



o-, *m*-, and *p*-Pyridyl isomer effects on construction of 1D loop-and-chains: Silver(I) coordination polymers with Y-type tridentate ligands

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ARTICLE INFO

Article history:

Received 25 March 2016

Received in revised form

30 May 2016

Accepted 30 May 2016

Available online 31 May 2016

Keywords:

Coordination geometry

Loop-and-chain coordination polymers

Silver(I) complexes

Y-type tridentate ligand

ABSTRACT

Self-assembly of silver(I) hexafluorophosphate with unique Y-type tridentate ligands (2,6-bis[(2-**picolinoyloxy**-5-methylphenyl)methyl]-*p*-tolylpicolinate (*o*-L), 2-**nicotinoyloxy**- (*m*-L), and 2-**isonicotinoyloxy**- (*p*-L)) produces single crystals consisting of 1D loop-and-chain coordination polymers of [Ag(*o*-L)](PF₆)·Me₂CO·CHCl₃, [Ag(*m*-L)](PF₆)·Me₂CO, and [Ag₃(*p*-L)₂](PF₆)₃·2H₂O·2C₂H₅OH·4CH₂Cl₂ with quite different trigonal prismatic, trigonal, and linear silver(I) coordination geometry, respectively. Coordinating ability of the three ligands for AgPF₆ is in the order of *p*-L > *o*-L > *m*-L. The solvate molecules of [Ag(*o*-L)](PF₆)·Me₂CO·CHCl₃ can be removed, and be replaced reversibly in the order of acetone ≫ chloroform ≈ dichloromethane ≫ benzene, without destruction of its skeleton.

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1. Introduction

Dimensionality of metal-organic coordination polymers plays a key role in determination of their task-specific functions. Their dimensions have been generally driven by a suitable combination of the coordination geometry of metal center and the donor-numbers of linkers or by unpredictable weak interactions [1–6]. In particular, 1D skeleton is one of the simplest practical polymeric arrays including chains, loops, helices, and spiro-links which are useful to gas adsorption, mixed-valence system, photo-induced electron or energy transfer, magnetic exchange, semiconductors, catalysts, luminescent chemosensors, and ion-exchangers [7–9]. Thus, construction of desirable motif 1D coordination polymers via delicate manipulation of some reaction-components is a challengeable work in the field of supramolecular materials. Various motif 1D coordination polymers containing designed interesting bidentate ligands have been formed, but the systematic 1D coordination polymers containing *o*-, *m*-, and *p*-tridentate ligands are relatively rare. To date, such tridentate ligands have been usually employed for generating coordination cages or triangular module metal complexes for the past decade [10–17]. In order to construct the proof-of-concept 1D loop-and-chain coordination polymers, a

systematic ligand of Y-type tridentate *N*-donors, 2,6-bis[(2-**picolinoyloxy**-5-methylphenyl)methyl]-*p*-tolylpicolinate (*o*-L), 2-**nicotinoyloxy**- (*m*-L), and 2-**isonicotinoyloxy**- (*p*-L), were designed and employed. We report the construction and characteristic coordination chemistry of a new family of unique 1D loop-and-chain coordination polymers from self-assembly of silver(I) ion with the respective Y-type ligands. Their different coordination chemistry including mole ratio, coordination numbers, coordination ability, and solvent exchangeability has been investigated. The silver(I) ion utilized therein has been known to act as various directional units such as linear, T-shaped, tetrahedral, and octahedral geometries [18].

2. Experimental

2.1. Materials and measurements

All commercialized chemicals including 2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol, 2-pyridinecarbonyl chloride hydrochloride, nicotinoyl chloride hydrochloride, and silver(I) hexafluorophosphate were purchased from Aldrich, and used without further purification. The *p*-L was prepared by the same procedure available in the literature [19]. Elemental microanalyses (C, H, N) were performed on solid samples by the Pusan center, KBSI, using a Vario-EL III. Thermal analyses were undertaken under a nitrogen atmosphere at a scan rate of 10 °C/min using a Labsys

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TGA-DSC 1600. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrometer with samples prepared as KBr pellets. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Mercury Plus 300. Scanning electron microscopy (SEM) images were obtained on a Tescan VEGA 3.

