Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Mononuclear and coordination polymer of silver(I) complexes: design, synthesis, and crystal structure analysis

Nur R.A. Rahazat, Rosenani A. Haque, Seik W. Ng & Mohd. R. Razali

To cite this article: Nur R.A. Rahazat, Rosenani A. Haque, Seik W. Ng & Mohd. R. Razali (2015) Mononuclear and coordination polymer of silver(I) complexes: design, synthesis, and crystal structure analysis, Journal of Coordination Chemistry, 68:8, 1317-1331, DOI: 10.1080/00958972.2015.1014348

To link to this article: http://dx.doi.org/10.1080/00958972.2015.1014348

Journal of Coordination Chemistry, 2015
Vol. 68, No. 8, 1317–1331, http://dx.doi.org/10.1080/00958972.2015.1014348

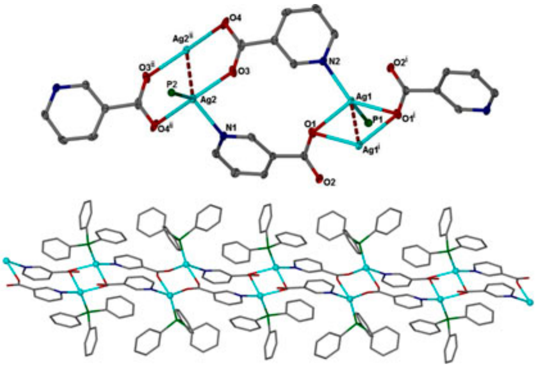
Taylor & Francis
Taylor & Francis Group

Mononuclear and coordination polymer of silver(I) complexes: design, synthesis, and crystal structure analysis

NUR R.A. RAHAZAT†, ROSENANI A. HAQUE†, SEIK W. NG‡ and
MOHD. R. RAZALI†*

†School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia
‡Department of Chemistry, University Malaya, Kuala Lumpur, Malaysia

(*Received 22 July 2014; accepted 10 November 2014*)



A series of mononuclear structures and coordination polymers of silver(I) has been synthesized and characterized by IR spectroscopy, NMR spectroscopy, and single-crystal X-ray diffraction. Reaction of the silver(I) precursor [Ag(PPh$_3$)$_2$(OAc)] with 2,3-pyridinedicarboxylic acid (2,3-pyCOOH), 2,6-pyridinedicarboxylic acid (2,6-pyCOOH), 3-pyridinecarboxylic acid (3-pyCOOH), and 4-pyridinecarboxylic acid (4-pyCOOH) afforded mononuclear complexes [Ag(PPh$_3$)$_2$(2,3-COO)] (**1**), [Ag(PPh$_3$)$_2$(2,6-COO)]·EtOH·MeCN (**2**), [Ag(PPh$_3$)$_2$(3-COO)]·H$_2$O (**3**), and [Ag(PPh$_3$)$_2$(4-COO)] (**4**), respectively. Coordination polymers [Ag(PPh$_3$)(2,3-COO)]$_n$ (**5**), [Ag$_2$(PPh$_3$)$_2$(3-pyCOO)$_2$]$_n$ (**6**), and [Ag(PPh$_3$)$_2$(4-COO)]$_n$·EtOH (**7**) were obtained from reaction of Ag(OAc), PPh$_3$, and pyridinedicarboxylic acid or pyridinecarboxylic acid. Even though the formation of **5** can be achieved by hydrothermal reaction using similar reactants to those in formation of **1**, the percentage yield and by-products of the final product prohibit further analysis of the compound. Complexes **5** and **6** are 1-D zigzag and ladder type structures, respectively, with argentophilic interactions, Ag···Ag, dominating the stability of **6**. Complex **7** shows a 2-D layer structure with three-connected 4.8^2-*fes* topology.

Keywords: Coordination polymer; Argentophilic interactions; Ladder-like structure

---

*Corresponding author. Email: mohd.rizal@usm.my

1. Introduction

Coordination polymers have attracted interest for potential applications in photoluminescence and porous frameworks for gas storage [1]. Structural studies of coordination polymers reveal fascinating interpenetration networks and topologies [2]. Reactions and selectivity of the ligands are crucial to obtain desired complexes. Carboxylic acid ligands are widely used for formation of coordination polymers, owing to their tendency as bridging ligands [3].

Our recent work has focused on silver(I) complexes because of variety of coordination number and extensive use in catalysis, medicine, and luminescent materials [4]. The flexibility of silver(I) may lead to different molecular architectures in the presence of chelating and bridging ligands, which can result in interesting structures and potentially useful chemical and physical properties [5]. Mononuclear silver(I) complexes are known for potential applications with biological activities or luminescence properties [6].

Many silver coordination polymers exhibit Ag···Ag interactions. Such behavior is observed in the structure of $\{[Ag(L^1)](BF_4)\}_n$ (where L^1 = 2-(3,5-dimethylpyrazol-1-yl)-1,10-phenanthroline) in which each repeating unit is linked by Ag···Ag interactions and further stabilized by $\pi \cdots \pi$ interactions between phenyl/pyrazole rings [7]. Ag···π, Ag···C, and C–H···Ag are also possible interactions that can occur in silver(I) complexes with aromatic ligands [8].

This work is based on previous work by Amini *et al.* in reaction between $[Ag(PPh_3)_2(OAc)]$ with 2-pyridinecarboxylic acid (2-pyCOOH) [9]. The resulting mononuclear product, $[Ag(PPh_3)_2(2\text{-pyCOO})]$, with 2-pyCOO$^-$ displays a N,O-chelating mode with silver(I). Thus, we proposed that with the presence of extra carboxylic group on the pyridyl ring, the assembly may form coordination polymers, owing to the ability of the extra carboxylic group to bind adjacent silver(I) ions. Such coordination modes offered by this type of ligands are known [10]. This is also due to silver(I) being flexible, adopting coordination numbers between two and six, and geometries from linear to octahedral [11]. This may result in formation of various coordination structures depending on the position of the second carboxylic group.

Reaction between $[Ag(PPh_3)_2(OAc)]$ and *n*-pyridinecarboxylic acid (where $n = 3$ or 4) may also result in formation of coordination polymers, since the ability to form a five-membered chelation ring, Ag–O–C–C–N, is not favored. While both oxygens in *n*-pyCOOH could bind to the silver(I), the nitrogen atom of pyridyl ring may coordinate to the adjacent silver(I) ions, as previously observed for this type of ligand [12, 13]. Thus, by varying the position of carboxylic acid in the pyridyl ring, numerous coordination polymers with different features may be obtained. Herein, we report the syntheses and structures of mononuclear complexes (**1–4**) and coordination polymers (**5–7**) of silver(I) based on pyridinedicarboxylic acids and pyridinecarboxylic acids.

2. Experimental

2.1. *Synthesis*

Elemental analyses (CHN) were performed with a Thermo Finnigan Flash-1112EA microanalyzer. The melting points of complexes were determined by Stuart Melting Point

SMP11. IR spectra were recorded from 4000 to 650 cm^{-1} on a Perkin Elmer Spectrum 100 FT-IR spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker AVANCE 500 MHz instrument. All syntheses were carried out with commercially available reagents, used as received. $[Ag(PPh_3)_2(CH_3COO)]$ was synthesized as reported [14].

