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SYNTHESIS AND CHARACTERIZATION OF NEW SILVER(I) COORDINATION POLYMERS INCORPORATING A BIS(TRIAZOLYL)-TYPE LIGAND

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Abstract

This paper reports the synthesis and characterization of six new coordination polymers having the following stoechiometric formulations: $Ag_2(tr_2ad)(NO_3)_2\cdot H_2O$ (**1**), $Ag_3(tr_2ad)_2(ClO_4)_3\cdot EtOH$ (**2**), $Ag(tr_2ad)(PF_6)\cdot H_2O$ (**3**), $Ag_3(tr_2ad)_2(BF_4)_3\cdot H_2O$ (**4**), $Ag_2(tr_2ad)(CH_3SO_3)_2\cdot 3H_2O$ (**5**) and $Ag_3(tr_2ad)_2(CF_3SO_3)_3\cdot EtOH$ (**6**) (EtOH = ethanol). The compounds were obtained from the interaction between the 1,3-bis(1,2,4-triazol-4-yl) adamantane ligand (tr_2ad) and silver(I) salts with different counteranions, in alcoholic ambient at room temperature. All the compounds are air- and moisture-stable, insoluble in most common solvents and do not melt, but only decompose upon heating to high temperatures, thus suggesting their polymeric nature. Fourier transform infrared spectroscopy (FTIR) was employed in order to reveal both the changes in the absorbtion bands of the ligand upon coordination to silver(I) ions and the binding modes of the counteranions.

Keywords: coordination polymers, bis(triazolyl) ligand, silver (I), counteranions, infrared spectra

1. INTRODUCTION

Inorganic-organic hybrid materials, also named coordination polymers (CPs) and metal-organic frameworks (MOFs), have been developed rapidly due to their potential uses [1,2]. Their prominent applications span from heterogeneous catalysis [3] to magnetism [4], conductivity [5], gas storage/ separation [6], and luminescence [7]. In recent years, the attention shifted to silver(I)-based coordination polymers due to the variety of applications from one compound alone, ranking from photoluminescence [8] to antibacterial activity [9]. The synthesis of silver(I)-based coordination polymers depends on several factors, such as ligand functionality [10], metal:ligand ratio [11], reaction conditions [12] and the nature of counterions [13], thus making this metal a suitable candidate for the fabrication of special CPs. Nitrogen-donor ligands represent typical linkers for designing this class of materials due to their strong electron-donating ability and rich coordination chemistry, since these ligands can provide the N^1,N^2-connection between two closely separated metal ions [14]. In this context, bis(triazoles) have been proven to be remarkable linkers.

The toxicity of silver(I)-based compounds has been successfully tested against different bacteria like, for example, *E. coli* and showed positive effects [15]. Currently, numerous applications have been reported in which silver or silver(I) derivatives are involved against the inclusion into antimicrobial ceramics [16] or catheters [17]. Nomiya and coworkers reported some promising results on the antibacterial activity of silver(I)-based coordination polymers, who demonstrated that [Ag(1,3-imidazole)] displays great activity towards bacteria and fungi [18].

The present paper reports the synthesis and preliminary structural characterization through infrared spectroscopy of six new silver (I) coordination polymers incorporating the 1,3-bis (1,2,4-triazol-4-yl) adamantane ligand (tr_2ad).

2. EXPERIMENTAL

Materials and Methods

All the chemicals and reagents were purchased from Sigma Aldrich Co. and used as received without further purification. The 1,3-bis(1,2,4-triazol-4-yl) adamantane ligand (tr_2ad) was synthesized according to an already reported procedure in the literature [19]. All the solvents were distilled prior to use. FTIR spectra were recorded from 4000 to 650 cm^{-1} with a Perkin-Elmer Spectrum 100 instrument by attenuated total reflectance (ATR) on a CdSe crystal. In the following, the IR bands are classified as broad (br), very weak (vw), weak (w), medium (m), strong (s) and very strong (vs). Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyzer. Before performing the analytical characterization, all samples were dried in vacuum (50 ºC, $\sim 10^{-4}$ bar) until a constant weight was reached. Melting points were recorded with an SMP3 Stuart instrument mounting a capillary apparatus.

