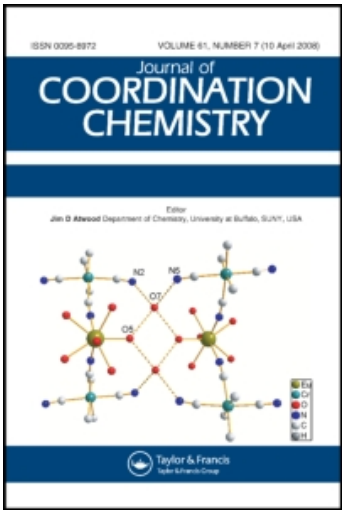

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A one-dimensional zigzag coordination polymer: {[Ag(2-amino-3-methylpyridine)](ClO_4)}$_\infty$

Zhen-Feng Chen[a]; Bing Liu[a]; Hong Liang[a]; Rui-Xiang Hu[a]; Zhong-Yuan Zhou[b]
[a] College of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin, Guangxi 541004, P.R. China [b] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, P.R. China

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A one-dimensional zigzag coordination polymer: $\{[Ag(2\text{-amino-3-methylpyridine})](ClO_4)\}_\infty$

ZHEN-FENG CHEN†, BING LIU†, HONG LIANG†*,
RUI-XIANG HU† and ZHONG-YUAN ZHOU‡

†College of Chemistry and Chemical Engineering, Guangxi Normal University,
Guilin, Guangxi 541004, P.R. China
‡Department of Applied Biology and Chemical Technology,
Hong Kong Polytechnic University, Hung Hom,
Kowloon, Hong Kong, P.R. China

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The reaction of silver perchlorate with 2-amino-3-methylpyridine gives a one-dimensional zigzag coordination polymer $\{[Ag(2\text{-amino-3-methylpyridine})](ClO_4)\}_\infty$ (**1**) consisting of single chains. The geometry of all Ag(I) cations is linear: each ion links together two 2-pyridyl (Ag1) rings and two 2-amino (Ag2) groups, with the ligand exhibiting a 'head-to-head' orientation. Crystal data: monoclinic $P2(1)/c$, $a = 5.2296(8)$, $b = 20.668(3)$, $c = 8.8716(14)$ Å, $\beta = 100.359(3)^\circ$, $V = 943.3(3)$ Å^3, $Z = 2$, $D_c = 2.214$ Mg/m^3, $\mu = 2.409$ mm^{-1}, $F(000) = 612$, $R1 = 0.0426$, $wR1 = 0.0980$ [$I > 2\sigma(I)$], $S = 0.969$.

Keywords: Silver(I); Coordination polymer; Crystal structure

1. Introduction

Metal coordination polymers derived from polydentate nitrogen ligands are an area of increasing interest because of their intriguing structural diversity and possible applications as electrical conductors, molecular magnets and antibacterial agents [1]. Coordination polymers based on Ag(I) cations, in particular, are attracting attention [2]. Because of the high lability of the Ag-donor atom bond [3] the process of coordination polymer formation is reversible; the resulting Ag(I) coordination polymers can generally be crystallized, allowing investigation by single-crystal X-ray diffraction. The coordination sphere of Ag(I) is very flexible and can adopt linear, trigonal, tetrahedral, trigonal pyramidal and octahedral geometries [4]. The design and structure of coordination polymers derived from Ag(I) with N-donor ligands and their role in the investigation of weak noncovalent interactions in the solid state has been reviewed by Khlobystov *et al.* [5]. The use of amino-pyridine as a bridging ligand coordinating

*Corresponding author. Email: chenzfgxnu@yahoo.com

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to Ag(I) to construct supramolecular species has yet not been reported. We report here the synthesis and X-ray structure of a one-dimensional zigzag coordination polymer, $\{[Ag(2\text{-amino-3-methylpyridine})](ClO_4)\}_\infty$ (**1**).

2. Experimental

2.1. *Materials and instrumentation*

2-Amino-3-methylpyridine was purchased from Acros and used without further purification. $AgClO_4$ was synthesized using AgOH and $HClO_4$. All solvents were of analytical grade. **CAUTION:** Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

IR spectra were recorded in the range 4000–500 cm^{-1} on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400/II automatic analyzer.

