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Ag-based Coordination Polymers Based on Metalloligands and Their Catalytic Performance in Multi-Component A³–Coupling Reactions

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Abstract: Two silver(I) based coordination polymers (CPs) namely, **1-Ag** and **2-Ag**, have been synthesized by the reaction of Cobased metalloligands offering appended pyridyl groups. X-ray diffraction analyses revealed 3D architectures for both **1-Ag** and **2-Ag** due to the coordination of Ag(I) ions to that of appended pyridyl groups. In case of **1-Ag**, transition from 2D network to the final 3D network was manifested due to the presence of argentophilic interactions. Both CPs illustrated noteworthy structural differences and interesting topologies as a result of coordination of Ag(I) ions to the metalloligands. Both CPs acted as the heterogeneous catalysts for A^3 -coupling reactions of aldehydes, secondary amines and alkynes. Recyclability experiments substantiated the stable nature of CPs in promoting the A^3 -coupling reactions heterogeneously.

Introduction

Coordination polymers (CPs) have been the subject of immense interest due to their remarkable structural features often controlling their interesting physical and chemical properties.¹ As a special class of designer porous materials, CPs offer noteworthy applications in the field of sorption,^{2–3} separation,⁴ catalysis,^{5–7} sensing,^{8–9} ion-exchange,^{10–11} transport,^{12–13} magnetism,^{14–15} and proton and hydroxide conduction.^{16–18} One of the major challenges being faced in CPs research is to improvise the design concepts so as to improve their performance.^{19–}

²¹ In this context, metalloligands have been found to be quite impressive in controlling the structural aspects so as to move towards predictable architectures.^{1,22} Importantly, metalloligand strategy typically generates stable CPs with minimum sensitivity to the structural collapse as a result of the loss of solvates.²³⁻³⁰ More importantly, metalloligands tend to generate non-interpenetrated networks therefore significantly improving the analyte and/or substrate accessibility.³¹⁻³⁴ These structural features have produced some noteworthy catalytic CPs based on the metalloligands.^{35,36}

Compared to the most of transition metals, silver has a stronger affinity for N-donor ligands while supporting variable coordination numbers and multifaceted geometries, ranging from linear and T-shaped to all the way to octahedral ones.^{37–39} Furthermore, Ag(I) ion with a d¹⁰ closed-shell electronic configuration often displays argentophilic interactions which further assist in the stabilization of polymetallic architectures.^{40–44} These structural features have been extensively used in the construction of assorted architectures.^{45–50}

A³-coupling led synthesis of substituted propargylamines is significant as such molecules are not only important structural synthons in natural products and pharmaceuticals but are also versatile intermediates in assorted organic reactions.⁵⁰⁻⁵⁵ Although several methods have been developed for their synthesis but efficient and cost-effective protocols are still limited.^{56,57} The importance of such reactions increases manifold if reusable catalysts could be used, particularly under heterogeneous reaction conditions for the facile product separation.^{58,59} For promoting such reactions, several homogeneous catalysts, such as salts of Zn, Cu, Fe, Ag, and Au have been

used.⁵⁶⁻⁶⁴ However, there are multiple drawbacks associated with these metal salts, such as their poor effectiveness, limited stability and water sensitivity, that have restricted their wider applications.^{65,66} Along the similar line, reusability is a major concern with most of the homogenous catalysts.^{67–70} Therefore, efforts have been made to immobilize catalytic metals on various solid supports, such as zeolite, silica, as well as organ-ic polymers.^{59,71-74} However, most of such immobilized materials suffer from cumbersome preparative routes, high temperature requirement, long reaction time, leaching of catalytic metals, and poor catalytic performance.^{62,75-78} In this context, CPs offer promising heterogeneous catalytic possibilities for various organic transformations.⁷⁹⁻⁸³ Such an advantageous situation is primarily due to their ability to retain their structural architecture during the catalysis, thermal stability and their reusability.⁸⁴⁻⁸⁷ In this work, two Ag(I) based CPs have been synthesized using two different Co³⁺-based metalloligands offering appended pyridyl groups (Scheme 1). Both CPs illustrate interesting three-dimensional (3D) architectures including argentophillic interactions-led stabilization of 3D network in one case. Both Ag-based CPs function as the reusable heterogeneous catalysts for the synthesis of propargylamines applying one-pot-three-component (A^3) coupling.

$$R = (1) \xrightarrow{Ag^{+}} [\{(1)Ag_{2}(H_{2}O)_{2}\}.2H_{2}O]_{n}(1-Ag)$$

$$R = (1) \xrightarrow{Ag^{+}} [\{(1)Ag_{2}(H_{2}O)_{2}\}.2H_{2}O]_{n}(1-Ag)$$

$$R = (1) \xrightarrow{Ag^{+}} [\{(2)_{2}Ag_{3}\}.2H_{2}O.2DMSO]_{n}(2-Ag)$$

Scheme 1. Preparative route for the synthesis of coordination polymers, 1-Ag and 2-Ag.