2.1.1. Synthesis of $[Ag(PPh_3)_2(2,3\text{-}pyCOO)]$ (1). $[Ag(PPh_3)_2(CH_3COO)]$ (0.70 g, 1 mM) and 2,3-pyridinedicarboxylic acid (0.17 g, 1 mM) were dissolved in a mixture of ethanol/water (20 mL, 50/50 v/v) and left to reflux for 2 h. The clear solution was filtered and the filtrate left for slow evaporation in the dark. Clear crystals formed within 3–4 days which were then recrystallized with acetonitrile. The crystals were isolated and washed with diethyl ether, water, and air-dried. Yield: 0.95 g, 75%. m.p. 192–196 °C. Anal. Calcd for $C_{43}H_{34}AgNO_4P_2$: C, 64.68; H, 4.29; N, 1.75%. Found: C, 64.95; H, 4.25; N, 1.79%. ATR-IR: 1688 w, 1559 w, 1479 m, 1431 m, 1363 m, 1182 m, 1161 m, 1092 m, 997 m, 805 m, 744 s, 691 s. ^{1}H NMR ($CDCl_3$, ppm): 7.27–7.37 (m, 24H, C_6H_5), 7.38–7.42 (m, 6H, C_6H_5), 8.12–8.16 (m, 3H, 2,3pyCOO). ^{13}C NMR ($CDCl_3$, ppm): 125.62, 128.99–129.06, 130.46, 131.68, 131.90, 132.74, 133.52–133.65, 143.99, 149.84, 150.41, 166.38, 168.24. ^{31}P ($CDCl_3$, ppm): 10.51.

2.1.2. Synthesis of $[Ag(PPh_3)_2(2,6\text{-}pyCOO)]\cdot EtOH\cdot MeCN$ (2). The preparation was similar to **1** except using 2,6-pyCOOH (0.17 g, 1 mM) instead of 2,3-pyCOOH. Yield: 0.86 g, 68%. m.p. 200–205 °C. Anal. Calcd for $C_{47}H_{43}AgN_2O_5P_2$: C, 63.73; H, 4.86; N, 3.16%. Found: C, 63.40; H, 4.52; N, 3.26%. ATR-IR: 1696 w, 1613 w, 1582 m, 1479 m, 1433 m, 1371 m, 1307 m, 1260 m, 1,94 w, 1026 m, 997 w, 880 w, 741 s, 692 s. ^{1}H NMR ($CDCl_3$, ppm): 7.17–7.37 (m, 24H, C_6H_5), 7.83–7.86 (m, 6H, C_6H_5), 8.30–8.33 (m, 3H, 2,6-py-COO). ^{13}C NMR ($CDCl_3$, ppm): 126.87, 128.73–128.81, 130.02, 132.08–132.59, 133.80–133.94, 138.55, 149.42, 167.16. ^{31}P ($CDCl_3$, ppm): 8.43.

2.1.3. Synthesis of $[Ag(PPh_3)_2(3\text{-}pyCOO)]\cdot H_2O$ (3). The preparation was similar to **1** except using 3-pyCOOH (0.12 g, 1 mM) instead of 2,3-pyCOOH. Yield: 0.84 g, 70%. m.p. 184–189 °C. Anal. Calcd for $C_{42}H_{34}AgNO_2P_2$: C, 66.86; H, 4.54; N, 1.86%. Found: C, 66.30; H, 4.27; N, 1.84%. ATR-IR: 1597 m, 1556 m, 1478 m, 1434 m, 1381 m, 1094 m, 1027 m, 997 m, 840 m, 744 s, 692 s. ^{1}H NMR ($CDCl_3$, ppm): 7.26–7.45 (m, 30H, C_6H_5), 8.28–8.30 (s, 2H, C_5H_4 N), 8.60–8.61 (s, 2H, C_5H_4 N), 9.24–9.25 (s, 1H, C_5H_4 N). ^{13}C NMR ($CDCl_3$, ppm): 122.63, 128.82–128.89, 130.19, 132.08, 132.29, 132.81, 133.86–133.99, 136.99, 150.34, 151.23, 171.34. ^{31}P ($CDCl_3$, ppm): 9.31.

2.1.4. Synthesis of $[Ag(PPh_3)_2(4\text{-}pyCOO)]$ (4). The preparation was similar to **1** except using 4-pyCOOH (0.12 g, 1 mM) instead of 2,3-pyCOOH. Yield: 0.86 g, 72%. m.p. 190–195 °C. Anal. Calcd for $C_{42}H_{34}AgNO_2P_2$: C, 66.86; H, 4.54; N, 1.86%. Found: C, 66.43; H, 4.49; N, 1.92 %. ATR-IR: 1603 m, 1544 m, 1478 m, 1433 m, 1365 m, 1092 m, 1026 m, 996 m, 743 m, 693 m. ^{1}H NMR ($CDCl_3$, ppm): 7.18–7.29 (m, 12H, C_6H_5), 7.31–7.39 (m, 9H, C_6H_5), 7.71–7.81 (m, 10H, C_6H_5), 8.52–8.53 (2, 2H, C_5H_4 N). ^{13}C NMR ($CDCl_3$, ppm): 123.63, 128.87–128.94, 130.33, 131.78–132.01, 133.85–133.98, 145.09, 149.70, 171.36. ^{31}P ($CDCl_3$, ppm): 10.20.

2.1.5. Synthesis of [Ag(PPh_3)(2,3-py(COO)]$_n$ (5). Silver acetate (0.16 g, 1 mM) and PPh_3 (0.26 g, 1 mM) dissolved in a mixture of ethanol/water (20 mL, 50/50 v/v) was refluxed until the reactants were completely dissolved. To the stirring solution, 2,3-py-COOH (0.17 g, 1 mM) dissolved in ethanol (10 mL) was added dropwise. Upon completion, the solution mixture then was left to reflux for 2 h. The resulting colorless solution was filtered and the filtrate left for slow evaporation in a dark place. Clear crystals formed after 3–4 days. The crystals were isolated and washed with diethyl ether, water, and air-dried. Yield: 0.24 g, 76%, m.p. 190–195 °C. Anal. Calcd for $C_{25}H_{19}AgNO_4P_2$: C, 56.10; H, 3.39; N, 2.62. Found: C, 56.17; H, 3.36; N, 2.88%. ATR-IR: 1544 s, 1480 m, 1435 s, 1359 s, 1100 m, 1057 w, 1014 w, 997 w, 838 w, 741 s, 684 s. ^1H NMR ($CDCl_3$, ppm): 7.46–7.53 (m, 15H, C_6H_5), 7.94–7.95 (s, 1H, C_5H_3 N), 8.69–8.71 (s, 1H, C_5H_3 N). ^{13}C NMR ($CDCl_3$, ppm): 123.877, 129.332, 130.331, 131.183, 133.984, 143.126, 150.144, 172.558. ^{31}P ($CDCl_3$, ppm): 16.14.

2.1.6. Alternative method to synthesis 5. [Ag(PPh_3)$_2$(CH_3COO)] (0.70 g, 1 mM) and 2,3-pyridinedicarboxylic acid (0.17 g, 1 mM) were dissolved in a mixture of ethanol/water (10 mL) and heated at 110 °C for 2 days in a sealed Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled to room temperature, very small colorless crystals formed concomitantly with white and pale yellow powder. The formation of **5** is confirmed by IR spectra and unit cell determination on the crystals. We were unable to separate the products and, thus, insufficient quantities of **5** via this method could be obtained for further analysis.

2.1.7. Synthesis of [Ag_2(PPh_3)$_2$(3-pyCOO)$_2$]$_n$ (6). The preparation was similar to **5** (Section 2.1.5) except using 3-pyCOOH (0.12 g, 1 mM) instead of 2,3-pyCOOH. Yield: 0.22 g, 76%, m.p. 228–231 °C. Anal. Calcd for $C_{24}H_{20}AgNO_2P$: C, 58.44; H, 4.09; N, 2.84%. Found: C, 58.55; H, 4.08; N, 2.74%. ATR-IR: 3434 w, 1662 w, 1583 m, 1558 s, 1478 m, 1435 s, 1379 s, 1190 w, 1096 s, 1043 m, 997 m, 846 s, 752 s, 691 s. ^1H NMR ($CDCl_3$, ppm): 7.33–7.51 (m, 15H, C_6H_5), 8.34–8.36 (m, 4H, C_5H_3 N). ^{13}C NMR ($CDCl_3$, ppm): 123.09, 128.73, 129.30, 130.44, 130.87, 131.39, 131.65, 132.32, 134.24, 137.64, 151.56, 170.78. ^{31}P ($CDCl_3$, ppm): 13.12.

