

Anion-Directed Assembly of Two Ag^I Complexes Based on 2,2'-(4H-1,2,4-triazole-3,4-diyl)dipyridine¹

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Abstract—Reaction of the Ag⁺ ions with 2,2'-(4H-1,2,4-triazole-3,4-diyl)dipyridine (L²²) in the presence of NO₃⁻ and CH₃SO₃⁻, respectively, affords two silver(I) coordination compounds, namely {[Ag₃(NO₃)₂(C₁₂H₉N₅)₂](NO₃)_n}_n (I) and [Ag(CH₃SO₃)(C₁₂H₉N₅)₂] (II). Both complexes have been characterized by single-crystal X-ray diffraction (CIF file CCDC nos. 1051589 (I) and 1051590 (II)). In complex I, the adjacent metal centers are interconnected via L²² ligands to afford a 1D coordination chain. Complex II shows the discrete cage-like binuclear coordination pattern with the Ag···Ag distance of 4.358(1) Å.

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INTRODUCTION

Over the past decades, chemists and material scientists have been focusing their research on exploring the synthesis of coordination polymers not only due to their intriguing structural versatility but also because of their potential applications [1–3]. To date, a large number of functional metal complexes with diverse topology and properties have been prepared, which can be controlled by external factors such as the coordination environments of metal centers, the organic ligands, solvent, pH, temperature, counter-anions, and so on [4–6]. Among these factors, anions play extraordinary roles in shaping up the overall supramolecular architectures of coordination polymers. On one hand, anions can influence the resultant supramolecular architectures either by coordinating directly to the metal centers or by acting as the templates with a wide range of geometries. Furthermore, anions play an important role in balancing the charge of the coordination framework, especially for the complexes constructed by the neutral ligands.

Our group has been working on the synthesis of various coordination assemblies with various of dipyridyl ligands, and a great diversity of discrete or infinite coordination architectures have been constructed [7–10]. As part of our ongoing study of coordination complexes of dipyridyl ligands, 2,2'-(4H-1,2,4-triazole-3,4-diyl)dipyridine (L²²) was used to react with AgNO₃ and Ag(CH₃SO₃), respectively, to investigate the influence of counter anion on the struc-

tural assembly and diversity, affording 1D {[Ag₃(NO₃)₂(C₁₂H₉N₅)₂](NO₃)_n}_n (I) and binuclear [Ag(CH₃SO₃)(C₁₂H₉N₅)₂] (II). The results indicate that the nitrate (NO₃⁻) and methanesulfonate (CH₃SO₃⁻) anions significantly influence the coordination modes of L²² from (η⁴, μ³) to (η³, μ²) fashions, and hence affect the final coordination motifs and the arrangement of supramolecular arrays.

EXPERIMENTAL

With the exception of the ligand L²², which was prepared according to the literature method [11], all reagents and solvents were commercially available and used as received. Elemental analyses of C, H, and N were performed by using a CE-440 (Leemanlabs) analyzer. FT-IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer.

Synthesis of I. A CH₃CN solution (6 mL) of AgNO₃ (8.5 mg, 0.05 mmol) was carefully layered onto a buffer solution of acetic ether, and underlying which was a CH₂Cl₂ solution of L²² (11.2 mg, 0.05 mmol) in a straight glass tube. After evaporating the solvents slowly for two weeks, the suitable colorless block single crystals for X-ray analysis were produced in a yield of 68% (10.8 mg, based on AgNO₃).

For C₂₄H₁₈N₁₃O₉Ag₃ (I)

anal. calcd., %: C, 30.15; H, 1.90; N, 19.05.

Found, %: C, 30.19; H, 1.83; N, 19.11.

¹ The article is published in the original.