Experimental Section

Materials and Reagents

All chemicals and reagents of analytical grades were used without further purification unless otherwise stated. Standard literature methods were used for the purification of organic solvents.^{88,89} Metalloligands $[Co(L^{4Py})_2]^-$ (1) and $[Co(L^{3Py})_2]^-$ (2) (where H_2L^{4Py} : 2,6-bis(*N*-(4-pyridyl)carbamoyl)pyridine

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and H_2L^{3Py} : 2,6-bis(*N*-(3-pyridyl)carbamoyl)pyridine), as their tetraethyl ammonium salt, were synthesized according to our earlier report.⁹⁰

Syntheses

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[{(1)Ag₂(H₂O)₂}.2H₂O]_n (1-Ag). A DMSO solution (3 mL) of metalloligand 1 (100 mg, 0.1004 mmol) was layered over an aqueous solution of Ag(CF₃COO) (59 mg, 0.3036 mmol) with an intermediate layer of *tert*-butanol. Visible light was avoided during the crystallization. Light-green crystalline material was obtained after 5–7 d which was filtered, washed with diethyl ether and dried under vacuum. Yield: 208 mg (83 %). $C_{34}H_{30}CoAg_2N_{10}O_8$, (981.34): calcd. C, 41.61; H, 3.08; N, 14.27. Found C, 41.19; H, 3.64; N, 14.79. FTIR spectrum (Zn–Se ATR, selected peaks): (v/cm⁻¹) = 3380 (H₂O); 1573 (C=O).

[{(2)₂Ag₃}·2H₂O·2DMSO]_n (2-Ag). 2-Ag was synthesized identically as mentioned for 1-Ag; however, using metalloligand 2. Yield: 215 mg (88 %). $C_{72}H_{60}Ag_3Co_2N_{20}O_{12}S_2$ (1902.99): calcd. C, 45.44; H, 3.18; N, 14.27; S, 3.37. Found C, 45.19; H, 3.44; N, 14.67. FTIR spectrum (Zn–Se ATR, selected peaks): (v/cm⁻¹) = (H₂O): 3380; 1593, 1556 (C=O); v(S=O, DMSO): 1040.

Physical Measurements

Elemental analysis data were obtained with an Elementar Analysen Systeme GmbH Vario EL-III instrument. FTIR spectra were recorded with a Perkin-Elmer Spectrum-Two spectrometer having Zn-Se ATR. NMR spectroscopic measurements were carried out with a Jeol 400 MHz spectrometer. Perkin Elmer Clarus-580 and Shimadzu QP-2010 instruments were respectively used for the gas chromatography (GC) and GC-MS studies having RTX-5 SIL-MS column. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with Shimadzu DTG-60 and TADSC Q200 instruments, respectively, under the nitrogen atmosphere. X-ray powder diffraction (XRPD) studies were performed either with an X'Pert Pro from PANanalytical or a Bruker AXS D8 Discover instrument (Cu–K α radiation, λ = 1.54184 Å). The samples were ground and subjected to 5-35° θ range at a slow scan rate at room temperature.

Crystallography

38 X-ray diffraction data for 1-Ag and 2-Ag were colected on an 39 Oxford Xcalibur CCD diffractometer equipped with a graphite 40 monochromatic MoK α radiation ($\lambda = 0.71073$ Å).⁹¹ The 41 frames were collected at 293(2) K. An empirical absorption 42 correction was applied using spherical harmonics implemented 43 in SCALE3 ABSPACK scaling algorithm.⁹¹ The structures 44 were solved by the direct methods using SIR-97⁹² and refined by the full-matrix least-squares refinement techniques on F^2 45 using SHELXL-2016/4⁹³ incorporated in WINGX 1.8.05 crystallographic package.⁹⁴ The hydrogen atoms were fixed at 46 47 the calculated positions with isotropic thermal parameters 48 whereas non-hydrogen atoms were refined anisotropically. 49 The hydrogen atoms of the coordinated as well as 50 uncoordinated water molecules could not be located from the 51 Fourier map; however, their contributions are included in the 52 empirical formulae. As there was a large amount of diffused 53 electron density, the model was SQUEEZED for better con-54 vergence and to remove any diffused electron density by using the PLATON SQUEEZE procedure.95 This procedure signifi-55 cantly improved the structural convergence both for 1-Ag (R =56 0.067) and 2-Ag (R = 0.101). Details of the crystallographic 57

data collection and structural solution parameter are provided in Table 1. Topological analysis for **1-Ag** and **2-Ag** was carried out by using ToposPro 5.1.0.7 software.^{96–98}

Table 1. Crystallographic data collection and structure re-finement parameters for 1-Ag and 2-Ag.