Synthesis of the silver(I) CPs: general procedure

The tr_2ad ligand (0.1 mmol) was dissolved in 10 mL of ethanol. After several minutes of stirring at room temperature, AgX (X = NO_3^-, **1**; ClO_4^-, **2**; PF_6^-, **3**; BF_4^-, **4**; $CH_3SO_3^-$, **5**; $CF_3SO_3^-$, **6**) (0.2 mmol) was added and the solution was left under continuous stirring at room temperature for 24 hours. The white precipitate so obtained was filtered off, washed three times with ethanol and dried in an oven at 50 ºC under vacuum. In the following, some analytical data, along with the main absorption bands taken from the FTIR spectra, are provided for each compound.

$Ag_2(tr_2ad)(NO_3)_2 \cdot H_2O$ (1). Yield: 70%. **1** is insoluble in alcohols, dimethylsulfoxide, acetone, acetonitrile, dimethylformamide and water. Elem. Anal. calc. for $C_{14}H_{20}Ag_2N_8O_7$ (FW = 628.09 g/mol): N, 17.84; C, 26.77; H, 3.21%. Found: N, 16.71; C, 26.26; H, 3.07%. IR (cm^{-1}): 3417(br) ν(H-O); 3110(m) ν(C-$H_{aromatic}$), 3000-2900(w) ν(C-$H_{aliphatic}$), 1530(m) ν(C=C + C=N), 1316(vs) ν (NO_3).

$Ag_3(tr_2ad)_2(ClO_4)_3 \cdot EtOH$ (2). Yield: 60%. **2** is insoluble in alcohols, dimethylsulfoxide, acetone, acetonitrile, dimethylformamide and water. Elem. Anal. calc. for $C_{30}H_{43}Ag_3Cl_3N_{12}O_{13}$ (FW = 1208.69 g/mol): N, 13.91; C, 29.81; H, 3.50%. Found: N, 14.22; C, 30.10; H, 3.41%. IR (cm^{-1}): 3559(br) ν(H-O); 3133(m) ν(C-$H_{aromatic}$), 3000-2900(w) ν(C-$H_{aliphatic}$), 1537(m) ν(C=C + C=N); 1196(s), 1076(vs) ν(ClO_4).

$Ag(tr_2ad)(PF_6) \cdot H_2O$ (3). Yield: 60%. **3** is insoluble in alcohols, dimethylsulfoxide, acetone, acetonitrile, dimethylformamide and water. Elem. Anal. calc. for $C_{14}H_{20}AgF_6N_6OP$ (FW = 541.18 g/mol): N, 15.53; C, 31.07; H, 3.72%. Found: N, 14.90; C, 31.82; H, 3.74%. IR (cm^{-1}): 3164(w) ν(C-$H_{aromatic}$), 3000-2900(w) ν(C-$H_{aliphatic}$), 1525(m) ν(C=C + C=N), 824(vs) ν(PF_6).

$Ag_3(tr_2ad)_2(BF_4)_3 \cdot H_2O$ (4). Yield: 65%. **4** is insoluble in alcohols, dimethylsulfoxide, acetone, acetonitrile, dimethylformamide and water. Elem. Anal. calc. for $C_{28}H_{38}Ag_3B_3F_{12}N_{12}O$ (FW = 1142.70 g/mol): N, 14.71; C, 29.43; H, 3.35%. Found: N, 14.28; C, 30.15%; H, 3.67%. IR (cm^{-1}): 3606(br) ν(H-O); 3143(w) ν(C-$H_{aromatic}$), 3000-2900(w) ν(C-$H_{aliphatic}$), 1540(m), ν(C=C + C=N), 1046(vs), 1024(vs) ν(BF_4).

$Ag_2(tr_2ad)(CH_3SO_3)_2 \cdot 3H_2O$ (5). Yield: 50%. **5** is insoluble in alcohols, dimethylsulfoxide, acetone, acetonitrile, dimethylformamide and water. Elem. Anal. calc. for $C_{16}H_{30}Ag_2N_6O_9S_2$ (FW = 730.31 g/mol): N, 11.51; C, 26.31; H, 4.14%. Found: N, 11.09; C, 26.19; H, 3.60%. IR (cm^{-1}): 3415(br) ν(H-O); 3103(w) ν(C-$H_{aromatic}$), 3000-2900(w) ν(C-$H_{aliphatic}$), 1535(m) ν(C=C + C=N), 1152(vs), 1032(vs) ν(CH_3–SO_3).