2.2. Preparation of 2,6-bis[(2-picolinoxy-5-methylphenyl)methyl]-*p*-tolylpicolinate (*o*-L)

Triethylamine (2.45 mL, 17.6 mmol) in chloroform (10 mL) was slowly added to a mixture of 2,6-bis(2-hydroxy-5-methylphenyl)methyl-4-methylphenol (0.70 g, 2.0 mmol) and picolinoyl chloride hydrochloride (1.42 g, 8 mmol) in chloroform (120 mL). The reaction mixture was refluxed for 24 h. The solution was filtered, and then the filtrate was washed with water several times. The chloroform layer was dried over MgSO_4 and filtered. Evaporation of the chloroform gave pale orange solid. Yield: 71%. M.p. 240 °C. Anal. Calcd for $\text{C}_{41}\text{H}_{33}\text{N}_3\text{O}_6$ (%): C, 74.19; H, 5.01; N, 6.33. Found: C, 74.10; H, 4.98; N, 6.21. IR (KBr, cm^{-1}): 1754 (w), 1736 (s), 1583 (w), 1499 (w), 1474 (w), 1437 (w), 1303 (s), 1291 (s), 1243 (m), 1197 (s), 1136 (m), 1112 (m), 1088 (m), 1042 (w), 993 (w), 870 (w), 747 (m), 701 (m), 617 (w). ^1H NMR (300 MHz, CDCl_3 , δ): 8.80 (m, overlapped, 3H), 7.99 (d, $J = 7.5$ Hz, 2H), 7.85–7.78 (m, overlapped, 4H), 7.54–7.46 (m, overlapped, 3H), 7.01 (s, overlapped, 4H), 6.92 (s, 2H), 6.76 (s, 2H), 3.79 (s, 4H), 2.14 (s, 6H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , δ): 163.28, 162.56, 149.95, 149.92, 147.15, 146.97, 146.83, 145.53, 137.07, 136.93, 135.80, 135.74, 131.77, 131.60, 131.10, 129.95, 128.11, 127.17, 125.72, 121.87, 31.53, 20.68, 20.51.

2.3. Preparation of 2,6-bis[(2-nicotinoxy-5-methylphenyl)methyl]-*p*-tolylnicotinate (*m*-L)

Triethylamine (6.14 mL, 44.0 mmol) in chloroform (10 mL) was slowly added to a mixture of 2,6-bis(2-hydroxy-5-methylphenyl)methyl-4-methylphenol (1.74 g, 5.0 mmol) and nicotinoyl chloride hydrochloride (3.56 g, 20 mmol) in chloroform (120 mL). The reaction mixture was refluxed for 24 h. The solution was filtered, and then the filtrate was washed with water several times. The chloroform layer was dried over MgSO_4 and filtered. Evaporation of the chloroform gave pale yellow solid. Yield: 87%. M.p. 154 °C. Anal. Calcd for $\text{C}_{41}\text{H}_{33}\text{N}_3\text{O}_6$ (%): C, 74.19; H, 5.01; N, 6.33. Found: C, 73.90; H, 4.98; N, 6.21. IR (KBr, cm^{-1}): 1740 (s), 1591 (m), 1499 (w), 1475 (w), 1420 (m), 1276 (s), 1197 (s), 1111 (m), 1083 (m), 1021 (s), 873 (w), 807 (w), 733 (m), 701 (m), 621 (w). ^1H NMR (300 MHz, CDCl_3 , δ): 9.11 (s, 2H), 8.88 (s, 1H), 8.80 (m, overlapped, 3H), 8.18 (d, $J = 7.5$ Hz, 2H), 7.98 (d, $J = 7.5$ Hz, 1H), 7.41–7.35 (m, 3H), 7.01 (d, $J = 8.1$ Hz, 2H), 6.92 (d, $J = 8.1$ Hz, 2H), 6.85 (s, 2H), 6.74 (s, 2H), 3.71 (s, 4H), 2.12 (s, 6H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , δ): 163.46, 162.61, 153.83, 153.78, 151.27, 151.16, 146.49, 145.08, 137.51, 137.38, 136.12, 136.07, 131.89, 131.75, 131.02, 130.13, 128.35, 125.34, 124.95, 123.39, 123.25, 122.07, 32.45, 20.73, 20.57.

2.4. Synthesis of $[\text{Ag}(\text{o-L})](\text{PF}_6)\cdot\text{Me}_2\text{CO}\cdot\text{CHCl}_3$

An acetone solution (2 mL) of AgPF_6 (13 mg, 0.05 mM) was layered onto a chloroform solution (2 mL) of *o*-L (33 mg, 0.05 mM). After 3 days, colorless crystals suitable for single crystal X-ray diffraction were obtained in an 81% yield (37 mg) based on silver(I) ion. M.p. 279 °C (dec.). Anal. Calcd for $\text{C}_{45}\text{H}_{40}\text{N}_3\text{O}_7\text{Cl}_3\text{F}_6\text{PAg}$ (%): C, 49.40; H, 3.69; N, 3.84. Found: C, 49.10; H, 3.60; N, 3.80. IR (KBr, cm^{-1}): 1743 (m), 1732 (m), 1705 (w), 1591 (w), 1499 (w), 1306 (m), 1290 (m), 1246 (w), 1196 (m), 1132 (m), 1085 (w), 843 (s, $\nu(\text{PF}_6^-)$), 750 (w), 691 (w), 558 (w).