	1-Ag	2-Ag
Empirical formula	$C_{34}H_{22}Ag_2CoN_{10}O_8$	$C_{72}H_{56}Ag_3Co_2N_{20}O_{12}S_2$
FW	973.29	1898.95
T(K)	293(2) K	293(2) K
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnna	Pbca
<i>a</i> (Å)	18.302(5)	15.5552(8)
<i>b</i> (Å)	18.201(5)	16.0646(8)
<i>c</i> (Å)	14.536(5)	31.4260(12)
$\alpha = \beta = \gamma (°)$	90	90
$V(\text{\AA})^3$	4842(3)	7853.0(6)
Ζ	4	4
$d (\text{g cm}^{-3})$	1.3350	1.606
$\mu \ (\mathrm{mm}^{-1})$	1.189	1.274
F(000)	1924	3804
<i>R</i> (int.)	0.1097	0.1328
Final <i>R</i> indices ^a	$R_1 = 0.0670$	0.1011
[<i>I</i> >2 <i>σ</i> (<i>I</i>)]	$wR_2 = 0.1669$	0.2690
R indices	$R_1 = 0.1443$	0.1481
All data	$wR_2 = 0.2063$	0.3116
GOF on F^2	0.928	0.992
CCDC No.	1846547	1846548

Typical procedure for A³-coupling reaction

In a typical reaction, an aldehyde, an amine, and an alkyne were allowed to react in 1.0:1.5:1.5 ratio under the solventfree conditions in presence of 2-mol% of a catalyst (1-Ag or 2-Ag). The progress of the reaction was monitored by thin layer chromatography (TLC) and/or gas chromatography (GC) techniques. After 1 h, ethyl acetate was added that resulted in the separation of solid catalyst which was filtered off and dried under vacuum. The recovered catalysts were characterised by FTIR spectra as well as PXRD studies. The ethyl acetate layer was washed with water (2x) and dried over anhyd. Na₂SO₄. The solvent was evaporated under vacuum to isolate the organic products. This product was purified using the flash column chromatography on silica gel with 5% EtOAc/hexanes as the eluent. The organic products were analyzed and/or quantified by the GC/GC-MS techniques and proton NMR spectra (Figures S1 – S16, SI).

Characterization data for a few representative A^3 -coupling products:

1-(1,3-diphenylprop-2-n-1-yl)pyrrolidine. ¹H NMR spectrum (400 MHz, CDCl₃) δ 7.62 (d, J = 7.2 Hz, 2H), 7.50 (dd, J = 6.3, 2.9 Hz, 2H), 7.40–7.34 (m, 2H), 7.34–7.27 (m, 4H), 4.90 (s, 1H), 2.71 (t, J = 6.7 Hz, 4H), 1.81 (t, J = 6.3 Hz, 4H).

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¹³C NMR spectrum (100 MHz, CDCl₃) δ 139.39, 131.89, 128.35, 127.7, 87.0, 86.6, 59.2, 50.3, 23.5.

1-(1-4-methoxyphenyl)-3-phenylprop-2-yn-1-

3yl)pyrrolidine. ¹H NMR spectrum (400 MHz, CDCl₃) δ 7.52–47.44 (m, 4H), 7.32–7.28 (m, 3H), 6.90–6.86 (m, 2H), 4.80 (s,51H), 3.80 (d, J = 3.5 Hz, 3H), 2.66 (t, J = 6.7 Hz, 4H), 1.78 (t,6J = 6.2 Hz, 4H). ¹³C NMR spectrum (100 MHz, CDCl₃) δ 7159.0, 131.8, 129.4, 128.3, 128.1, 123.3, 113.6, 87.0, 86.7,855.3, 50.3, 23.5.

9 1-(1-(4-cholorophenyl)-3-phenylprop-2-yn-1-

10yl)pyrrolidine. 1 H NMR spectrum (400 MHz, CdCl₃) δ 7.55 –117.42 (m, 4H), 7.34 – 7.28 (m, 3H), 6.92 – 6.82 (m, 2H), 4.8012(s, 1H), 3.80 (s, 3H), 2.66 (t, J = 6.7 Hz, 4H), 1.78 (t, J = 6.213Hz, 4H). 13 C NMR spectrum (100 MHz, CdCl₃) δ 138.16,1413.36, 131.87, 129.69, 128.61 – 128.21, 123.02, 87.36,1586.05, 58.45, 50.22, 23.54.

15 1-(3-(4-(*tert*-butyl)phenyl)-1-phenylprop-2-yn-1-

1616(3)-(4-(arr-buty))-(arr)

221-(3-(4-(*tert*-butyl)phenyl)-1-(4-cholorophenyl)prop-2-yn-1-23yl)pyrrolidine. 1 H NMR spectrum (400 MHz, CDCl₃) & 7.5424(d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.35–7.28 (m,254H), 4.85 (s, 1H), 2.65 (dd, J = 10.4, 5.9 Hz, 4H), 1.77 (t, J =266.1 Hz, 4H), 1.30 (s, 9H). 13 C NMR spectrum (100 MHz,27CDCl₃) & 151.6, 138.3, 133.2, 131.5, 129.6, 128.4, 125.4,28120.0, 85.3, 58.4, 50.1, 34.8, 31.2, 23.5.

