

Article

A One-Dimensional Coordination Polymer Containing Cyclic [Ag₄] Clusters Supported by a Hybrid Pyridine and Thioether Functionalized 1,2,3-Triazole

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Abstract: A pyridine and thioether co-supported triazole ligand **L** (**L** = 2-((4-(3-(cyclopentylthio)propyl)-1H-1,2,3-triazol-1-yl)methyl)pyridine) has been synthesized using the CuAAC click reaction. This ligand supports the formation of a thermally stable, one-dimensional coordination polymer [L₂Ag₄]_n·4n(BF₄) (**1**) possessing a cationic polymeric structure with [Ag₄] metallomacrocycles, in which the ligand **L** displays chelate/bridging coordination modes using all four potential donors of nitrogen (N) and thioether (S). The dominant direction of the prism crystals of **1** aligns with the propagation of the chain in the lattice.

Keywords: hybrid ligand; click reaction; [Ag₄] metallomacrocycle; coordination polymer; crystal morphology

1. Introduction

Coordination polymers are well-defined molecular materials consisting of metal centers and organic ligands, and have received considerable attention because of their fascinating crystalline structures and wide range of applications, including as luminescent sensors, catalysts, and porous and electrochemical materials [1–5]. The formation and dimensionality of coordination polymers are governed by the coordination number and geometry of the metal centers and the nature and arrangement of donor atoms on the ligand. Reaction conditions—such as temperature, solvent, metal-to-ligand ratio, and counter ions—also influence coordination diversity [6,7]. Many synthetic chemists have dedicated themselves to the construction of new organic ligands and coordination polymers, from which to discover the principles of controlled self-assembly. Significant effort has been devoted to the complementarity of metal precursor and rationally designed organic ligands [8–12]. Ag(I) with d¹⁰ electronic configuration, multiple coordination geometries and luminescence resulting from Ag···Ag interactions is especially attractive to crystal engineers [13–17]. Ag(I) is a soft metal and so favored to N, O, and S donor ligands [18–21]. N-heterocyclic pyridine, pyrazole, imidazole, triazole, and multidentate ligands have been employed to support Ag(I) ions and clusters. We have a particular interest in hybrid ligands with different chemical donors that demonstrate hemilability for the design of new functional materials [22,23]. Schiff-base-, pyrazole-, and thioether-functionalized pyridines have been used to construct magnetic and luminescent coordination polymers of Mn^{II}, Ni^{II}, Cu^{II/I}, and Zn^{II} [24–30]. The copper-catalyzed azide-alkyne cycloaddition (CuAAC) reactions provide access to versatile, multidirectional 1,2,3-triazole ligands and we have used these ligands to make copper-iodide cluster-based coordination compounds and study the relationship between lattice weak interactions and crystal growth [31,32]. Different substituents on the ligands can be used to tune the possible coordination modes and these weak lattice interactions. The distance between two coordination sites (e.g., thioether (S) and pyridine–triazole NN groups) is also appropriate for

stabilizing different sized copper-iodide clusters. As a continuation of this work, we herein report a new pyridine and thioether supported 1,2,3-triazole ligand **L** synthesized using the click reaction. This neutral ligand employs pyridine–triazole chelate-bridging and thioether bridging modes to stabilize Ag(I) centers and form a polymeric, cationic chain with cyclic [Ag₄] clusters.

2. Materials and Methods

All reagents were used as received. Infrared spectra were obtained on a PerkinElmer Spectrum 2000 FT-IR spectrometer from a sample in KBr disc. Elemental analyses were performed on a thermo electron corporation flash EA 1112 series analyzer. Electrospray ionization mass spectrometry (ESI-MS) was recorded in positive ion mode using a Shimadzu LCMS-IT-TOF mass spectrometer. UV–vis absorption spectrum was recorded on a Shimadzu UV-2501PC UV–vis recording spectrophotometer. Photoluminescence spectrum was measured on a Shimadzu RF-5301 PC spectrofluorophotometer. Powder X-ray diffraction data was collected on a Bruker D8 Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). Thermogravimetric analysis (TGA) was carried out in an air stream using a TA Instruments TGA Q500 analyzer with a heating rate of 20 °C per min.