Table 1. Crystallographic data and structure refinement details for complexes **I** and **II**

| Parameter | Value | |
|---|---|---|
| | I | II |
| Formula mass | 956.12 | 852.41 |
| Crystal size, mm | 0.18 × 0.14 × 0.13 | 0.18 × 0.17 × 0.16 |
| Crystal system | Monoclinic | Triclinic |
| <i>a</i> , Å | 18.946(8) | 7.6257(18) |
| <i>b</i> , Å | 8.682(4) | 7.9844(19) |
| <i>c</i> , Å | 18.802(8) | 12.269(3) |
| α, deg | 90.00 | 96.381(5) |
| β, deg | 101.560(5) | 92.222(4) |
| γ, deg | 90.00 | 92.793(4) |
| <i>V</i> , Å ³ | 3030(2) | 740.8(3) |
| Temperature, K | 296(2) | 296(2) |
| Space group | <i>C</i> 2/ <i>c</i> | <i>P</i> 1 |
| <i>Z</i> | 4 | 1 |
| ρ _{calcd} , mg m ⁻³ | 2.096 | 1.911 |
| μ(MoK _α), mm ⁻¹ | 2.0 | 1.52 |
| <i>F</i> (000) | 1864 | 424 |
| θ Range, deg | 2.2–25.0 | 1.7–25.0 |
| Index ranges <i>h</i> , <i>k</i> , <i>l</i> | –22 ≤ <i>h</i> ≤ 17 –10 ≤ <i>k</i> ≤ 10 –17 ≤ <i>l</i> ≤ 22 | –9 ≤ <i>h</i> ≤ 9 –9 ≤ <i>k</i> ≤ 9 –11 ≤ <i>l</i> ≤ 14 |
| Reflections measured | 7703 | 4334 |
| Independent reflections | 2681 | 2618 |
| <i>R</i> _{int} | 0.0215 | 0.0216 |
| Reflections with <i>I</i> ≥ 2σ, <i>I</i> | 2218 | 2394 |
| Number of refinement parameters | 237 | 209 |
| GOOF | 1.034 | 1.070 |
| Final <i>R</i> ₁ , <i>wR</i> (<i>F</i> ²) values, <i>I</i> > 2σ, <i>I</i> | 0.0275, 0.0630 | 0.0276, 0.0673 |
| Final <i>R</i> ₁ , <i>wR</i> (<i>F</i> ²) values, all data | 0.0374, 0.0670 | 0.0305, 0.0697 |
| Largest difference peak and hole, <i>e</i> Å ⁻³ | 0.53/–0.57 | 0.37/–0.77 |

Table 2. Selected bond lengths (Å) and bond angles (deg) in structures **I** and **II***

| Bond | <i>d</i> , Å | Bond | <i>d</i> , Å | Bond | <i>d</i> , Å |
|-------------------------|--------------|-------------------------|--------------|----------------------|--------------|
| I | | | | | |
| Ag(1)–N(5 <i>A</i>) | 2.339 (3) | Ag(1)–N(1) | 2.391 (3) | Ag(1)–N(2) | 2.426 (3) |
| Ag(1)–O(1) | 2.506 (6) | Ag(2)–N(3) | 2.173 (3) | Ag(2)–N(3 <i>B</i>) | 2.173 (3) |
| II | | | | | |
| Ag(1)–N(3 <i>A</i>) | 2.231 (2) | Ag(1)–N(1) | 2.284 (2) | Ag(1)–N(2) | 2.511 (3) |
| Ag(1)–O(1) | 2.552 (2) | | | | |
| Angle | ω, deg | Angle | ω, deg | Angle | ω, deg |
| I | | | | | |
| N(5 <i>A</i>)Ag(1)N(1) | 120.49 (10) | N(5 <i>A</i>)Ag(1)N(2) | 121.59 (9) | N(1)Ag(1)N(2) | 69.18 (9) |
| N(5 <i>A</i>)Ag(1)O(1) | 94.26 (19) | N(1)Ag(1)O(1) | 144.34 (17) | N(2)Ag(1)O(1) | 100.7 (2) |
| N(3)Ag(2)N(3 <i>B</i>) | 179.998 (1) | | | | |
| II | | | | | |
| N(3 <i>A</i>)Ag(1)N(1) | 166.99 (8) | N(3 <i>A</i>)Ag(1)N(2) | 102.04 (8) | N(1)Ag(1)N(2) | 71.26 (8) |
| N(3 <i>A</i>)Ag(1)O(1) | 88.89 (8) | N(1)Ag(1)O(1) | 104.04 (8) | N(2)Ag(1)O(1) | 115.78 (8) |

* Symmetry transformation: (*A*) $-x + 2, -y + 1, -z + 2$; (*B*) $-x + 2, -y, -z + 2$ (**I**); (*A*) $-x, -y + 1, -z + 1$ (**II**).