$Ag_3(tr_2ad)_2(CF_3SO_3)_3 \cdot EtOH$ (6). Yield: 55%. **6** is insoluble in alcohols, dimethylsulfoxide, acetone, acetonitrile, dimethylformamide and water. Elem. Anal. calc. for $C_{33}H_{42}Ag_3F_9N_{12}O_{10}S_3$ (FW = 1357.54 g/mol): N, 12.38; C, 29.19; H, 3.12%. Found: N, 12.75; C, 29.01; H, 3.35%. IR (cm^{-1}): 3493(br) ν(H-O); 3125(m) ν(C-$H_{aromatic}$), 3000-2900(w) ν(C-$H_{aliphatic}$), 1526(m) ν(C=C + C=N), 1247(vs), 1156(vs), 1024(vs) ν(CF_3–SO_3).

3. RESULTS AND DISCUSSION

The synthesis of the 1,3-bis(1,2,4-triazol-4-yl)adamantane ligand (tr_2ad) was accomplished by functionalizing adamantane to the aim at preparing the corresponding amines, followed by an acid-catalyzed condensation with N,N-dimethylformamideazine, finally yielding the desired ditopic bis(triazolyl)-type ligand [19]. The FTIR spectrum of this ligand (Fig. 1) reveals the main stretching vibration bands that are in accordance with the corresponding structure: stretching vibration of the C–H bonds from the aromatic triazolyl rings at 3125 cm^{-1} and of the C–H aliphatic bonds from the adamantane core, along with the stretching vibration of the C=C and C=N double bonds from the triazolyl rings at 1517 cm^{-1}.

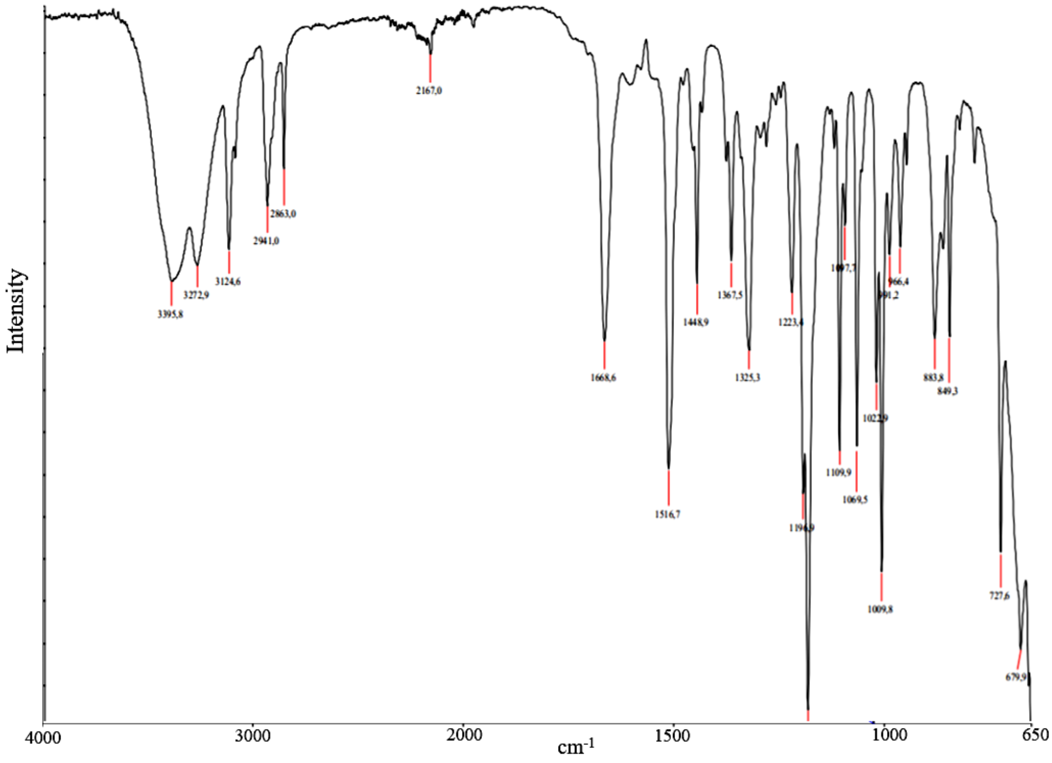
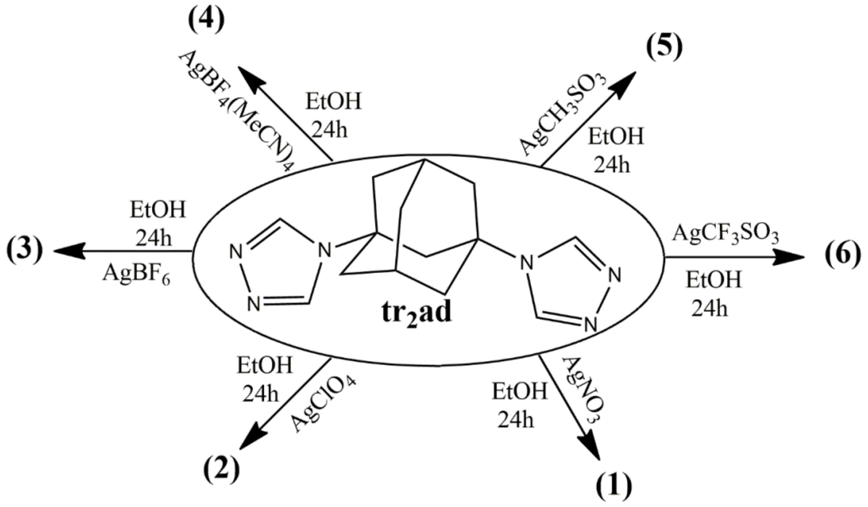