2.1.8. Synthesis of [Ag(PPh_3)(4-pyCOO)]$_n$·EtOH (7). The preparation was similar to **5** (section 2.1.5) except using 4-pyCOOH (0.12 g, 1 mM) instead of 2,3-pyCOOH. Yield: 0.20 g, 68%. m.p. 178–182 °C. Anal. Calcd for: $C_{26}H_{26}Ag$ NO_3P: C, 58.01; H, 4.68; N, 2.60%. Found: C, 58.17; H, 4.69; N, 2.71%. ATR-IR: 3055 w, 1597 m, 1478 m, 1433 m, 1369 w, 1306 w, 1178 w, 1089 m, 1025 m, 997 m, 744 s, 692 s. ^1H NMR ($CDCl_3$, ppm): 7.46–7.72 (m, 15H), 8.29–8.31 (m, 4H, C_5H_3 N). ^{13}C NMR ($CDCl_3$, ppm): 122.912, 128.610, 129.361, 132.163, 133.901, 134.973, 137.433, 150.892. ^{31}P ($CDCl_3$, ppm): 19.48.

2.2. *Crystallographic details*

Crystals were mounted on fine glass fiber or metal pin using viscous hydrocarbon oil. Data were collected on a Bruker-Smart ApexII-2009 CCD diffractometer (**1**, **2,** and **7**) or Oxford CrysAlis Pro (**3**, **5,** and **6**) equipped with graphite monochromated Mo-Kα ($\lambda = 0.71073$)

radiation. Data collection temperatures were maintained at 100 K using open flow N_2 cryostreams. For data collected on the Bruker ApexII-2009 diffractometer, integration was carried out by SAINT using the APEX^{II} software [15]. For data collected on the Oxford CrysAlis Pro, data collection and processing was carried by the CrysAlis^{Pro} software.

Solutions were obtained by direct methods using SHELXS 97, followed by successive refinements using full-matrix least-squares method against F^2 using SHELXL 97 [16]. The program X-seed was used as a graphical SHELX interface [17].

2.2.1. [Ag(PPh$_3$)$_2$(2,3-pyCOO)] (1). $C_{43}H_{34}NAgO_4P_2$: $M = 798.52$, colorless, 0.47 × 0.37 × 0.26 mm^3, monoclinic, $P2_1/n$, $a = 13.4215(2)$, $b = 12.9555(2)$, $c = 21.6556(4)$, $\alpha = 90$, $\beta = 99.155(2)$, $\gamma = 90$, $V = 3717.56(11)$, $Z = 4$, $\rho_{cacl} = 1.427$ g cm^{-3}, $F_{000} = 1632$, 38,756 reflections collected, 8578 unique ($R_{int} = 0.0218$), Final $GooF = 1.022$, $R1 = 0.0243$, $wR2 = 0.0598$, R indices based on 7723 reflections with $I > 2\sigma(I)$, 464 parameters, 1 restraints, $\mu = 0.672$.

2.2.2. [Ag(PPh$_3$)$_2$(2,6-pyCOO)]·EtOH·MeCN (2). $C_{45}H_{39.25}AgN_{1.25}O_{4.75}P_2$: $M = 843.34$, colorless, 0.30 × 0.05 × 0.05 mm^3, monoclinic, $P2_1/n$, $a = 11.1275(2)$, $b = 23.6375(4)$, $c = 15.3022(3)$, $\alpha = 90$, $\beta = 100.209(2)$, $\gamma = 90$, $V = 3961.16(12)$, $Z = 4$, $\rho_{cacl} = 1.414$ g cm^{-3}, $F_{000} = 1732$, 48,548 reflections collected, 17,504 unique ($R_{int} = 0.0367$), Final $GooF = 0.996$, $R1 = 0.0325$, $wR2 = 0.0748$, R indices based on 9161 reflections with $I > 2\sigma(I)$, 519 parameters, 29 restraints, $\mu = 0.636$. Residual electron density in the lattice was assigned as disordered ethanol and acetonitrile molecules.

2.2.3. [Ag(PPh$_3$)$_2$(3-pyCOO)]·H$_2$O (3). $C_{42}H_{36}AgNO_3P_2$: $M = 772.53$, colorless, 0.40 × 0.31 × 0.18 mm^3, monoclinic, $P2_1/n$, $a = 9.1223(2)$, $b = 19.5270(5)$, $c = 20.2272(5)$, $\alpha = 90$, $\beta = 90.0100(10)$, $\gamma = 90$, $V = 3602.54(15)$, $Z = 4$, $\rho_{cacl} = 1.424$ g cm^{-3}, $F_{000} = 1584$, 32,430 reflections collected, 6339 unique ($R_{int} = 0.0398$), Final $GooF = 1.121$, $R1 = 0.06444$, $wR2 = 0.1450$, R indices based on 5330 reflections with $I > 2\sigma(I)$, 442 parameters, 0 restraints, $\mu = 0.689$.

2.2.4. [Ag(PPh$_3$)(2,3-py(COO)]$_n$ (5). $C_{25}H_{18}AgNO_4P$: $M = 535.24$, colorless, 0.40 × 0.30 × 0.30 mm^3, monoclinic, $P2_1/c$, $a = 12.8937(16)$, $b = 12.5081(15)$, $c = 14.7682(18)$, $\alpha = 90$, $\beta = 108.990(2)$, $\gamma = 90$, $V = 2252.1(5)$, $Z = 4$, $\rho_{cacl} = 1.579$ g cm^{-3}, $F_{000} = 1076$, 16,741 reflections collected, 5137 unique ($R_{int} = 0.0258$), Final $GooF = 1.076$, $R1 = 0.0357$, $wR2 = 0.1089$, R indices based on 4125 reflections with $I > 2\sigma(I)$, 289 parameters, 0 restraints, $\mu = 0.998$.

2.2.5. [Ag$_2$(PPh$_3$)$_2$(3-pyCOO)$_2$]$_n$ (6). $C_{24}H_{19}AgNO_2P$: $M = 492.24$, colorless, 0.30 × 0.20 × 0.10 mm^3, monoclinic, $P2_1/c$, $a = 15.8458(4)$, $b = 17.9803(5)$, $c = 14.3366(4)$, $\alpha = 90$, $\beta = 96.098(2)$, $\gamma = 90$, $V = 4061.56(19)$, $Z = 4$, $\rho_{cacl} = 1.610$ g cm^{-3}, $F_{000} = 1984$, 56,551 reflections collected, 9405 unique ($R_{int} = 0.0453$), Final $GooF = 1.011$, $R1 = 0.0340$, $wR2 = 0.0701$, R indices based on 6753 reflections with $I > 2\sigma(I)$, 523 parameters, 0 restraints, $\mu = 1.092$.