2.2. *Synthesis of $\{[Ag(2\text{-amino-3-methylpyridine})](ClO_4)\}_\infty$*

Solutions of $AgClO_4$ (1 mmol, 0.207 g) in water (10 mL) and 2-amino-3-methylpyridine (1 mmol, 0.108 g) in ethanol (20 mL) were mixed together. Avoiding light, the mixture was stirred for 2 h at room temperature and the filtrate was allowed to stand for 6 days at ambient temperature; colorless plate crystals of **1** were obtained. Yield: 52% based on silver. Anal. Calcd. for $C_{12}H_{14}Ag_2Cl_2N_4O_8$(%): C, 22.92; H, 2.24; N, 8.90. Found: C, 22.89; H, 2.30; N, 9.02. Main IR (KBr, cm^{-1}) data: 3419(m) ν(N–H), 1600(s), 1572(m), 1099(s) ν(Cl–O), 637(m), 613(w), 408(w).

2.3. *X-ray crystallography*

Crystallographic data for **1** were collected with a Bruker CCD area detector diffractometer equipped with graphite-monochromatized Mo Kα X-ray radiation ($\lambda = 0.71073$ Å, 50 kV, 150 mA) using the ω–θ scan mode in the range $2.58 \le \theta \le 27.54$ at 293 K. Raw frame data were integrated with the SAINT [6] program. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97 [7]. An empirical absorption correction was applied with the program SADABS [8]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. All calculations and graphics were performed with SHELXTL [7].

Crystallographic data for compound **1**: Crystal dimensions $0.30 \times 0.20 \times 0.18$ mm, $C_{12}H_{14}Ag_2Cl_2N_4O_8$, $M_r = 628.91$, monoclinic, $P2_1/c$, $a = 5.2296(8)$, $b = 20.668(3)$, $c = 8.8716(14)$ Å, $\beta = 100.359(3)^\circ$, $V = 943.3(3)$ Å^3, $Z = 2$, $D_c = 2.214$ Mg m^{-3}, $\mu = 2.409$ mm^{-1}, $R1 = 0.043$, $wR2 = 0.098$ [$I \ge 2\sigma(I)$], goodness-of-fit 0.969. A total of 6342 reflections are collected with 2172 independent reflections ($R_{int} = 0.0484$). The largest peak and hole on the final difference-Fourier map are 0.598 and -0.664 e Å^{-3}, respectively. CCDC deposition number: 218143.

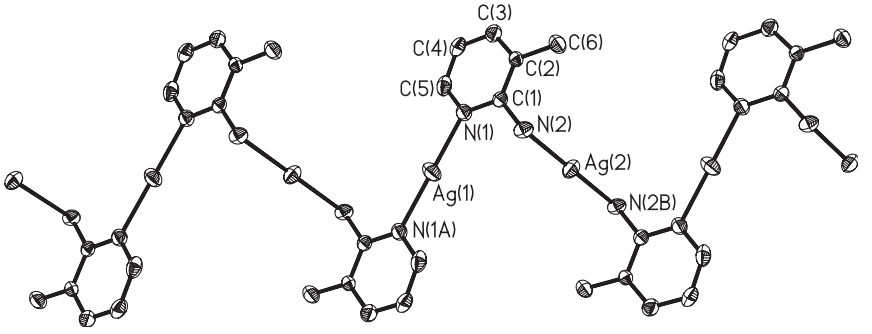

Figure 1. Fragment of the zigzag one-dimensional chain of $\{[Ag(2\text{-amino-3-methylpyridine})](ClO_4)\}_\infty$. Perchlorate anions are omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)–N(1A) 2.186(4), Ag(1)–N(1) 2.186(4), Ag(2)–N(2) 2.288(3), Ag(2)–N(2B) 2.288(3); N(1A)–Ag(1)–N(1) 180.000(1), N(2)–Ag(2)–N(2B) 180.00(19).

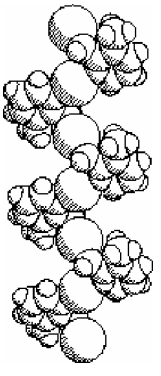

Figure 2. Space-filling drawing of complex **1**. The perchlorate anions are omitted for clarity.

3. Results and discussion

An ORTEP drawing, a space-filling drawing and a packing view of compound **1** are shown in figures 1, 2 and 3, respectively. The important bond distances and angles are shown in figure 1.