IR (KBr; ν , cm^{-1}): 1591 s, 1473 m, 1384 s, 1308 w, 1248 w, 1199 m, 1149 w, 1092 w, 1044 w, 992 w, 868 w, 825 w, 787 s, 744 m, 707 m, 663 w, 621 w, 569 m.

Synthesis of II. The same synthetic method as that for complex **I** was used except that AgNO₃ was replaced by Ag(CH₃SO₃) (10.2 mg, 0.05 mmol), producing colorless block single crystals of complex **II** in a yield of 62% (13.2 mg).

For C₂₆H₂₄N₁₀O₆S₂Ag₂ (**II**)

anal. calcd., %: C, 36.64; H, 2.84; N, 16.43.
Found, %: C, 36.68; H, 2.80; N, 16.47.

IR (KBr; ν , cm^{-1}): 1591 s, 1525 w, 1484 s, 1443 s, 1386 s, 1332 m, 1287 w, 1195 v.s, 1111 w, 1054 v.s, 958 m, 868 m, 786 v.s, 743 m, 708 m, 665 m, 621 w, 563 s, 534 m, 415 m.

X-ray crystallography. X-ray single-crystal diffraction data for both complexes were collected on a Bruker Apex II CCD diffractometer at room temperature with MoK_α radiation ($\lambda = 0.71073$ Å). Both structures were solved by direct methods with SHELXS and refined with SHELXL [12, 13]. The

final refinements were achieved by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms on F^2 . Hydrogen atoms were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. In the structure of complex **I**, the coordinated nitrate anion is disordered over two positions with partial site-occupancies of 0.683 and 0.317. Further crystallographic details are summarized in Table 1, and selected bond lengths and angles are shown in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1051589 (**I**) and 1051590 (**II**); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The asymmetric unit of complex **I** is composed of one and a half Ag(I) center, one coordinated nitrate anion, one L²² ligand, and half a lattice nitrate anion. As can be seen in Fig. 1a, Ag(1) represents a distorted tetrahedral geometry, which is surrounded by three nitrogen atoms from a chelating triazole-pyridyl segment (Ag(1)–N(1) 2.391(3), Ag(1)–N(2) 2.426(3) Å)