2.2.6. [Ag(PPh$_3$)(4-pyCOO)]$_n$·EtOH (7). $C_{26}H_{25}AgNO_3P$: $M = 538.31$, colorless, 0.45 × 0.35 × 0.05 mm^3, monoclinic, $P2_1/c$, $a = 15.7848(10)$, $b = 12.9426(5)$, $c = 12.4989(6)$, $\alpha = 90$, $\beta = 111.695(7)$, $\gamma = 90$, $V = 2372.6(2)$, $Z = 4$, $\rho_{cacl} = 1.507$ g cm^{-3}, $F_{000} = 1096$, 26,061 reflections collected, 5505 unique ($R_{int} = 0.0587$), Final $GooF = 1.044$, $R1 = 0.0398$, $wR2 = 0.0953$, R indices based on 4283 reflections with $I > 2\sigma(I)$, 293 parameters, 2 restraints, $\mu = 0.944$.

3. Results and discussion

3.1. *Synthesis*

Reaction of [Ag(PPh$_3$)$_2$(OAc)] with either 2,3-pyridinedicarboxylic acid or 2,6-pyridinedicarboxylic acid yielded mononuclear complexes [Ag(PPh$_3$)$_2$(2,3-pyCOO] (**1**) and [Ag(PPh$_3$)$_2$(2,6-pyCOO]·EtOH·MeCN (**2**), respectively. Reactions were conducted as reported with the molar ratio of the reactants being 1 : 1. A similar reaction procedure, using either 3-pyCOOH or 4-pyCOOH instead of pyridinedicarboxylic acid derivatives, also resulted in mononuclear [Ag(PPh$_3$)$_2$(3-pyCOO)] (**3**) and [Ag(PPh$_3$)$_2$(4-pyCOO)] (**4**), respectively. These reactions did not yield the expected coordination polymer.

Similar reactants were also left to react in a solvothermal oven under more forcing conditions, beneficial in synthesizing coordination polymers. Solvothermal/hydrothermal has also been applied to increase the ability of the ligand to coordinate with the metal center [18]. Similar reactants used to synthesize **1** via hydrothermal synthesis yielded [Ag(PPh$_3$)(2,3-COO)]$_n$ (**5**) as tiny colorless crystals in very low-yield. This product concomitantly exists with white and yellow powder, which could not be separated, prohibiting further analysis of this complex. Other reactions yielded either oily products or clear solutions which yielded brown oily product upon evaporating the solvent at room temperature.

Based on the molecular structure of **5** obtained via hydrothermal synthesis, a few changes were made in the reaction procedure. While Ag(OAc), PPh$_3$, and 2,3-pyCOOH or *n*-pyCOOH (*n* = 3 or 4) as starting materials in 1 : 1 : 1 M ratio, coordination polymers [Ag(PPh$_3$)(2,3-COO)]$_n$ (**5**), [Ag$_2$(PPh$_3$)$_2$(3-pyCOO)$_2$]$_n$ (**6**), and [Ag(PPh$_3$)(4-COO)]$_n$·EtOH (**7**) were obtained in good yield as pure colorless crystals. Similar reactions, with different molar ratio of reactants, such as 1 : 2 : 2 or 1 : 2 : 1 resulted in formation of similar mononuclear structures. Reactions in excess 2,3-pyCOOH or *n*-COOH (1 : 1 : 2 or 1 : 1 : 3 M ratio) yielded the known structures, [$Ag_6(C_7H_4NO_4)_2(C_7H_3NO_4)_2(H_2O)_4$] [19], [Ag(3-pyCOO)] [20], and [Ag(4-pyCOO)(4-pyCOOH)]·H$_2$O [21], respectively. These results indicate that the molar ratio of reactants is a crucial aspect in synthesizing these coordination polymers.

We have found that pyridinedicarboxylic acid or pyridinecarboxylic acid must be added slowly to a solution of Ag(OAc) and PPh$_3$ while stirring at elevated temperature. This is due to the tendency of Ag(I) to bind with two PPh$_3$, which then leads to the respective mononuclear complexes. Attempts to synthesize coordination polymers consisting of 2,6-pyCOOH and crystals of **4** were unsuccessful.

3.2. *Crystal structure*

[Ag(PPh$_3$)$_2$(2,3-pyCOO)] (**1**) crystallizes in the monoclinic space group $P2_1/_n$ with the entire molecule in the asymmetric unit. Ag(I) is four coordinate and possesses tetrahedral geometry (figure 1). The 2,3-pyCOO$^-$ chelates Ag(I) through N-pyridyl nitrogen and deprotonated carboxylic group, similar to [Ag(PPh$_3$)$_2$(2-pyCOO)] [6]. The remaining carboxylic groups are uncoordinated. The behavior of 2,6-pyCOO$^-$ in this structure is somewhat similar with dimethylpyridine-2,6-dicarboxylate in [Ag(L)NO$_3$]$_n$, in which nitrate is bridging in the coordination polymer [22]. Even though 2,3-pyCOOH obtains two carboxylic groups, only one is deprotonated and coordinated to metal, thus sharing similar coordination mode with 2-pyCOO$^-$ in the aforementioned structure. The Ag1–O1 and Ag1–N1 distances are 2.364(8) Å and 2.421(7) Å, respectively (table 1). Intramolecular hydrogen bond is observed with O2 as hydrogen bond acceptor to an adjacent carboxylic group, O4.

[Ag(PPh$_3$)$_2$(2,6-pyCOO)]·EtOH·MeCN (**2**) crystallized in the monoclinic space group $P2_1/n$ with the asymmetric unit containing the entire molecule. Ag(I) is four coordinate tetrahedral (figure 2). The coordination sphere around Ag(I) and coordination mode of the ligand are similar to that in **1** with the distance between Ag1–O1 and Ag1–N1, 2.470(5) Å and 2.365(8) Å, respectively. Unlike **1**, intermolecular hydrogen bonds are observed in which hydrogen of carboxylic group is a hydrogen bond donor to ethanol in the lattice, forming the 1-D hydrogen bond network.

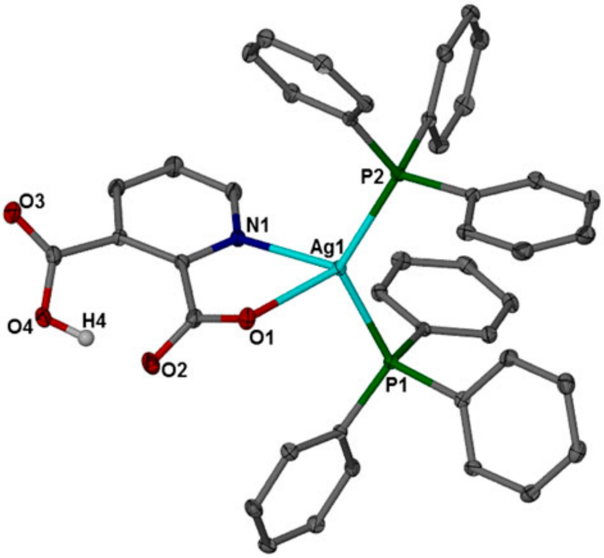


Figure 1. Structure of [Ag(PPh$_3$)$_2$(2,3-pyCOO)] (**1**) with ellipsoids shown at 50% probability. Hydrogens are omitted for clarity.

Table 1. Selected bond lengths and angles for **1–3**.