29 1-(3-(4-fluorophenyl)-1-(4-meyhoxyphenyl)prop-2-yn-

1yl)pyrrolidine.¹H NMR spectrum (400 MHz, CDCl₃) δ 7.50(d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.80 (s, 1H), 3.80 (s, 3H),2.65 (s, 4H), 1.77 (t, J = 5.6 Hz, 4H), 1.30 (s, 9H)."spectrum (100 MHz, CDCl₃) δ 159.0, 151.3, 131.9, 131.5,129.4, 125.3, 120.3, 113.6, 86.7, 86.3, 58.5, 55.3, 50.2, 34.8,35

1-(3-(4-fluorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine. H NMR spectrum (400 MHz, CDCl₃) δ 7.57 (d, J = 7.3 Hz,

382H), 7.45 (dd, J = 8.5, 5.4 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H),397.29 (d, J = 7.1 Hz, 1H), 7.00 (dd, J = 14.2, 5.5 Hz, 2H), 4.8440(s, 1H), 2.67 (s, 4H), 1.80 (d, J = 5.9 Hz, 4H).41trum (100 MHz, CDCl₃) δ 133.7, 128.3, 127.7, 115.7, 115.4,4292.5, 84.4, 59.2, 50.4, 23.5.

1-(1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-yn-1

yl)pyrrolidine. ¹H NMR spectrum (400 MHz, CDCl₃) δ 7.52 (d, J = 8.4 Hz, 2H), 7.44 (dd, J = 8.6, 5.5 Hz, 2H), 7.36–7.28 (m, 2H), 7.00 (dd, J = 12.2, 5.1 Hz, 2H), 4.82 (s, 1H), 2.63 (s, 4H), 1.79 (d, J = 5.9 Hz, 4H). ¹³C NMR spectrum (100 MHz, CDCl₃) δ 138.1, 133.7, 133.4, 129.6, 128.5, 115.7, 115.5, 86.2, 85.8, 58.4, 50.3, 23.5.

Results and Discussion

Pale green–coloured crystalline **1-Ag** and **2-Ag** were respectively synthesized from metalloligands **1** and **2**. Both CPs show broad v_{0-H} stretches in the range of 3360–3410 cm⁻¹ due to the presence of coordinated water in **1-Ag** and lattice water molecules in **2-Ag** (Figures S17 and S18, SI).^{99,100} Strong bands in the region of 1545–1565 cm⁻¹ corresponds to the amidic $v_{C=0}$ stretches.^{99,100} For both CPs, TGA supports the

presence of either coordinated or lattice water molecules by displaying weight loss in the temperature range of 60-150 °C (Figures S19 and S20, SI). For 1-Ag, an observed weight change of 7.95% fits nicely with the calculated value of 7.33% corresponding to the loss of one coordinated and one lattice water molecule. In case of 2-Ag, observed weight loss of 4.70% is in close match with the calculated value of 5.06% for the loss of one water and one DMSO molecule present in lattice. DSC plots for both CPs exhibit broad exothermic features in the region of 60-150 °C for the loss of solvent molecules thereby supporting TGA results. Thermal studies further suggest that both CPs are thermally stable up to ca. 350 °C. Diffuse-reflectance absorption spectra of both CPs display broad features at 453-458 nm and 634-654 nm (Figure S21, SI). The low-energy spectral band has been assigned to be based on Co^{3+} -based metalloligand.¹⁰¹⁻¹⁰³ X-ray powder diffraction (XRPD) studies were used to confirm the crystalline homogeneity and bulk purity of the CPs. The experimental XRPD patterns closely match the ones simulated from the single crystal diffraction data for both CPs (Figures S22 and S23, SI) thereby inferring a single crystalline phase.



Figure. 1 (a) Asymmetric unit of **1-Ag**, a lattice water molecule and hydrogen atoms are omitted for clarity. Selected bond distances (Å): Co1–N(1), 1.954(5); Co1–N(2), 1.869(5); Co1–N(3), 1.984(5); Ag1–N(4), 2.148(6); Ag1–O2W, 2.093(6); Selected bond angles (°): N(1)– Co1–N(2), 81.2(2); N(1)–Co1–N(3), 162.1(2); N(2)–Co1–N(3), 80.9. (b) Partial crystal structure of **1-Ag** illustrating the coordination of pyridyl fragments to the secondary Ag(I) ions. (c) A combination of metalloligands (shown in different colors) to that of silver atoms generates a 2D network. (d) Weak argentophilic interactions between adjacent Ag(I) ions from two different layers (shown in red and green colors, respectively) connect two parallel 2D layers together. (e) Topological representation of **1-Ag** where yellow and green nodes respectively represent silver atoms and metalloligands.