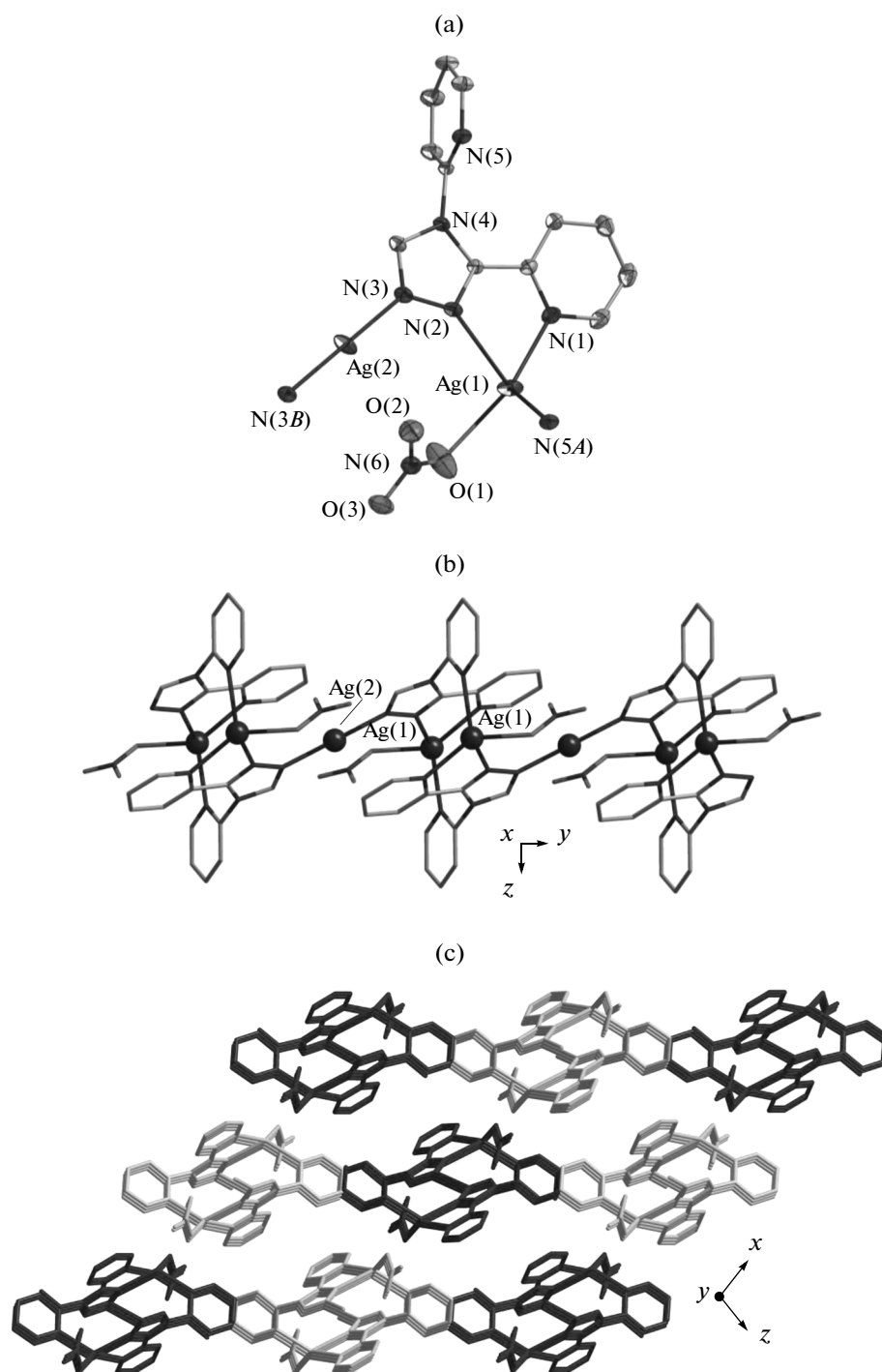


Fig. 1. The coordination environment of $\{[\text{Ag}_3(\text{NO}_3)_2(\text{L}^{22})_2](\text{NO}_3)\}_n$. Displacement ellipsoids are drawn at the 30% probability level (symmetry codes: (A) $-x + 2, -y + 1, -z + 2$; (B) $-x + 2, -y, -z + 2$) (a); view of the 1D coordination chain of complex I (b); a 3D packing diagram of complex I (c).

and one 2-pyridyl group ($\text{Ag}(1)\text{--N}(5A)$ 2.339(3) Å) from two L^{22} ligands, and one oxygen atom ($\text{Ag}(1)\text{--O}(1)$ 2.506(6) Å) from the monodentate NO_3^- . The half-occupied $\text{Ag}(2)$ center adopts approximately linear coordination geometry consisting of tri-

azole nitrogen atoms ($\text{Ag}(2)\text{--N}(3)/\text{N}(3B)$ 2.173(3) Å) from two L^{22} ligands. Each L^{22} ligand is coordinated to three $\text{Ag}(1)$ centers via the pyridyl and triazole groups adopting the (η^4, μ^3) coordination mode. Notably, the adjacent $\text{Ag}(1)$ centers are connected via the chelating