	1	**2**	**3**
Ag–O1	2.364(8)	2.470(5)	2.378(7)
Ag–N1/O2	2.421(7)	2.365(8)	2.635(5)
Ag–P1	2.450(7)	2.444(8)	2.482(5)
Ag–P2	2.411(5)	2.448(3)	2.456(6)
O1–Ag–N1/O2	69.21(9)	68.71(4)	51.72(9)
P1–Ag1–P2	124.69(5)	122.77(6)	130.49(9)

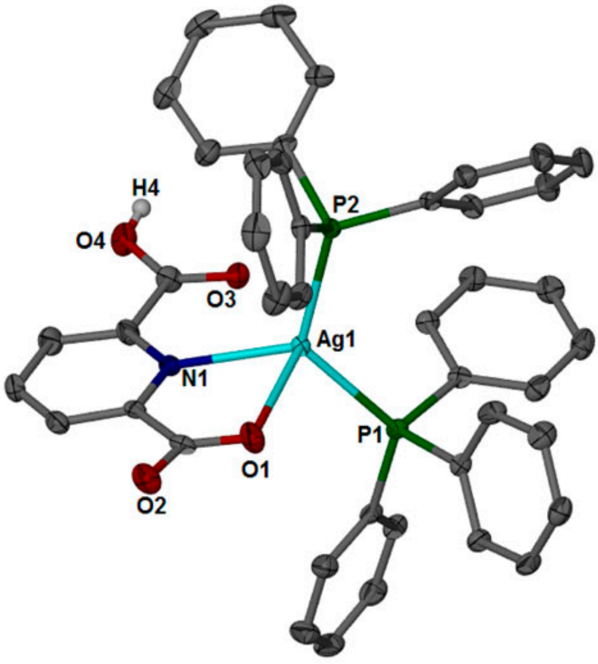


Figure 2. Structure of $[Ag(PPh_3)_2(2,6\text{-}pyCOO)]\cdot EtOH\cdot MeCN$ (**2**) with ellipsoids shown at 50% probability. Hydrogens are omitted for clarity.

$[Ag(PPh_3)_2(3\text{-}pyCOO)]\cdot H_2O$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with the entire molecule in the asymmetric unit. Ag(I) is tetrahedral with two PPh_3 ligands and two oxygens of $3\text{-}pyCOO^-$ [figure 3(a)]. The Ag1–O1 and Ag1–O2 bond lengths are 2.378 (7) Å and 2.635(5) Å, while the distances between Ag(I) to P1 and P2 are 2.482(5) Å and 2.456(6) Å, respectively (table 1). The nitrogen of pyridyl ring are not involved in coordination with Ag(I). The chelate angle of $3pyCOO^-$ to Ag(I), O1–Ag1–O2 is 51.72 (9)°, smaller compared to the two previous structures.

The presence of hydrogen bonds between these monomeric structures with water in the lattice plays an important role in stabilizing the entire molecule. A water in the lattice is a hydrogen bond donor to uncoordinated carbonyl oxygen, O2 and nitrogen of pyridyl in the adjacent molecule, leading to formation of a 1-D hydrogen bond network structure [figure 3(b)].

$[Ag(PPh_3)(2,3\text{-}py(COO)]_n$ (**5**) crystallized in the monoclinic space group $P2_1/c$ with the asymmetric unit containing one Ag(I), one PPh_3, and one $2,3\text{-}pyCOO^{2-}$. Unlike **1**, both carboxylic groups are deprotonated and coordinate. Each Ag(I) is four coordinate, tetrahedral [figure 4(a)]. The Ag1–O1 and Ag1–N1 distances are 2.317(2) Å and 2.295(2) Å, respectively. The $2,3\text{-}pyCOO^{2-}$ has a $\mu_2\text{-}\kappa^2(N,O)Ag{:}\kappa^1(O')Ag'$ coordination mode, bridging two Ag(I) ions via two doubly deprotonated carboxylates with Ag1–O4i distance of 2.530(3) Å (table 2). The extended structure of **5** can be viewed as a 1-D zigzag chain structure [figure 4(b)]. Viewed down the *b* axis, 1-D chains are arranged such that PPh_3 ligands align interdigitating to each other, giving π–π interactions between unsaturated carbon rings with the distance of 3.820 Å and 3.871 Å [figure 4(c)].

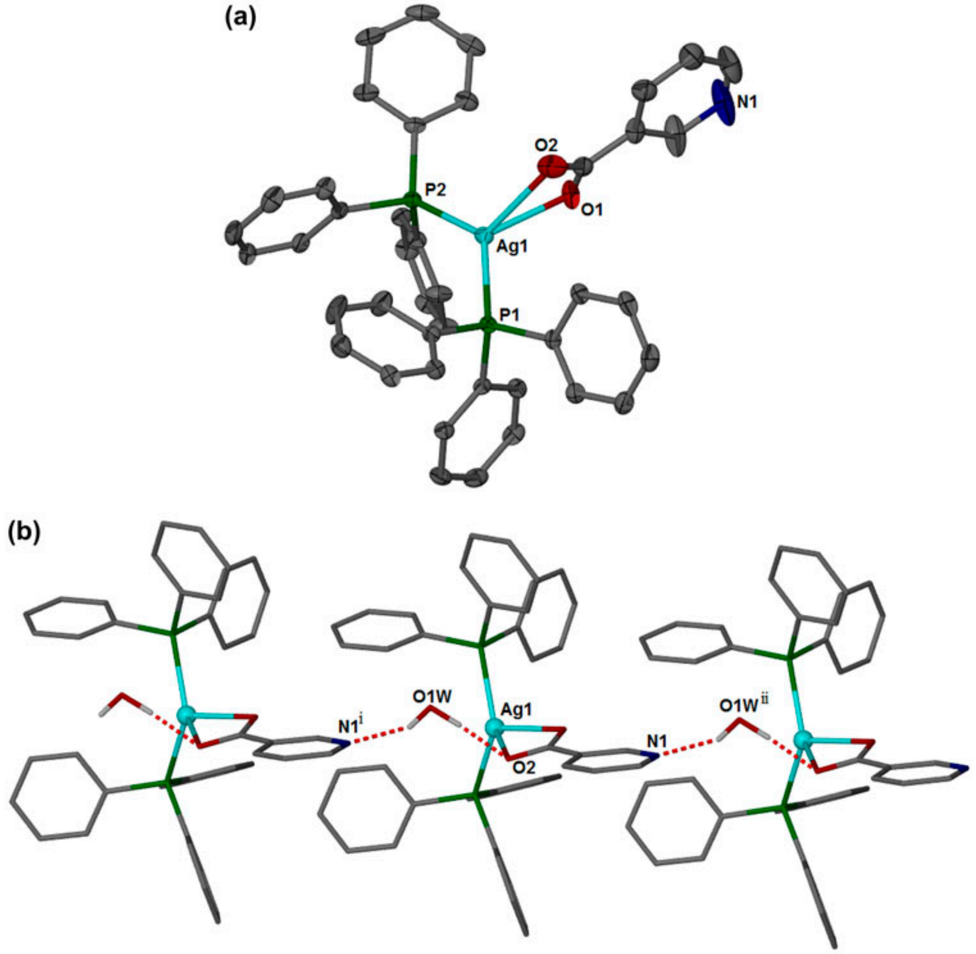


Figure 3. (a) Structure of $[Ag(PPh_3)_2(3\text{-pyCOO})]\cdot H_2O$ (**3**) with ellipsoids shown at 50% probability. Hydrogens are omitted for clarity. (b) Hydrogen bond networks for **3**.

$[Ag_2(PPh_3)_2(3\text{-pyCOO})_2]_n$ (**6**) crystallized in the monoclinic space group $P2_1/c$ with two Ag(I), two PPh_3, and two 3-pyCOO^- in the asymmetric unit. Each Ag(I) is tetrahedral, surrounded by two oxygens, one PPh_3, and a nitrogen of pyridyl [figure 5(a)]. Ag···Ag interactions are observed in this structure, with the distances of $Ag1\cdots Ag1^i$ and $Ag2\cdots Ag2^i$, 2.969 (3) Å and 3.244(6) Å, respectively (table 3). The Ag···Ag separations are significant as the value is smaller than twice the van der Waals' radius sum of silver(I) (3.44 Å) and agree with reported structures [23]. The interactions are also present in dimeric and polymeric silver(I) complexes with definite Ag···Ag attractive forces recognized as argentophilic interactions [24].