Crystal Structures

Both CPs, 1-Ag and 2-Ag, were crystallographically characterized and their structures are shown in Figures 1 and 2, respectively. CP 1-Ag was crystallized in orthorhombic cell with *Pnna* space group. The asymmetric unit of **1-Ag** is consisted of half Co-based metalloligand, one silver atom, one coordinated water molecule, and a lattice water molecule (Figure 1a). Every metalloligand provides one negative charge which is balanced by one Ag⁺ ion. A metalloligand illustrates two tridentate ligands arranged meridionally around the Co³⁺ ion maintaining a compressed octahedral geometry (Figure 1b). The Co^{3+} ion is coordinated by four N_{amide} atoms in a distorted basal plane whereas two $N_{pyridine}$ atoms occupy the axial positions. $^{104-107}$ The Co– N_{amide} (avg. 1.952 Å) bond distances were longer than that of Co-N_{pyridine} distances (avg. 1.860 Å).¹⁰⁴⁻¹⁰⁷ The Ag(I) ion exhibits T-shaped geometry where two coordinations come from two pyridyl groups from two different metalloligands whereas the remaining one site is ligated by a water molecule (Figures 1b and 1c).

A metalloligand offers four appended pyridyl groups that coordinate to four different Ag(I) ions in different directions therefore generating a two-dimensional (2D) sheet-like architecture. Importantly, crystal structure of **1-Ag** exhibits prominent argentophilic interactions with $d_{Ag\cdots Ag}$ of 3.375 Å. These Ag...Ag interactions are present between two silver atoms from two parallel sheets (Fig. 1d). As a result, two 2D sheets (shown by red and green colors in Figure 1d) are further connected to each other and generate a three-dimensional (3D) architecture. Thus, argentophilic interactions play a critical role in controlling the overall 3D structure of **1-Ag**. The 3D nature of **1-Ag** as a result of argentophilic interactions is clearly visible in the resultant topology (Figure 1e).¹⁰⁸ Herein, a SBU is composed of a silver atom coordinated by two pyridyl rings (shown in yellow color) whereas two parallel sheets are further connected as a result of argentophilic interactions. Such SBUs are connected to the Co³⁺–based building blocks acting as tetratopic nodes (shown in green color) while parallel sheets are held together due to argentophilic interactions, therefore generating a 3D network. Topologically, **1-Ag** illustrates a 3D network with two nodal net and point symbol **{8².12}** (Figure 1e).⁹⁶⁻⁹⁸



Figure. 2 (a) Asymmetric unit of **2-Ag**, one lattice water, a DMSO molecules and hydrogen atoms are omitted for clarity. Selected bond distances (Å): Co1–N(1), 1.957(8); Co1–N(2), 1.852(8); Co1–N(3), 1.953(9); Co1–N(4), 1.979(8); Co1–N(5), 1.876(8); Co1–N(6), 1.969(9); Ag1–N(10), 2.228(9); Ag2–N(8), 2.192(12); Selected bond angles (°): N(2)–Co1–N(5), 177.9(4); N(2)–Co1–N(3), 81.29(5); N(5)–Co1–N(3), 96.7(4); N(10)–Ag1–N9, 110.9(4); N(10)–Ag1–N(7), 145.1(3); N(8)–Ag1–N(8), 180.0. (b) Partial crystal structure of **2**-Ag illustrating the coordination of pyridyl fragments to the secondary silver metals. (c) Coordination environment around the Ag1 and Ag2 atoms and its bonding to N_{pyridyl} groups from different metalloligands. (d) A combination of metalloligands (shown in different colors) and silver atoms give rise to a network which is actually composed of two individual parts shown on left and right sides; see text for details. (e) Topological representation (view along 001) of **2-Ag** where yellow and green nodes respectively represent silver atoms and metalloligands. (f) A different orientation of topological representation illustrating a layer-based structure.

Notably, Ag...Ag distance in silver metal is 2.88 Å whereas sum of van der Waals radii for two Ag atoms is 3.44 Å.¹⁰⁹ Strong argentophilic interactions are typically <3.0Å whereas distances >3.3Å are considered to be weak argentophilic interactions.¹¹⁰ A comparison suggests that **1-Ag** illustrates weak argentophilic interactions.¹¹⁰⁻¹¹²

Importantly, **1-Ag** exhibits the presence of pores in the resultant 3D network with dimensions of 13.62 x 8.21 Å². Such pores are arranged into channels throughout the network and accommodate lattice water molecules. Such a unique structural feature is expected to enhance substrate accessibility during the catalytic applications.