X-ray crystal structure analysis reveals that compound **1** is a one-dimensional zigzag coordination polymer consisting of repeating $[Ag_2(2\text{-amino-3-methylpyridine})_2](ClO_4)_2$ units (figure 1). As shown in figure 1, similar to $\{Ag(2,4'\text{-pyph})(PF_6)MeCN\}_\infty$ [5], the geometry of all Ag(I) cations is linear and the ligands exhibit a 'head-to-head' orientation. There are two types of silver(I) ions in complex **1**. Ag(1) is strongly coordinated by two nitrogen atoms, N(1) and N(1A), of pyridine rings from two different ligands. Ag(2) is strongly coordinated by two nitrogen atoms, N(2) and N(2B), of amino groups from two different ligands. The perchlorate remains uncoordinated. The bond distances Ag(1)–N(1) and Ag(1)–N(1A) are 2.186(4) Å and shorter than those of silver(I)–nitrogen bonds from pyridine- or pyrazine-based systems such as $[Ag(pesp)]_n^{n-}$ and $[Ag(PIP)]_n^{n+4(e)}$. The N(1)–Ag(1)–N(1A) bond angle is 180.000(1)°, indicating the linear geometry of Ag(1). However, the bond distances of Ag(2)–N(2) and Ag(2)–N(2A) are 2.288(3) Å, very close to that of $[Ag_2(L)](ClO_4)_2$ [L = 2,3-bis

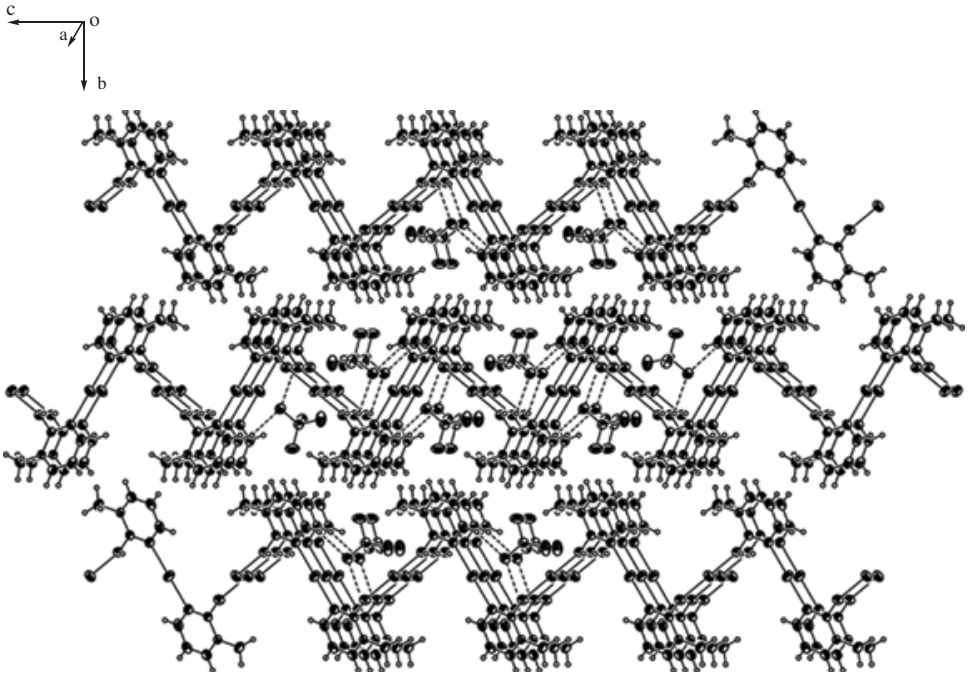

Figure 3. Packing view of complex **1** from the *boc* plane.

(6′-methyl-2′-pyridylmethylsulfanylmethyl)pyrazine] [9]. The N(2)–Ag(2)–N(2A) bond angle is 180.00(19)°, indicating the ideal linear coordination geometry of Ag(2) in **1**. Obviously, no metal–metal interaction occurs as a result of the long distances between the neighboring silver(I) ions [4.436 Å for Ag(1)···Ag(2)]. In addition, because of the strong hydrogen-bonding interaction between amino groups of the ligand and counter-ion $ClO\overline{4}$ [e.g. N(2)–H(2A)···O(4) 2.922(5) Å], a two-dimensional network is constructed (figure 3).

In conclusion, we have demonstrated the formation of a one-dimensional zigzag coordination polymer derived from 2-amino-3-methylpyridine and silver(I) ion.

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