Pairs of Ag(I) centers are bridged by two 3-pyCOO^- ligands in two different coordination modes. One is $\mu_3\text{-}\kappa^2(O)Ag,Ag':\kappa^1(N)Ag''$ while another 3-pyCOO^- has $\mu_3\text{-}\kappa^1(O)Ag:\kappa^1(O')Ag':\kappa^1(N)Ag''$ coordination. These then lead to a 1-D network with the network simplified as a ladder-like structure [figure 5(b)].

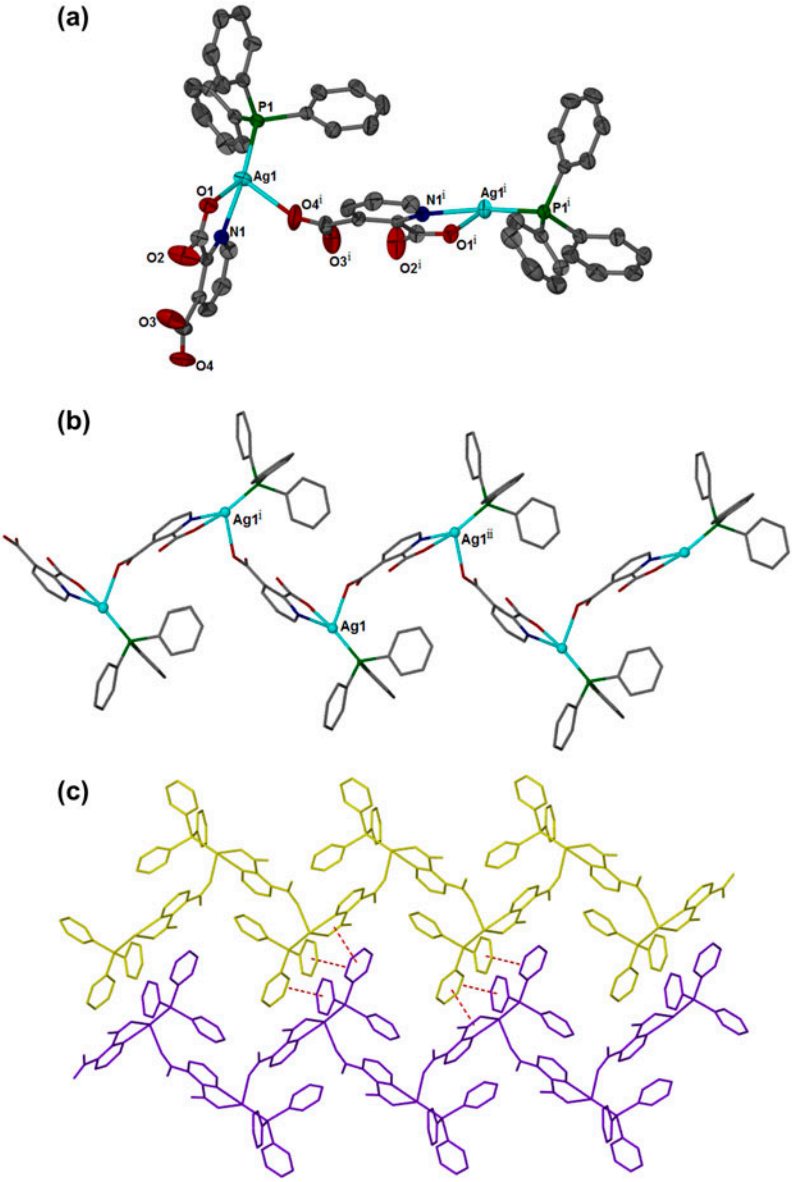


Figure 4. (a) Structure of $[Ag(PPh_3)(2,3\text{-}py(COO)]_n$ (**5**) with ellipsoids shown at 50% probability. Hydrogens are omitted for clarity. Symmetry element used: $^{i} = 2 - x$, $½ + y$, $½ - z$. (b) 1-D zigzag chain structure of **5**. Symmetry elements used: $^{i} = 2 - x$, $y - ½$, $½ - z$; $^{ii} = 2 - x$, $½ + y$, $½ - z$. (c) Interdigitating interaction between 1-D zigzag structure of **5**. Interactions between aromatic rings are shown as dashed lines representing face-to-face and edge-to-face interactions.

$[Ag(PPh_3)(4\text{-}pyCOO)]_n \cdot EtOH$ (**7**) crystallized in the monoclinic space group $P2_1/c$ with one Ag(I), one PPh_3, and one 4-pyCOO$^-$ in the asymmetric unit. Ag(I) is tetrahedral and unlike 3-pyCOO$^-$ in **6**, 4-pyCOO$^-$ shows only one bridging mode, μ_3-κ^2(O)Ag,Ag′:κ^1(N)Ag″ - bridging three Ag(I) ions via oxygen and nitrogen of pyridyl ring [figure 6(a)].

Table 2. Selected bond lengths and angles for **5**[a].

Ag1–O1	2.317(2)	Ag1–N1	2.295(2)
Ag1–O4^{i}	2.530(3)	Ag1–P1	2.333(2)
O1–Ag1–N1	69.54(7)	O1–Ag1–O4^{i}	81.85(9)
O1–Ag1–P1	141.35(5)	N1–Ag1–O4^{i}	81.89(10)
N1–Ag1–P1	140.12(6)	P1–Ag1–O4^{i}	119.43(8)

[a] Symmetry element used: $^{i}= 2 - x, ½ + y, ½ - z$.

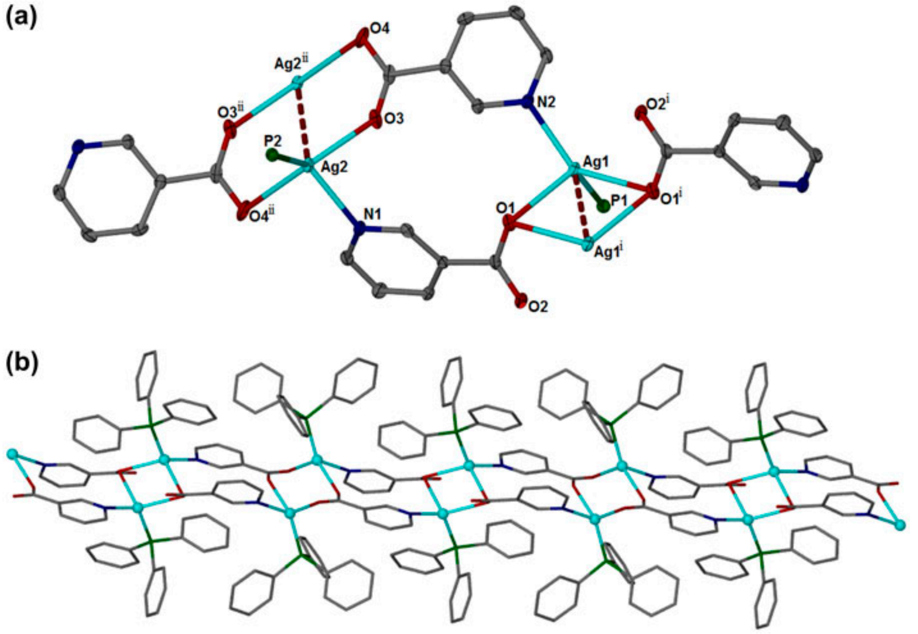


Figure 5. (a) Structure of $[Ag_2(PPh_3)_2(3\text{-}pyCOO)_2]_n$ (**6**) with ellipsoids shown at 50% probability. Phenyl rings attached to phosphorus and hydrogens are omitted for clarity. Ag···Ag interactions are shown by dashed lines. Symmetry elements used: $^{i} = 1 - x, 1 - y, 1 - z$; $^{ii} = -x, 1-y, 1 - z$. (b) A 1-D ladder-like structure of **6**.