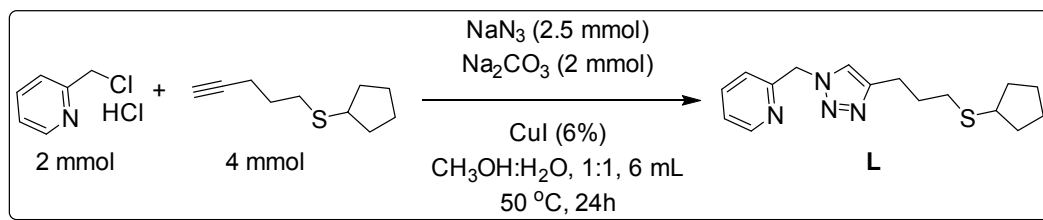
X-ray Crystallography

Single-crystal X-ray diffraction data were collected using a Bruker AXS SMART APEXII CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data integration and scaling were performed using Bruker SAINT [33]. The empirical absorption correction was performed by SADABS [34]. The space group determination, structure solution, and least-squares refinements on $|F|^2$ were carried out with the Bruker SHELXL [35]. The structure was solved by direct method to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically. CCDC reference number: 1587041 (1). Crystal Data for C₃₂H₄₄Ag₄B₄F₁₆N₈S₂ (M = 1383.57 g/mol): monoclinic, space group P2₁/c, a = 15.6371(4) Å, b = 9.1234(3) Å, c = 16.6824(5) Å, $\beta = 101.648(1)^\circ$, V = 2331.0(1) Å³, Z = 2, T = 296(2) K, D_{calc} = 1.971 g/cm³, 39572 reflections measured ($1.33^\circ \leq \Theta \leq 27.12^\circ$), 5147 unique ($R_{\text{int}} = 0.0277$) which were used in all calculations. The final R₁ was 0.0733 ($I > 2\sigma(I)$) and wR₂ was 0.2093 (all data).