Single crystal X-ray diffraction of 2-Ag revealed that it crystallized in orthorhombic cell with Pbca space group. The asymmetric unit of 2-Ag contains one metalloligand, two half occupancy silver atoms, one water and a DMSO molecule in the crystal lattice (Figure 2a). Every metalloligand generates one negative charge which is balanced by two half occupancy Ag(I) ions. As seen in 1-Ag, Co³⁺ ion displays a compressed octahedral geometry coordinated by two meridional tridentate ligands (Figure 2b).¹⁰⁴⁻¹⁰⁷ Interestingly, in **2-Ag**, silver exhibits two different coordination geometries; three-coordinated distorted triangular planar geometry and two-coordinated linear geometry (Figure 2c). Importantly, in both cases, all coordination sites are satisfied by N_{pvridyl} groups. The overall 3D network is composed of two parts. Initially, a 2D sheet-like structure is created by the involvement of three-coordinated Ag(I)ions (right side of Figure 2d). Subsequently, such 2D sheets are perpendicularly connected via two-coordinated Ag(I) ions (left side of Figure 2d) therefore producing a 3D network. Such a packing between metalloligands and Ag(I) ions produces a densely packed 3D structure (Figure 2d). Topology of 2-Ag (Figure 2e) clearly exhibits both two-coordinated (as 2connected node) as well as three-coordinated (as 3-connected nodes) Ag atoms. Such nodes act as the SBUs in the resultant network whereas metalloligands function as the tetra-topic nodes. A combination of two provides five nodal net and point symbol {10.16.18}₂{10³}₄{10}₂{16} (Fig. 1e).⁹⁶⁻⁹⁸

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There are several notable structural differences between the two CPs. In 1-Ag, all silver atoms offered identical coordination environment where two coordinations come from the metalloligands while the third one was satisfied by a water molecule. The presence of a water molecule may assist in its facile removal and/or exchange and such a situation is likely to assist in catalysis (vide infra). In contrast, silver atoms in 2-Ag displayed two types of coordination environments that resulted in densely packed molecular components when compared to 1-Ag. We anticipate that such a difference between two CPs may result in considerable difference in their catalytic performance (vide infra).

Exchange, Adsorption and Inclusion Studies

As 1-Ag displayed a coordinated water molecules to the Ag(I) center, solvent–exchange studies were carried out to evaluate its possible exchange or replacement with potential substrate and/or reagents.^{113,114} For such a study, 1-Ag was heated up to 80 °C under vacuum for 6 h to remove both coordinated and lattice water molecules. Subsequently, desolvated 1-Ag was allowed to equilibrate in a sealed environment of D₂O vapours. Such a sample exhibited v_{O-D} stretches at ca. 2500 cm⁻¹ ($\Delta = 900$ cm⁻¹) and potentially suggest the exchange of ligated H₂O with D₂O (Figure S24, SI).^{115–117} A similar exchange using CH₃OH vapours displayed v_{C-O} stretch for the ligated CH₃OH at 1020 cm⁻¹ (Figure S25, SI).

The desolvated sample of **1-Ag** was further used to investigate possible inclusion of molecular iodine within its pores and channels. Notably, a 20 mg sample of **1-Ag** was able to adsorb nearly 2 mg of I_2 which corresponded to ca. 10.0% weight change. Such an adsorption resulted in a distinct colour change from green (**1-Ag**) to dark brown (**1-Ag+I**₂) (Figure S26, SI).^{118,119} Importantly, iodine adsorption process was reversible as the green coloured **1-Ag** was regenerated after evacuating the dark brown solid indicating the stable nature of network in accommodating and releasing molecular iodine from its pores and channels.

We also investigated inclusion of benzaldehyde (subsequently used in A³-coupling) both with 1-Ag and 2-Ag. For such studies, de-solvated samples were impregnated by dipping crystals in a CH₂Cl₂ solution of benzaldehyde. Such impregnated samples were investigated by FTIR spectra, XRPD patterns as well as SEM and optical images. The FTIR spectra suggested the inclusion of benzaldehyde within the crystal lattice as noted by the red-shifted $v_{C=0}$ stretches of benzaldehyde (Figures S27 and S28, SI). Interestingly, inclusion of benzaldehyde resulted in a visible color change of the crystals from green to black (Figures S29 and S30, SI). However, SEM images did not show noticeable morphological changes to the crystal surface (Figures S31 and S32, SI) suggesting that the inclusion has not significantly affected the crystallinity. The convincing proof about the stability of the crystalline samples was obtained from the XRPD studies that did not show measurable changes to that of pristine samples (Figures S33 and S34, SI). Collectively, these studies strongly suggest the inclusion of benzaldehyde within the crystal lattice without compromising the crystallinity.

Catalytic A³–Coupling Reactions

The presence of low-coordinated Ag(I) ions both in 1-Ag and 2-Ag suggest that a suitable substrate and/or reagent could potentially approach such metals whereas exchange and sorption studies with 1-Ag indeed proves such a point. On the other hand, 3D polymeric nature of two CPs suggests their potential utilization as the heterogeneous catalysts. Therefore, both 1-Ag and 2-Ag were screened as the heterogeneous catalysts for the synthesis of propargylamines via A³-coupling of aldehydes, amines and alkynes.