Fig. 1. FTIR spectrum of 1,3-bis(1,2,4-triazol-4-yl)adamantane (tr_2ad)

The isolation of the six new silver(I) coordination polymers required room temperature conditions in alcoholic ambient (ethanol) for 24 h. Elemental analyses allowed to propose the stoechiometric formulations for the obtained silver(I) coordination polymers, that is, $Ag_2(tr_2ad)(NO_3)_2 \cdot H_2O$ (**1**), $Ag_3(tr_2ad)_2(ClO_4)_3 \cdot EtOH$ (**2**), $Ag(tr_2ad)(PF_6) \cdot H_2O$ (**3**), $Ag_3(tr_2ad)_2(BF_4)_3 \cdot H_2O$ (**4**), $Ag_2(tr_2ad)(CH_3SO_3)_2 \cdot 3H_2O$ (**5**) and $Ag_3(tr_2ad)_2(CF_3SO_3)_3 \cdot EtOH$ (**6**). The reactions were carried out in the metal:ligand ratio = 2:1 and, despite the ratio used in the syntheses, the formulae derived from the elemental analyses were independent of such a metal:ligand ratio (Scheme 1). All the compounds are in the form of white powders, air- and moisture-stable, and are insoluble in most common organic solvents and water and do not melt, but only decompose at elevate temperatures. This occurrence suggests their polymeric nature. Worthy of note, the same formulated compounds could also be obtained if methanol was employed as a solvent instead of ethanol, in the same reaction conditions.



Scheme 1. Synthesis of the new silver(I) coordination polymers incorporating the tr$_2$ad ligand

After coordination to the silver(I) ions, in each prepared coordination polymer, the FTIR spectrum of the ligand shows different patterns and the main absorption bands of the ligand are shifted to higher or lower wavenumbers, thus indicating the success of each synthesis, also taking into consideration the influence of the counteranion. In Figs. 2-4, the FTIR spectra of the newly obtained silver(I) coordination polymers are given.