3. Results and Discussion

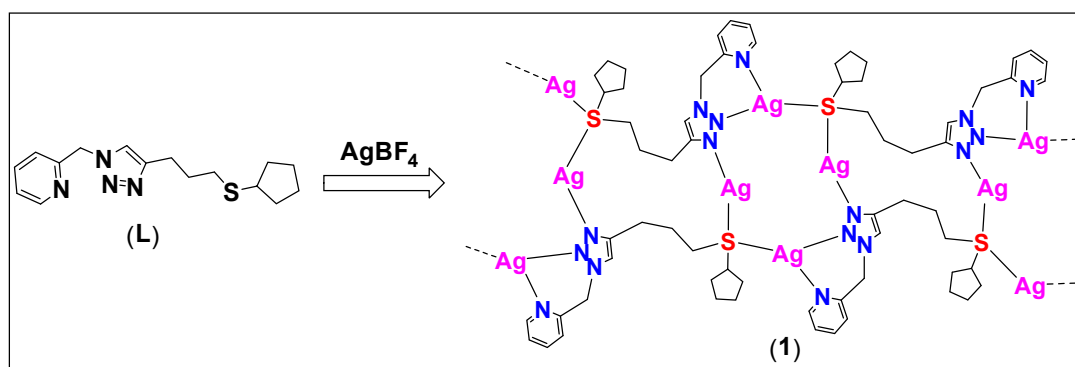
3.1. Synthesis

Sodium azide is potentially explosive. Only micro-scaled reactions should be performed. The alkyne precursor (4-pentyn-1-ylthio)-cyclopentane was prepared following literature procedures for thioether formation [28,32]. The crude alkyne was placed in a round bottom flask containing 2-(chloromethyl)pyridine hydrochloride (328 mg, 2 mmol), Na₂CO₃ (210 mg, 2 mmol), NaN₃ (156 mg, 2.5 mmol), CuI (23 mg, 0.12 mmol), and CH₃OH/H₂O (1:1 v:v, 6 mL) (Scheme 1). The reaction was stirred at 50 °C for 24 h. The residue was extracted with ethyl acetate (150 mL) and the organic layer was washed with water (3 × 20 mL), dried (with anhydrous Mg₂SO₄) and concentrated by rotary evaporator at 60 °C under vacuum. Column chromatography on silica gel with hexane/ethyl acetate (2:1 v:v) as eluent produced a band at R_f = 0.1 that was collected and the solvent removed by rotary evaporator at 40 °C under vacuum. The product (**L**) was a pale yellow oil. Yield: 330 mg, 55%. 2-((4-(3-(Cyclopentylthio)propyl)-1H-1,2,3-triazol-1-yl)methyl)pyridine (**L**), (C₁₆H₂₂N₄S, MW 302.44). ESI-MS (m/z, %): [L+H]⁺ (303, 100). ¹H NMR (CDCl₃, 500.2 MHz) δ : 8.56 (s, 1H, pyridine, NCH), 7.68–7.65(m, 1H), 7.45 (s, 1H, triazole), 7.25–7.23 (m, 1H), 7.16–7.13 (t, 1H), 5.61 (s, 2H, pyridine–CH₂–triazole), 3.06–3.01 (m, 1H, SCH), 2.81–2.78 (m, 2H), 2.56–2.52 (m, 2H), 1.97–1.91 (m, 4H), 1.69 (b, 2H), and 1.53–1.43 (m, 4H). ¹³C NMR (CDCl₃, 125.8 MHz): 154.7, 149.5, 147.9, 137.6, 123.5, 122.5, and 121.6 (C in pyridine and triazole groups), 55.4 (pyridine–CH₂–triazole), 43.8 (SCH), 33.9, 31.2, 29.4, and 24.9.



Scheme 1. Preparation of ligand L.

Complex **1** was prepared by mixing a methanol solution (5 mL) of ligand **L** (151 mg, 0.5 mmol) and a methanol solution (5 mL) of AgBF_4 (195 mg, 1 mmol). Single crystals were obtained by slow evaporation of the solvent over one week at room temperature (Scheme 2). The product was collected by filtration, washed with methanol and diethyl ether, and dried in vacuum oven for overnight at 60 °C. Yield: 270 mg, 78%. The powder sample of complex **1** is grey and no obvious solid-state luminescence was observed. Single crystals of **1** are prisms with a relative long axis. Anal. Calcd. for $\text{C}_{32}\text{H}_{44}\text{Ag}_4\text{B}_4\text{F}_{16}\text{N}_8\text{S}_2$ (1383.57): C, 27.78; H, 3.21; N, 8.10%. Found: C, 27.80; H, 3.27; N, 8.08%. Main IR bands (cm^{-1}): 3132(m), 3078(m), 2951(s), 2865(m), 1594(m), 1573(m), 1553(m), 1476(m), 1439(m), 1301(m), 1218(m), 1057(s, b, $\nu(\text{BF}_4^-)$), 756(m), 726(m), 596(m), 534(m), and 522(m). ESI-MS (m/z , %): $[\text{LAg}]^+$ (409, 100), $[\text{L}_2\text{Ag}]^+$ (713, 81).

Scheme 2. Formation of cationic coordination polymer **1**.

3.2. UV-Vis and Photoluminescent Spectra of Ligand L

An ethanol solution of ligand **L** absorbed UV-vis light at 203 nm and between 240–280 nm with a maximum at about 260 nm (Figure 1a) and exhibited a broad emission between 400–500 nm with a maximum at 442 nm upon excitation at 358 nm. Neat liquid gave a blue emission under UV 365 nm light. (Figure 1b, insert) Coordination polymer **1** was synthesized by the reaction of **L** and AgBF_4 in methanol at room temperature (Scheme 2). IR spectroscopy indicated characteristic absorption by the BF_4^- anion. The polymeric structure may be disassociated into small fragments (e.g., $[\text{LAg}]^+$ and $[\text{L}_2\text{Ag}]^+$) in solution which were detected by ESI-MS.

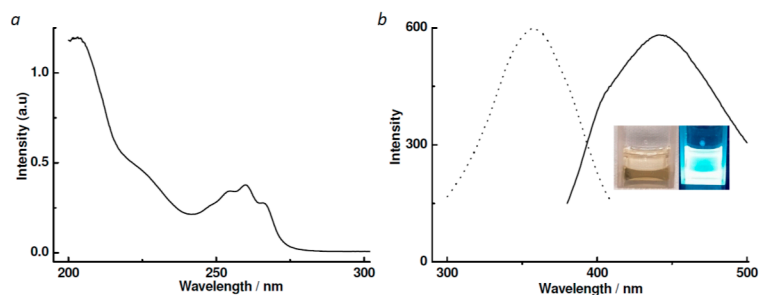


Figure 1. UV-vis (a) and excitation (dotted line) and emission (solid line) (b) spectra of ligand L in ethanol (0.1 M). (The inset images are ligand L in a quartz cuvette under normal and 365 nm lights, respectively).