Table 3. Selected bond lengths and angles for **6**[a].

Ag1···Ag1^{i}	2.969(3)	Ag1–P1	2.392(2)
Ag2···Ag2^{ii}	3.244(6)	Ag2–N1	2.323(3)
Ag1–O1	2.476(2)	Ag2–O3	2.376(2)
Ag1–O1^{i}	2.461(2)	Ag2–P2	2.399(2)
Ag1–N2	2.231(3)	Ag2–O4^{ii}	2.678(3)
O1–Ag1–O1^{i}	106.07(6)	O3–Ag2–O4^{ii}	119.82(8)
N2–Ag1–O1	91.40(9)	N1–Ag2–O3	78.28(9)
N2–Ag1–O1^{i}	128.44(8)	N1–Ag2–O4^{ii}	81.30(9)

[a] Symmetry elements used: $^{i}1 - x, 1 - y, 1 - z$; $^{ii}-x, 1 - y, 1 - z$.

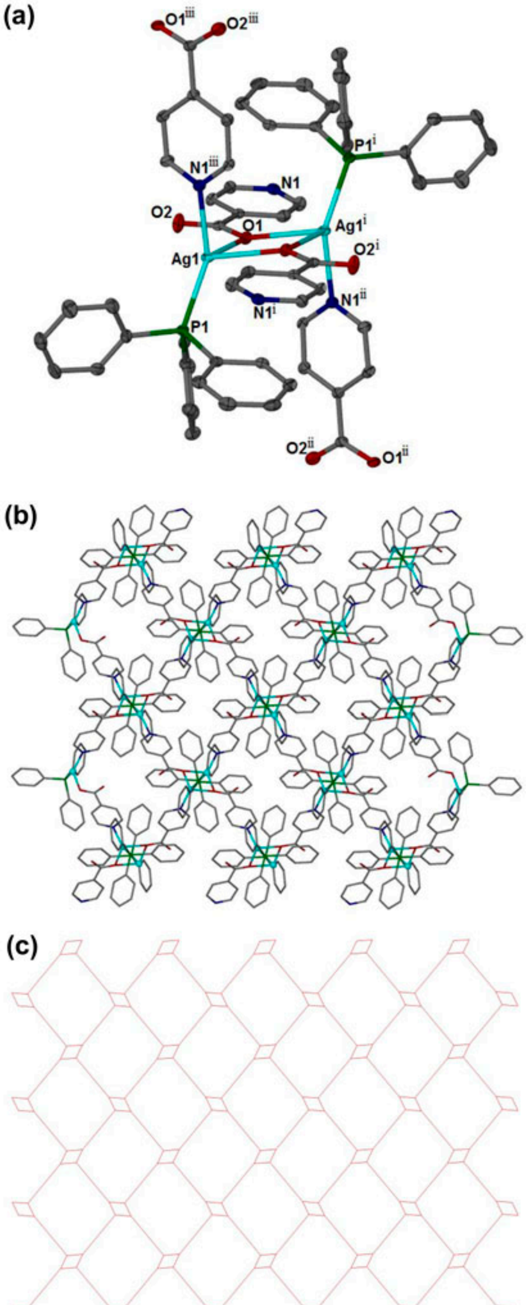


Figure 6. (a) Structure of $[Ag(PPh_3)(4\text{-pyCOO})]\cdot EtOH$ (**7**) with ellipsoids shown at 50% probability. Hydrogens are omitted for clarity. Symmetry elements used: $^{i} = 1 - x,\ 1 - y,\ 1 - z$; $^{ii} = x,\ ½ - y,\ z - ½$; $^{iii} = 1 - x,\ ½ + y,\ 3/2 - z$. (b) 2-D network structure of **7**, which can be simplified as (c) *fes* topology based on three connected nodes.

Table 4. Selected bond lengths and angles for **7**[a].

Ag1···Ag1[i]	3.732(3)	Ag1–P1	2.353(2)
Ag1–O1	2.351(2)	Ag1–N1[ii]	2.262(3)
Ag1–O1–Ag1[i]	98.16(8)	O1–Ag1–N1[ii]	91.23(9)
P1–Ag1–N1[ii]	146.81(8)	O1–Ag1–P1	119.83(6)

[a] Symmetry elements used: [i] 1−*x*, 1−*y*, 1−*z*; [ii] 1−*x*, ½ + *y*, 3/2−*z*.

The separation between Ag1···Ag1[i] is 3.732(3) Å, somewhat longer than in **6** (table 4). Complex **7** can be described as a 2-D network with the vertex symbol is 4.8^2 which correspond to *fes* topology [25]. The topology generated when each Ag(I) center and 4-pyCOO$^-$ ligand is a three connected topological node [figure 6(b) and (c)]. An ethanol in the lattice serves as a hydrogen bond donor to uncoordinated oxygen of 4-pyCOO$^-$, O2.

3.3. *IR and NMR spectroscopy*

In FTIR spectra of **3–7**, bands involved in O–H motions of the carboxylate group (O–H stretching of the COOH groups, the C–OH in-plane bending and out-of-plane O–H deformation modes) are absent. This clearly shows deprotonation of –COOH and coordination to the metal ions as disclosed by X-ray crystal structure analyses. For **1** and **2**, it can be postulated that one -COOH of 2,3-pyCOOH and 2,6-pyCOOH is not deprotonated, evidenced by the presence of peaks at 1688 and 1696 cm^{-1}, respectively, shifted a bit when compared with free 2,3-pyCOOH and 2,6-pyCOOH at 1713 cm^{-1}. Peaks at 1544–1597 cm^{-1} and 1359–1381 cm^{-1} can be assigned to the asymmetric stretch ν_{asym}(COO$^-$) and the symmetric stretch ν_{sym}(COO$^-$) of carboxyl groups, respectively.

^{1}H NMR spectra of **1–4** in $CDCl_3$ exhibit characteristic phenyl and pyridyl ring proton resonances at *ca.* 7.17–9.25 ppm. ^{13}C NMR spectra for all complexes displayed prominent peaks downfield at *ca.* 122.912–172.558 ppm, attributed to phenyl groups of PPh_3 and pyridyl ring. The ^{31}P spectra of **1–7** showed singlets at *ca.* 10.51, 8.43, 9.31, 10.20, 16.14, 13.12, and 19.48 ppm, respectively.

4. Conclusion

The syntheses and characterizations of seven silver(I) complexes are reported. Compounds **1–4** are mononuclear with all pyridine dicarboxylic acid and pyridine monocarboxylic acid showing bidentate chelation as a terminal ligand. The observation could be due to steric effects around silver, already occupied by two bulky PPh_3. This is supported by formation of several coordination polymers in the absence of such bulky ligands around the coordination sphere of silver(I) [26]. Compounds **5–7** are polymeric structures with molar ratio of reactants playing an important role in synthesizing these complexes. Structure elucidation via X-ray diffraction reveals that **5** exhibits as a 1-D zigzag structure while **6** exists as a 1-D ladder-type structure with significant Ag···Ag interactions, so-called argentophilic interactions. Compound **7** exists as a 2-D network with the vertex symbol is 4.8^2 which correspond to *fes* topology.

Supplementary material

CCDC 1015001–1015006 contain supplementary crystallographic data for **1–3** and **5–7**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment

The authors thank Universiti Sains Malaysia (USM) for the Short Term Grant 304/PKI-MIA/6312119.