Initially, reaction conditions were optimized to achieve maximum product formation using benzaldehyde, phenyl acetylene and pyrrolidine as the model coupling reagents utilizing only 1 mol% of 1-Ag as a representative catalyst (Table 2). Various solvents such as ethanol, water, THF, and toluene were screened to find out the best solvent (entries 1 -4); however, maximum product formation was observed without the use of any solvent (92%; entry 7). Temperature screening revealed that elevated temperature enhanced the product formation (entries 5 - 8). Although best results were obtained at 100 °C; subsequent reactions were only performed at 80 °C. The effect of assorted secondary amines as the nucleophile (pyrrolidine, piperidine, piperazine and morpholine) was also evaluated (entry 7-11) and the best product yield was noted with pyrrolidine when compared to other amines. The use of Ag(CF₃COO), Ag(OTf) and AgCl as the catalyst resulted in quite low product formation (entry 12-14). Such a fact suggests the significance of 1-Ag in promoting A³-coupling reactions. Finally, an identical reaction was carried out without the use of any catalyst that produced the respective product in only 12% yield (entry 15). Similarly, use of metalloligands 1 and 2 as the catalysts only produced desired product in 10 - 15% yield (entries 16–17). These reactions confirmed the importance of 1-Ag as a heterogeneous catalyst and rule out the leaching of Ag(I) ion from the CPs (vide infra).

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Table 2. Optimisation	n of the	reaction	conditions	for	the	A^3-
coupling reactions.						

ĺ	CHO + Amine +	- Cat	alyst 🕞		\bigcirc
S. No	Catalyst	Amine	T (° C)	Solvent	Yie (%
1	1-Ag	Pyrrolidine	80	EtOH	6
2	1-Ag	Pyrrolidine	80	H_2O	7
3	1-Ag	Pyrrolidine	80	THF	5
4	1-Ag	Pyrrolidine	80	Toluene	5
5	1-Ag	Pyrrolidine	40		3
6	1-Ag	Pyrrolidine	60		7
7	1-Ag	Pyrrolidine	80		9
8	1-Ag	Pyrrolidine	100		9
9	1-Ag	Piperidine	80		7
10	1-Ag	Piperazine	80		5
11	1-Ag	Morpholine	80		3
12	AgCOOCF ₃	Pyrrolidine	80		3
13	AgOTf	Pyrrolidine	80		2
14	AgCl	Pyrrolidine	80		2
15	No catalyst	Pyrrolidine	80		1
16	1	Pyrrolidine	80		1
17	2	Pyrrolidine	80		1

These control experiments paved the foundation to evaluate the scope as well as the versatility of both CPs as the heterogeneous catalysts in promoting multi-component coupling reactions using different coupling partners bearing electronic substituents (Table 3). To evaluate the effect of electronic subsituents (e-donating or e-withdrawing) on product yield, several para-substituted benzaldehydes as well as parasubstituted alkynes were used. It was observed that both electron rich as well as electron poor aldehydes were somewhat equally effective with both the catalysts. Although, presence of e-withdrawing substituent at the para-position of benzaldehyde did increase the product yield (entry 4); edonating group at para-position did not show much effect (entry 3) when compared to only benzaldehyde. Notably, an e -donating group at the para-position of ethynylbenzene increased the product conversion due to the enhanced nucleophilicity (entries 5-8). In contrast, when 1-ethynyl-4fluorobenzene was used in place of ethynylbenzene, product yield was reduced due to the lower nucleophilicity of alkyne (entries 9–12). In fact, nearly quantitative A³-coupling product was obtained using **1-Ag** as a catalyst when $-{}^{t}Bu$ and $-NO_{2}$ groups were respectively placed on the para position of ethynylbenzene and benzaldehyde (entry 8).

Table 3. A³-coupling reactions using 1-Ag and 2-Ag as the catalysts.



1	-H	-H	92	86	
2	-Cl	-H	93	77	
3	-OMe	-H	92	79	
4	-NO ₂	-H	98	91	
5	-H	- ^t Bu	94	84	
6	-Cl	- ^t Bu	96	84	
7	-OMe	- ^t Bu	91	87	
8	-NO ₂	- ^t Bu	99	88	
9	-H	-F	83	79	
10	-Cl	-F	84	79	
11	-OMe	-F	81	77	
12	-NO ₂	-F	91	87	
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Conditions: Catalyst: 1-mol%; Temperature: 80 °C; Time: 60 min.

We further extended A³-coupling reactions to a few challenging aldehydes of biological importance along with pyrrolidine and phenyl acetylene (Table 4). Importantly, both CPs, 1-Ag and 2-Ag, promoted such reactions smoothly to afford the respective propargylamines in yields ranging from 70 to 88 %.

Table 4. A³-coupling reaction of some biologically relevant aldehydes using 1-Ag and 2-Ag as the catalysts.



Conditions: Catalyst: 1-mol%; Temperature: 80 °C; Time: 60 min.