3.3. Molecular Structure of Complex 1

Coordination polymer **1** crystallized in a monoclinic crystal system with space group $P 2_1/c$. There is one neutral ligand L, two cationic Ag(I) centers and two lattice BF_4^- anions in the crystallographic asymmetric unit. (Figure 2a) Ag1 and Ag2 possess three-coordinated trigonal planar and two-coordinated linear geometries, respectively. Ag1 is surrounded by two chelating N donors from pyridine and triazole of ligand L and one bridging S donor from another ligand L. Ag2 is coordinated by one 3'-N_{triazole} of ligand L and one bridging S donor from another ligand L. These two S donors also bridge neighboring Ag1-Ag2 centers to form a $[\text{Ag}_4]$ metallomacrocycle. The cyclic $[\text{Ag}_4]$ units are further linked by double ligands and extend along the short *b* axis, which aligns with the dominant direction of the prism-shaped single crystals. (Figure 2c,d) The polymeric chains are parallel to each other in the lattice (Figure 2b). The counterions BF_4^- occupy the cavities created by the cationic polymeric chains. The Ag1...Ag2 distances are 4.28 and 4.04 Å in the $[\text{Ag}_4]$ metallomacrocycle. The shortest Ag...Ag distance of neighboring $[\text{Ag}_4]$ units is 6.06 Å. The shortest Ag...Ag distance of neighboring chains is 7.60 Å.

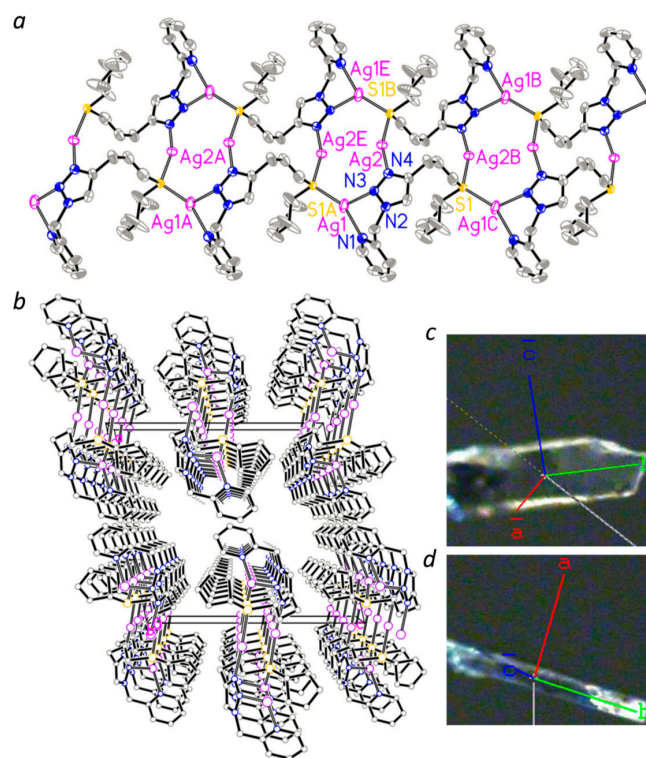


Figure 2. (a) Cationic and polymeric chain structure in **1**. (b) Packing structure in **1**. (BF_4^- anions are removed for clarity) (c,d) Single crystal indexes in different orientations of **1**.

3.4. Powder XRD and TGA

The experimental powder X-ray diffraction pattern for complex **1** showed good agreement with its simulated pattern determined from the single-crystal XRD experiment, supporting its phase purity (Figure 3). Thermogravimetric analysis (TGA) of **1** was conducted from room temperature to 900 °C under an air flow with a heating rate of 20 °C per min (Figure 4). Complex **1** is stable to about 230 °C. There are two weight loss stages between 230 and 890 °C, which correspond to the removal of ligand **L**, decomposition of BF_4 anion, and the formation of metallic silver with a residue amount of 31.5% (calcd. 31.2%).