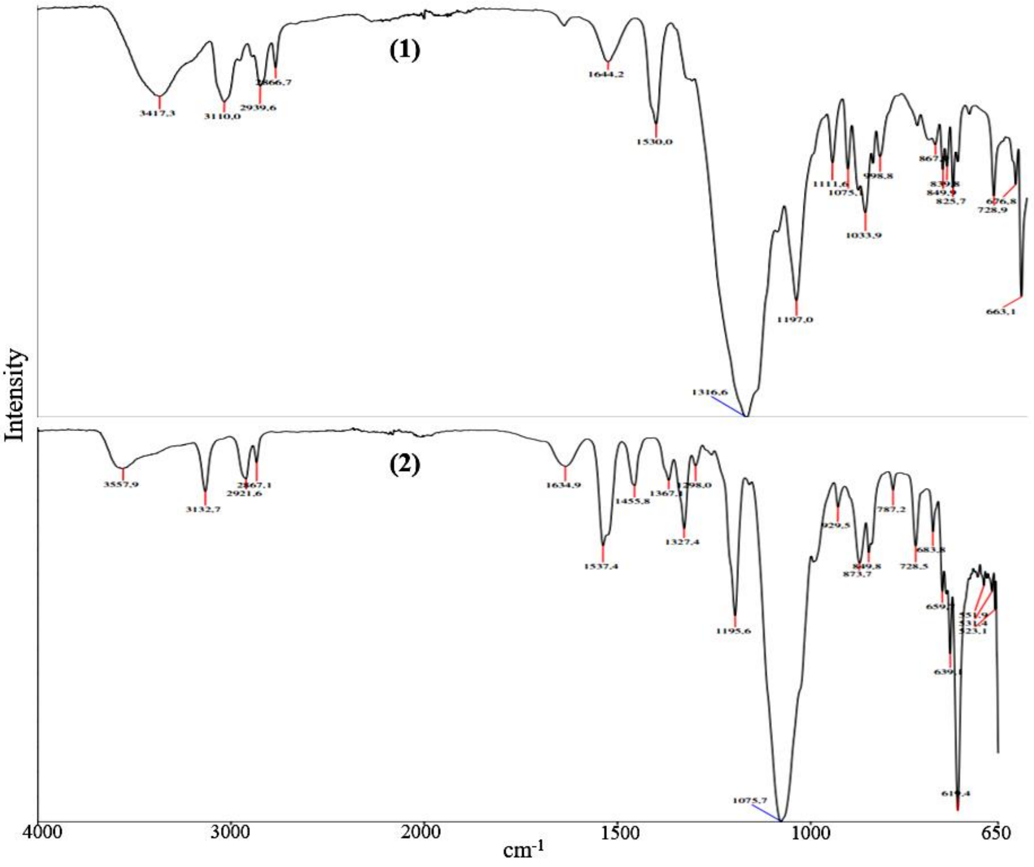


*Fig. 2. FTIR spectra of Ag$_2$(tr$_2$ad)(NO$_3$)$_2$·H$_2$O (**1**) and Ag$_3$(tr$_2$ad)$_2$(ClO$_4$)$_3$·EtOH (**2**)*

The FTIR spectra of all silver(I) CPs show a weak to medium broad band in the region 3400-3600 cm^{-1}, along with the weak to medium absorption band located in the region 1635-1658 cm^{-1}, which are attributed to the stretching vibration and the bending mode, respectively, of the hydroxyl group from either ethanol, methanol or water. These molecules are therefore acting as clathrated solvent molecules that remained trapped inside the crystalline network of the obtained species during their synthesis. The elemental analyses and FTIR spectra were unchanged after several weeks at room temperature, thus suggesting their remarkable stability. On the hand, the absorption bands observed in the region 2800-300 cm^{-1} have been assigned to the stretching vibration of the aliphatic C–H bonds from the adamantane's structure, whereas the band located at 3125 cm^{-1}, specific to the vibration of the aromatic C–H bonds from the structure of the triazolic rings of the free ligand, is somehow shifted to lower or high wavenumbers in all silver(I) CPs. The band observed at 1517 cm^{-1}, specific to the stretching vibration of the C=N double bond from the triazolic rings of the free ligand, is also shifted to slightly higher wavenumbers in all silver(I) CPs, this occurrence indicating the successful coordination of the tr_2ad ligand to the silver(I) ions, as well as the certain influence of the anions from each compound.

A careful analysis of the FTIR spectra of all the newly obtained silver(I) CPs was also performed in order to get clues, in the absence of X-ray structural characterization for reasons of their lack of crystallinity, about the possible interactions in which the anions may be involved within the corresponding structures. Thus, in the spectrum of **1**, the very strong band observed at 1317 cm^{-1} is ascribed to the nitrate group that is coordinated to the silver(I) ions in a unidentate mode [20]. In Fig. 5, a proposed chemical structure of compound **1** is given. The spectrum of **2** shows a very strong absorption band at 1076 cm^{-1} and a very sharp one at 619 cm^{-1} which are characteristic of the ionic perchlorate group [20]. In the spectrum of **3**, the very strong absorption band observed at 824 cm^{-1}, along with the presence of a medium sharp band at 661 cm^{-1}, are characteristic of the hexafluorophosphate anion which is in interaction with the silver(I) ions [21]. In the spectrum of **4**, the very strong broad band, finely splitted into two peaks at 1024 and 1046 cm^{-1}, was attributed to the coordinated tetrafluoroborate anion [21].