References

[1] For examples, see: (a) B.F. Hoskins, R. Robson. *J. Am. Chem. Soc.*, **111**, 5962 (1989); (b) R. Robson, B.F. Abrahams, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Liu. *ACS Symp. Ser.*, **499**, 526 (1992); (c) S. Kitagawa, M. Matsuyama, S. Munakata, T. Emori. *J. Chem. Soc., Dalton Trans.*, 2869 (1991); (d) M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994); (e) O.M. Yaghi, G.M. Li. *Angew. Chem. Int. Ed. Engl.*, **34**, 207 (1995); (f) S. Kitagawa, S. Kawata. *Coord. Chem. Rev.*, **11**, 224 (2002); (g) G.B. Gardner, D. Venkataraman, J.S. Moore, S. Lee. *Nature*, **374**, 792 (1995); (h) S.R. Batten, S.M. Neville, D.R. Turner. *Coordination Polymers: Design Analysis and Application*, Royal Society of Chemistry, Cambridge (2009).

[2] J.-C. Jin, N.-N. Yan, W.-G. Chang, J.-Q. Liu, Z.-C. Yin, G.-N. Xu, K.-F. Yue, Y.-Y. Wang. *J. Coord. Chem.*, **66**, 3509 (2013).

[3] For examples, see: (a) X. He, X.-P. Lu, Z.-F. Ju, C.-J. Li, Q.-K. Zhang, M.-X. Li. *CrystEngComm*, **15**, 2731 (2013); (b) F. Sun, Z. Yin, Q.-Q. Wang, D. Sun, M.-H. Zeng, M. Kurmoo. *Angew. Chem. Int. Ed.*, **52**, 4538 (2013); (c) S. Lipstman, I. Goldberg. *Cryst. Growth Des.*, **13**, 942 (2013); (d) R. Pandey, M. Yadav, P. Kumar, P.-Z. Li, S.K. Singh, Q. Xu, D.S. Pandey. *Inorg. Chim. Acta*, **376**, 195 (2011); (e) T. Taguchi, M.R. Daniels, K.A. Abboud, G. Christou. *Inorg. Chem.*, **48**, 9325 (2009).

[4] For examples, see: (a) S.-L. Zheng, M.-L. Tong, X.-M. Chen. *Coord. Chem. Rev.*, **246**, 185 (2003); (b) S.R. Batten, N.R. Champness, X.M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, J. Reedijk. *CrystEngComm*, **14**, 3001 (2012).

[5] For examples, see: (a) Y. Cui, C. He. *J. Am. Chem. Soc.*, **125**, 16202 (2003).; (b) M.B. Duriska, S.R. Batten, D.J. Price. *Aust. J. Chem.*, **59**, 26 (2006).

[6] For examples, see: (a) S.J. Berners-Price, R.K. Johnson, A.J. Giovenella, L.F. Faucette, C.K. Mirabelli, P.J. Sadler. *J. Inorg. Biochem.*, **33**, 285 (1988); (b) R.A. Haque, M.Z. Ghdhayeb, A.W. Salman, S. Budagumpi, M.B. Khadeer Ahamed, A.M.S. Abdul Majid. *Inorg. Chem. Commun.*, **22**, 113 (2012); (c) R.A. Haque, P.O. Asekunowo, M.R. Razali. *J. Coord. Chem.*, **67**, 2131 (2014); (d) Y.-Q. Wei, K.-C. Wu, B.-T. Zhuang, Z.-F. Zhou, M.-X. Chang, C.-P. Liu. *Z. Anorg. Allg. Chem.*, **631**, 1532 (2005).

[7] P. Yang, F. Cui, X.-J. Yang, B. Wu. *Cryst. Growth Des.*, **13**, 186 (2013).

[8] J. Zheng, D. Zhou, T.-H. Shi, Q.-Q. Guan, Y. Xu. *J. Coord. Chem.*, **67**, 533 (2014).

[9] M.M. Amini, O. Sadeghi, S.W. Ng. *J. Inorg. Organomet. Polym.*, **23**, 826 (2013).

[10] For examples, see: (a) H. Gao, L. Yi, B. Zhao, X. Zhao, P. Cheng, D. Liao. *Inorg. Chem.*, **45**, 5980 (2006); (b) S. Biswas, R. Saha, I.M. Steele, G. Mostafa. *Inorg. Chim. Acta*, **368**, 216 (2011); (c) P. Kanoo, G. Mostafa, R. Matsuda, S. Kitagawa, T.K. Maji. *Chem. Commun.*, **47**, 8106 (2011).

[11] A.N. Khlobystov, A. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder. *Coord. Chem. Rev.*, **222**, 155 (2001).

[12] J. Luo, F. Jiang, R. Wang, L. Han, Z. Lin, R. Cao, M. Hong. *J. Mol. Struct.*, **707**, 211 (2004).

[13] For examples, see: (a) F.-T. Xie, H.-Y. Bie, L.-M. Duan, G.-H. Li, X. Zhang, J.-Q. Xu. *J. Solid State Chem.*, **178**, 2858 (2005); (b) Z. Liu, P. Liu, Y. Chen, J. Wang, M. Huang. *New. J. Chem.*, **29**, 474 (2005); (c) A. Schoedel, L. Wojtas, S.P. Kelley, R.D. Rodgers, M. Eddaoudi, M.J. Zaworotko. *Angew. Chem., Int. Ed.*, **50**, 11421 (2011).

[14] S.W. Ng, A.H. Othman. *Acta Cryst. C*, **53**, 1397 (1997).

[15] APEXII, *V2.1.0*, Bruker AXS, Madison, WI (2005).

[16] G.M. Sheldrick. *Acta Crystallogr., Sect. A*, **64**, 112 (2008).

[17] L.J. Barbour. *J. Supramolecular Chemistry*, **1**, 189 (2001).

[18] M.R. Razali, A. Urbatsch, G.B. Deacon, S.R. Batten. *Polyhedron*, **64**, 352 (2013).

[19] F. Jaber, F. Charbonnier, R. Faure. *Polyhedron*, **15**, 2909 (1996).

[20] D.M. Chackraburtty. *Acta Cryst. E*, **10**, 128 (1957).

[21] F. Jaber, F. Chanbonnier, R. Faure, M. Petit-Ramel. *Z. Kristallogr.*, **209**, 536 (1994).
[22] M. Hakimi, K. Moeini, Z. Mardani, E. Schuh, F. Mohr. *J. Coord. Chem.*, **66**, 1124 (2013).
[23] For examples, see: (a) A.T. Colak, G. Pamuk, O.Z. Yesilel, F. Yilmaz. *Inorg. Chem. Commun.*, **14**, 1591 (2011); (b) S.H. Alisir, B. Sariboga, Y. Topcu, S.-Y. Yang. *J. Inorg. Organomet. Polym.*, **23**, 1061 (2013).
[24] P. Pyykkö. *Chem. Rev.*, **97**, 597 (1997).
[25] For examples, see: (a) T. Wu, J. Zhang, X. Bu, P. Feng. *Chem. Mater.*, **21**, 3830 (2009); (b) J. Liu, H.-B. Zhang, Y.-X. Tan, F. Wang, Y. Kang, J. Zhang. *Inorg. Chem.*, **53**, 1500 (2014).
[26] For examples, see: (a) X.-L. Chen, Y.-L. Qiao, L.-J. Gao, M.-L. Zhang. *J. Coord. Chem.*, **66**, 3749 (2013); (b) G.-F. Hou, Y.-H. Yu, X. Wang, J.-S. Gao, B. Wen, X.-D. Wang, P.-F. Yan. *J. Coord. Chem.*, **66**, 3402 (2013); (c) R. Meijboom, R.J. Bowen, S.J. Berners-Price. *Coord. Chem. Rev.*, **253**, 325 (2009); (d) G.K. Kole, C.K. Chin, G.K. Tan, J.J. Vittal. *Polyhedron*, **52**, 1440 (2013).