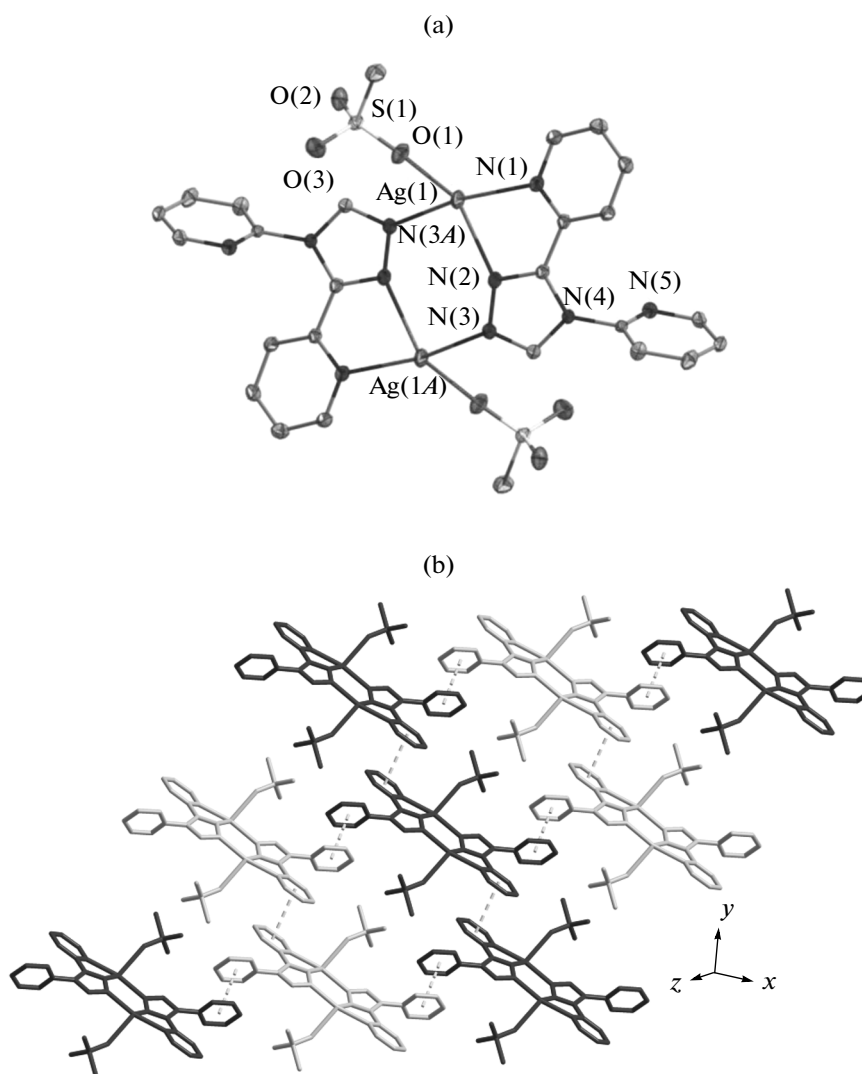


Fig. 2. The coordination environment of $[\text{Ag}(\text{CH}_3\text{SO}_3)(\text{L}_{22})]_2$. Displacement ellipsoids are drawn at the 30% probability level (symmetry codes: (A) $-x, -y + 1, -z + 1$) (a); the aromatic packing between the adjacent binuclear units of complex II (b).

pyridyl-triazole and 2-pyridyl groups from two L^{22} ligands to result in a binuclear unit with the $\text{Ag}(1)\cdots\text{Ag}(1)$ distance of $5.896(1)$ Å. Then the triazole groups of L^{22} further connect the $\text{Ag}(2)$ ions to result in a 1D double-chain along the *b* axis (Fig. 1b). Further analysis indicates that these 1D chains stack in a parallel fashion in the crystalline lattice without any significant interactions (Fig. 1c).

The replacement of AgNO_3 with $\text{Ag}(\text{CH}_3\text{SO}_3)$ in the reaction process affords a distinct binuclear coordination motif of complex II, the asymmetric coordination unit of which is composed of one Ag^+ ion, one L^{22} ligand, and one CH_3SO_3^- . As can be shown in Fig. 2a, the central Ag atom is tetrahedrally (ZnN_3O) coordinated to three nitrogen atoms from the chelating pyridyl-triazole ($\text{Ag}(1)-\text{N}(1)$ $2.284(2)$, $\text{Ag}(1)-\text{N}(2)$ $2.511(3)$ Å) and triazole ($\text{Ag}(1)-\text{N}(3A)$ $2.231(2)$ Å)

groups from two L^{22} ligands, and one oxygen atom ($\text{Ag}(1)-\text{O}(1)$ $2.552(2)$ Å) from the monodentate methanesulfonate anion. Each L^{22} ligand adopts the (η^3, μ^2) binding mode via the triazole and one 2-pyridyl groups to link two adjacent Ag^+ ions ($\text{Ag}\cdots\text{Ag}$ $4.358(1)$ Å) to constitute a centrosymmetric binuclear entity. These binuclear motifs are further extended by $\pi\cdots\pi$ stacking interactions between the parallel 2-pyridyl groups with the center-to-center distance of $3.562(1)$ Å, as well as the other pair of the parallel 2-pyridyl groups with the center-to-center distance of $3.665(2)$ Å, to result in a 2D network (Fig. 2b).

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