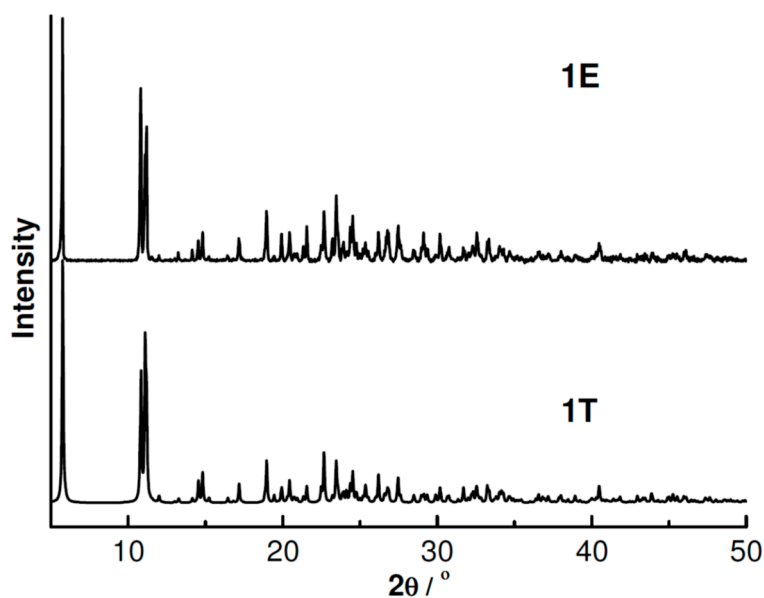


Figure 3. Powder XRD patterns of **1**. (T = theoretical profile referenced to the experimentally determined single-crystal XRD pattern; E = experimental data).

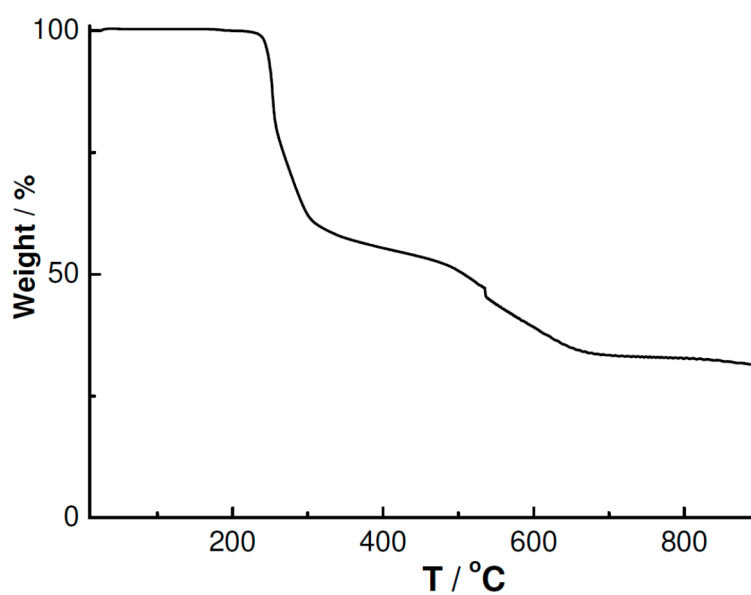


Figure 4. TGA curves of **1**.

4. Conclusions

In summary, a pyridine and thioether functionalized 1,2,3-triazole ligand with a relatively long methylene bridge ((CH₂)₃) between NN and S donors was synthesized using the CuAAC click reaction. The reaction of ligand L and AgBF₄ afforded a novel, thermally stable polymeric chain structure with [Ag₄] metallomacrocyclics. The propagation of these chains in the lattice aligns with the dominant growth direction of the prism crystals. The observation of two types of Ag(I) coordination geometries (linear and trigonal planar) further emphasizes the diversity of Ag(I) coordination chemistry.

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Author Contributions: Shiqiang Bai conceived and designed the experiments; Shiqiang Bai and Hoi Ka Ivy Wong performed the experiments; Shiqiang Bai wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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