2.5. Synthesis of $[\text{Ag}(\text{m-L})](\text{PF}_6)\cdot\text{Me}_2\text{CO}$

An acetone solution (2 mL) of AgPF_6 (13 mg, 0.05 mmol) was layered onto a dichloromethane solution (2 mL) of *m*-L (33 mg, 0.05 mmol). After 3 days, colorless crystals suitable for single crystal X-ray diffraction were obtained in a 75% yield (34 mg) based on silver(I) ion. M.p. 278 °C (dec.). Anal. Calcd for $\text{C}_{44}\text{H}_{37}\text{N}_3\text{O}_7\text{F}_6\text{PAg}$ (%): C, 54.34; H, 3.83; N, 4.32. Found: C, 55.00; H, 3.78; N, 4.30. IR (KBr, cm^{-1}): 1742 (s), 1600 (w), 1500 (w), 1476 (w), 1431 (w), 1284 (s), 1197 (s), 1139 (w), 1116 (w), 1086 (w), 1042 (w), 847 (s, $\nu(\text{PF}_6^-)$), 736 (m), 696 (w), 558 (m).

2.6. Synthesis of $[\text{Ag}_3(\text{p-L})_2](\text{PF}_6)_3\cdot 2\text{H}_2\text{O}\cdot 2\text{C}_2\text{H}_5\text{OH}\cdot 4\text{CH}_2\text{Cl}_2$

An ethanol solution (2 mL) of AgPF_6 (15 mg, 0.06 mmol) was layered onto a dichloromethane solution (2 mL) of *p*-L (27 mg, 0.04 mmol). After 1 day, colorless crystals suitable for single crystal X-ray diffraction were obtained in an 85% yield (35 mg) based on silver(I) ion. M.p. 286 °C (dec.). Anal. Calcd for $\text{C}_{90}\text{H}_{90}\text{N}_6\text{O}_{16}\text{Cl}_8\text{F}_{18}\text{P}_3\text{Ag}_3$ (%): C, 42.33; H, 3.55; N, 3.29. Found: C, 42.10; H, 3.50; N, 3.21. IR (KBr, cm^{-1}): 1747 (m), 1561 (w), 1498 (w), 1420 (w), 1328 (m), 1276 (m), 1196 (m), 1118 (w), 1062 (w), 842 (s, $\nu(\text{PF}_6^-)$), 757 (w), 695 (w), 558 (m).

2.7. Crystal structure determinations

X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) and a CCD detector at -25 °C. Thirty-six frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the multi-scan method (SADABS) [20]. The structures were solved by the direct method (SHELXS 2014) and refined by full-matrix least squares techniques (SHELXL 2014) [21]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic displacement parameters. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1.

3. Results and discussion

3.1. Synthesis

New Y-type tridentate *N*-donor ligands were synthesized and characterized. Loop-and-chain 1D silver(I) coordination polymers were constructed by self-assembly of AgPF_6 with respective *o*-L, *m*-L and *p*-L, yielding colorless single crystals suitable for X-ray crystallographic analyses, as depicted in Scheme 1. IR and chemical analytical results were consistent with formation of the proposed skeletons. The self-assemblies were performed originally in the 1:1 mol ratio of $\text{Ag}(\text{I}):\text{L}$, but the silver(I) products of *o*-L, *m*-L, and *p*-L were obtained as 1:1, 1:1, and 3:2 mol ratio, respectively. That is, formation of each product was not significantly affected by either the mole ratio, indicating that the products are thermodynamically stable. All the reactions afforded unique loop-and-chain 1D coordination polymeric species which show significant differences in both coordination numbers and bonding nature. It is noteworthy that their basic skeleton is a loop-and-chain 1D instead of 2D or 3D networks via self-assembly of the respective tridentate ligand and a variety of coordination geometries of silver(I) ion. In this light, the 1D silver(I) coordination polymers' formation might be attributable to the intrinsic properties of the rigid Y-type conformation of new ligands. The products were dissociated in *N,N*-dimethylformamide

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