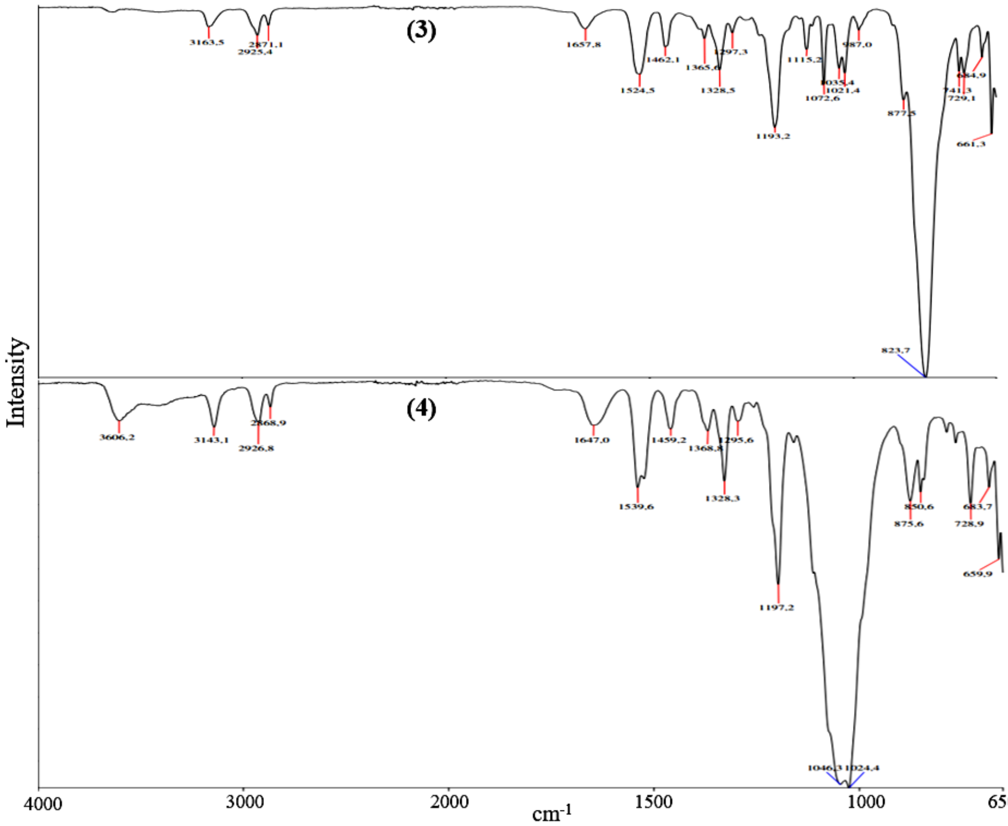


Fig. 3. FTIR spectra of $Ag(tr_2ad)(PF_6)\cdot H_2O$ *(**3**) and* $Ag_3(tr_2ad)_2(BF_4)_3\cdot H_2O$ *(**4**)*

The FTIR spectra of **5** and **6** show a number of strong absorptions in the 1032−1152 cm^{-1} region, which are specific of the asymmetric and symmetric vibrations of the SO_3^- group together with the vibration of the S−O bond from both the methanesulfonate and trifluoromethanesulfonate anions, and are indicative of unidentate coordination to the silver(I) centres through the oxygen atoms [22].

