position. With these approximations, the hydrodynamic diameter of **L** was found $d = 0.762 \pm 0.002$ nm (the uncertainty caused by the error of curve fitting).

With the same procedure as for **L**, diffusion coefficients and hydrodynamic diameters were also determined for compounds **1–3** in aqueous solutions. The data are shown in Table 3, the corresponding experimental results are shown on Figs. S9–S11.

With regard to compound **2**, it is noted, that the 2D transformation of the ^1H NMR signals of the tosylate anion showed unequivocally an independent diffusion of tosylate and **L** (Fig. S10B). Diffusion coefficients were determined as $6.92 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for tosylate, $5.51 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for **L**, and $1.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for D_2O , and the fitting error was smaller by two orders of magnitude (for tosylate) and by three orders of magnitude (for **L** and D_2O) than the fitted value.

Comparison of the values of the hydrodynamic diameters of **L** vs **1–3** in Table 3 leads to the conclusion, that coordination of the phosphabeta-taine **L** to $\text{Ag}(\text{I})$ results in shrinking of the total occupied space around the metal ion. Even with the approximations involved in the Einstein–Stokes equation, this result does not support the presence of high nuclearity species of coordination polymers **1–3** in aqueous solutions. Furthermore, dissolution of polymers usually leads to increased viscosity of the solutions related to the pure solvent, which results in slower

diffusion hence lower diffusion coefficient of the solvent. In contrast, in aqueous solutions of 1–3, the diffusion coefficient of the solvent is close to that of the literature value of pure D₂O. This finding again supports the disaggregation of 1–3 in aqueous solutions. Taking these results together with the ESI-MS data discussed above, it may be concluded that in solution the supramolecular coordination effects and second order bonding are not sufficiently strong to maintain the polymeric structures determined unambiguously in the crystalline state of compounds 1–3. These findings are in accord with the results of Kirillov and co-workers [24,26], who also came to the conclusion that related Ag-PTA-based coordination polymers disassembled in aqueous solutions and existed as oligomers, at most.

In summary, we have confirmed, that *P*-carboxyethyl-substituted derivatives of PTA may serve as new building blocks for novel self-assembling silver-organic networks. Depending on the nature of the anion of the Ag-salt used for building up the coordination polymers, significant differences can be obtained in the structure of the polymers as a result of the various possible N,N',O- or N,O,O'-coordination modes of the PTA-derived ligand. The obtained compounds extend a limited family of PTA-derived coordination polymers [7–9]. Furthermore, the high-yielding synthesis of **L** from acrylic acid and PTA in a ball-mill is in striking contrast to the unsuccessful attempts to obtain **L** in solution from the same reactants and demonstrates the effectiveness of mechanochemical synthesis.

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CRediT authorship contribution statement

Antal Udvardy: Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **Csenge Tamara Szolnoki:** Investigation. **Éva Kováts:** Investigation, Writing - original draft, Writing - review & editing. **Dávid Nyul:** Methodology, Investigation, Writing - original draft. **Gyula Tamás Gál:** Methodology, Investigation. **Gábor Papp:** Methodology, Writing - review & editing. **Ferenc Joó:** Writing - original draft, Writing - review & editing, Resources. **Ágnes Kathó:** Conceptualization, Writing - original draft, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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