Although both 1-Ag and 2-Ag efficiently carried out A³coupling of substituted benzaldehydes, substituted alkynes and pyrrolidine but it can precisely be noticed that 1-Ag is a better catalyst than 2-Ag. We believe that such a difference in catalysis is related to the structures of two CPs. 1-Ag offers open structure as a result of well-defined pores and channels throughout its 3D architecture that allows facile diffusion of substrates and reagents as was also illustrated by the exchange and adsorption studies. In contrast, 2-Ag presents somewhat densely packed structure that may not have effectively supported the substrate and reagents' diffusion that has resulted in comparatively poor product yield.

Recyclability Studies

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As catalytic reactions were carried out heterogeneously, both CPs can be conveniently recovered after the reactions. Such a fact provided the opportunity to test their reusability as well as stability before and after the catalytic reactions. Subsequently, **1-Ag**, as a representative example, was recovered from a reaction between benzaldehyde, pyrrolidine and phenyl acetylene in nearly quantitative yield and was reused five times without apparent loss in its catalytic performance (Figure 3).

A major disadvantage of heterogeneous catalysis is the potential leaching of the catalytically active species from a solid catalyst.^{120–122} Often, such a leached but a catalytically active species actually carries out a reaction. ¹²⁰⁻¹²² To test such a hypothesis, hot filtration test, in which solid catalyst is filtered off during the reaction while the filtrate is monitored for continued activity, was performed.¹⁰² A reaction involving benzaldehyde, pyrrolidine and phenylacetylene was taken as a model reaction for the hot filtration test in presence of 1-Ag as a representative catalyst (Figure 4). The reaction was allowed to coninue for 30 min and thereafter solid 1-Ag was removed via filtration while the reaction was further continued. As clearly visible, negligible product formation took place after the removal of 1-Ag. However, once 1-Ag was readded to the same reaction mixture at 60 min, the catalysis resumed producing the product in high yield. This simple test confirm the true heterogeneous nature of catalysis and rules out the leaching of any catalytically active species. Figure 4 also displays disappearance of benzaldehyde as a function of time (red dots) that correlates nicely with the formation of propargylamine, as the desired product (black squares). Such a fact rules out other undesirable reactions parallely taking place within the reaction mixture.

The recovered **1-Ag** was characterized and compared to that of pristine sample. FTIR spectrum of recovered **1-Ag** exhibited nearly identical resonances to that of as-synthesized **1-Ag** (Figure S35, SI). Furthermore, a comparison between the XRPD patterns of as synthesized **1-Ag** to that of recovered **1-Ag** after 2^{nd} cycle revealed that both crystallinity as well as the structural integrity of the sample is preserved during the catalytic cycles (Figure S36, SI). Collectively, these experiments convincingly point towards the stable and reusable nature of the present CPs in carrying out the A³-coupling reactions.

100 80 40 0 0 Numbers of catalytic runs **Figure 3.** Reusability of **1-Ag** as a catalyst for five consecutive runs for the A^3 -coupling reaction between benzaldehyde, pyrrolidine and phenyl acetylene.



Figure 4. (a) A^3 -coupling reaction of benzaldehyde, pyrrolidine and phenylacetylene in presence of 1-Ag as a catalyst. (b) Disappearance of benzaldehyde as a function of time. (c) Catalyst 1-Ag was filtered off after 30 min. leading to nearly termination of the catalytic reaction. (d) Catalyst 1-Ag was re-added at 60 min. causing commencement of the reaction.

Mechanistically, A³–coupling reactions proceed via the initial coupling between an aldehyde and an amine producing the corresponding iminium ion as the intermediate. Subsequently, phenyl acetylene attacks the iminium ion to form the propargylamine. In this context, nucleophilicity of phenyl acetylene becomes a decisive factor and e-donating groups on ethynylbenzene are likely to enhance product formation as was also noted in the present case (cf. Table 3).

Conclusions

This work has shown synthesis and characterization of two Ag-based CPs (1-Ag and 2-Ag) constructed by using two Cobased metalloligands decorated with appended pyridyl rings. Crystal structures of 1-Ag and 2-Ag displayed 3D architectures due to the coordination of Ag(I) ions by the appended pyridyl groups. In case of 1-Ag, transition from 2D sheets to a 3D network was manifested due to the presence of argentophilic interactions. Two CPs illustrated noteworthy structural differences and interesting topologies as a result of coordination of Ag(I) ions to the metalloligands. Both CPs acted as the heterogeneous catalysts for the A³-coupling reactions of aldehvdes, secondary amines and alkynes. Recyclability experiments substantiated the stable nature of CPs in promoting the A³-coupling reactions. This work has illustrated that the relative position of substituted pyridyl ring not only influenced the structural outcome but also the catalysis results.

ASSOCIATED CONTENT

Supporting Information. Figures for FTIR and NMR spectra; TGA; PXRD patterns; SEM and optical images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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Page 12 of 13

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Synopsis: Two Ag(I)-based 3D coordination polymers have been synthesized and utilized as the heterogeneous catalysts for A^3 -coupling reactions of assorted aldehydes, secondary amines and substituted alkynes.