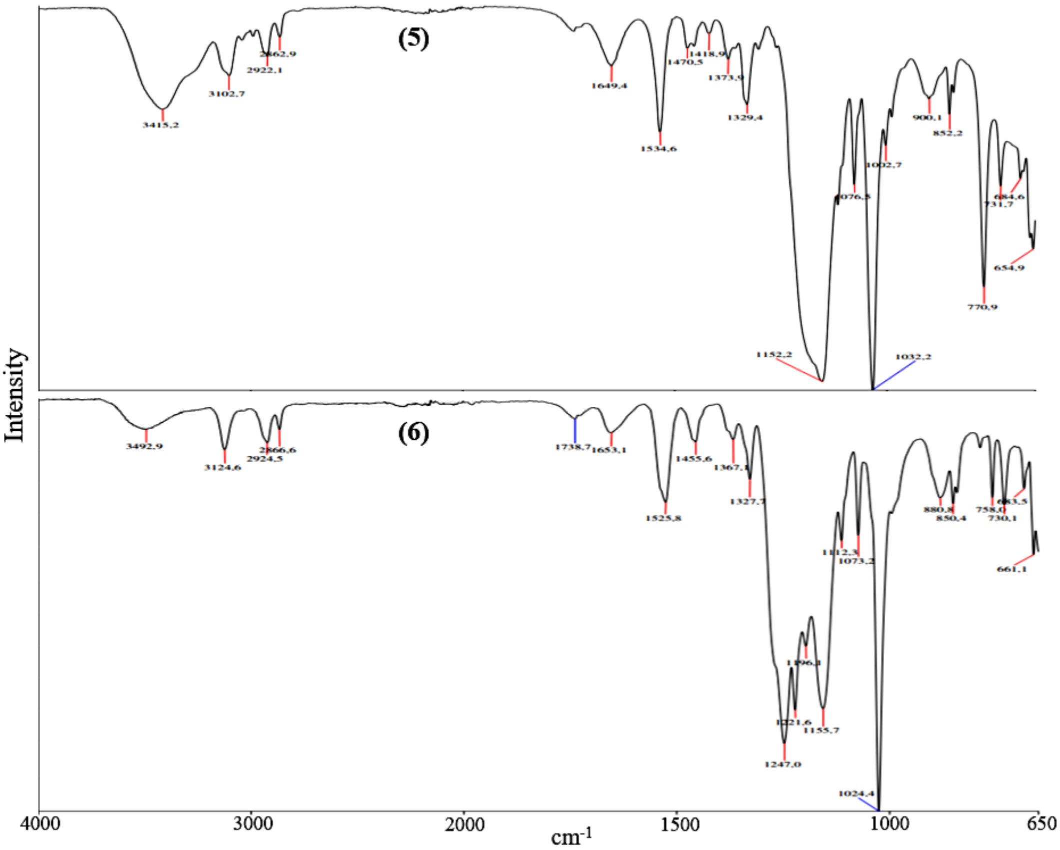


*Fig. 4. FTIR spectra of $Ag_2(tr_2ad)(CH_3SO_3)_2·3H_2O$ (**5**) and $Ag_3(tr_2ad)_2(CF_3SO_3)_3·EtOH$ (**6**)*

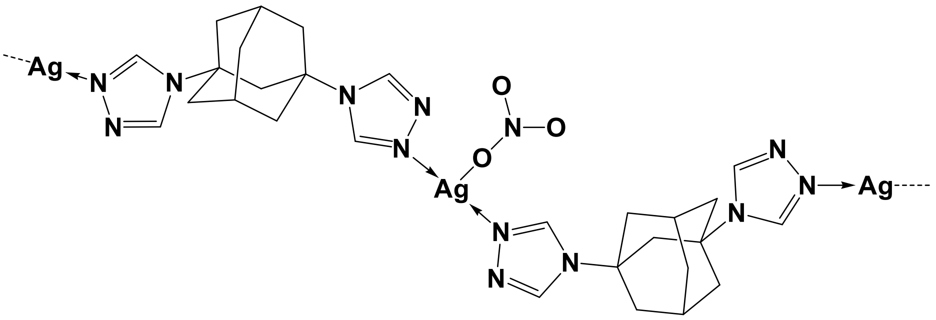


*Fig. 5. Proposed chemical structure of $Ag_2(tr_2ad)(NO_3)_2·H_2O$ (**1**)*

4. CONCLUSIONS

The reaction of the ditopic 1,3-bis(1,2,4-triazol-4-yl)adamantane ligand (tr_2ad) with different silver(I) salts afforded a new family of coordination polymers bearing the stoechiometric formulae $Ag_2(tr_2ad)(NO_3)_2·H_2O$ (**1**), $Ag_3(tr_2ad)_2(ClO_4)_3·EtOH$ (**2**), $Ag(tr_2ad)(PF_6)·H_2O$ (**3**), $Ag_3(tr_2ad)_2(BF_4)_3·H_2O$ (**4**), $Ag_2(tr_2ad)(CH_3SO_3)_2·3H_2O$ (**5**) and $Ag_3(tr_2ad)_2(CF_3SO_3)_3·EtOH$ (**6**), as were derived by means of elemental analyses. In the absence of crystallinity in the corresponding powdered solids, FTIR spectroscopy offered a useful help to reveal the success of each synthesis, together with the manner of anions involvement regarding their coordinating or noncoordinating ability to the silver(I) ions. Due to their prolonged stability and insolubility, the new silver(I) CPs will be subjected to antimicrobial tests, thus expecting to overcome the classical materials used to this aim.

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