Helical Silver(I)−2,4′-Bipyridine Chains Organized into 2-D Networks by Metal−Counterion or Metal−Metal Bonding. Structures of [Ag(2,4′-bipyridine)]X (X^- = NO_3^- or ClO_4^-)

Ming-Liang Tong, Xiao-Ming Chen,* and Bao-Hui Ye

Department of Chemistry, Zhongshan University, Guangzhou 510275, China

Seik Weng Ng

Institute of Postgraduate Studies and Research, University of Malaya, Kuala Lumpur 50603, Malaysia

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Two compounds, [Ag(2,4′-bpy)]NO_3 (**1**) and [Ag(2,4′-bpy)]ClO_4 (**2**), were obtained from self-assembly of AgX (X = NO_3^-, ClO_4^-) with 2,4′-bipyridine (2,4′-bpy). **1** crystallizes in the orthorhombic space group *Pbca*, with $a = 11.2884(7)$ Å, $b = 11.3981(10)$ Å, $c = 16.5299(13)$ Å, and $Z = 8$, while **2** crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.6361(4)$ Å, $b = 9.9896(4)$ Å, $c = 11.2661(6)$ Å, $\beta = 98.527(4)°$, and $Z = 4$. Both complexes consist of helical $[Ag(2,4'\text{-bpy})]_\infty$ chains that are surrounded by nitrate or perchlorate counterions. Adjacent helical chains are racemic. The Ag^I atom is linked to two nitrogen atoms of the 2-pyridyl and 4′-pyridyl groups from two different 2,4′-bpy ligands as well as to the oxygen atom of the counterion. In **1**, another oxygen atom of the counterion is weakly coordinated to the Ag^I atom of an adjacent chain, thus bridging the helical chains into a wavy 2-D network structure, whereas in **2**, adjacent helical chains are linked by the weak ligand-unsupported metal−metal interactions, resulting in an open 2-D network with compressed hexagons as building units. The structures of **1** and **2** imply the role that counterions may play in the framework construction.

Introduction

The crystal engineering of metal−organic coordination polymers is of considerable interest in the development of synthetic routes to novel 2-D and 3-D inorganic frameworks, and studies on such supramolecular assemblies organized by coordinate-covalent bonding,[1] hydrogen bonding,[2] or other intermolecular interactions[3] have yielded a plethora of potentially functional materials having cavities of diverse sizes and shapes.[4−10] Supramolecular compounds have been constructed largely with the use of symmetrically bridging ligands, although some asymmetric ligands, such as 2,3-substituted pyrazine and hexamethylenetetraamine, have also been used.[11,12] The adoption of an asymmetrically bridging ligand is one of several strategies that could be employed in the synthesis of frameworks having asymmetric cavities or channels for possible application in separation and catalysis. Supramolecular architectures, especially those displaying helical motifs, have particular relevance to biological systems and asymmetric catalysis.[13,14] In this report, we describe two helical silver(I)−2,4′-bipyridine chains, [Ag(2,4′-bpy)]NO_3 (**1**) and [Ag(2,4′-bpy)]ClO_4 (**2**)

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* To whom correspondence should be addressed. E-mail: cedc03@zsu.edu.cn. Fax: +86 20 8418-7564.

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(bpy = bipyridine), which are linked into 2-D networks by weak coordination bonds and weak metal−metal bonds in **1** and **2**, respectively.

Experimental Section

All reagents were commercially available and used as received. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 NMR spectrometer using $(CD_3)_2SO$ as solvent at room temperature; the $(CD_3)_2SO$ signal was used to lock the field, and all chemical shifts are given relative to TMS; ^{1}H NMR spectra were measured at 300.132 MHz and ^{13}C NMR spectra were obtained at 75.475 MHz using $(CD_3)_2SO$ as an internal standard with wide-band proton decoupling. The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Nicolet 5DX spectrometer.

Safety Notes. ***CAUTION!*** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.*

Synthesis. [Ag(2,4′-bpy)]NO$_3$ (1). A methanolic solution (10 cm^3) of 2,4′-bpy (0.078 g, 0.5 mmol) was added dropwise to a stirred methanolic solution (5 cm^3) of $AgNO_3$ (0.085 g, 0.5 mmol) at 50 °C to give a clear mixture. After several days the solution gave polyhedral crystals in 65% yield. ^{1}H NMR (ppm): 8.74−8.77, 8.20, 8.16, 8.02, 7.54. ^{13}C NMR (ppm): 152.82, 151.07, 150.05, 146.52, 137.71, 124.61, 121.33. Anal. Calcd for $C_{10}H_8AgN_3O_3$: C, 36.83; H, 2.47; N, 12.89. Found: C, 36.68; H, 2.34; N, 12.75. IR: 3460 m, 3068 w, 1602 s, 1581 s, 1546 w, 196 w, 1461 s, 1384 vs, 1278 m, 1215 m, 1159 m, 1110 vs, 1096 w, 1060 m, 990 m, 840 m, 772 vs, 730 s, 639 m, 610 m, 561 w, 442 w cm^{-1}.

[Ag(2,4′-bpy)]ClO$_4$ (2). The analogous reaction of $AgClO_4$ with 2,4′-bpy produced colorless block crystals of **2** in ca. 54% yield. ^{1}H NMR (ppm): 8.76−8.78, 8.23, 8.18, 8.03, 7.56. ^{13}C NMR (ppm): 152.72, 151.33, 150.15, 146.89, 124.76, 121.54. Anal. Calcd for $C_{10}H_8AgClN_2O_4$ (**2**): C, 33.16; H, 2.23; N, 7.74. Found: C, 32.96; H, 2.13; N, 7.64. FT-IR: 3458 m, 3071 w, 1602 s, 1553 w, 1468 m, 1412 m, 1328 w, 1291 w, 1222 w, 1145 vs, 1110 vs, 1089 vs, 842 w, 772 s, 730 w, 674 w, 625 s, 567 w, 512 w cm^{-1}.

X-ray Crystallography. Diffraction intensities for complexes **1** and **2** were collected at 20 °C on an Enraf-Nonius CAD4 diffractometer using the ω-scan technique. Lp and absorption corrections were applied.[15] The structures were solved with the direct methods of SHELXS-86[16] and refined with full-matrix least-squares techniques using the SHELXL-93 program.[17] Non-hydrogen atoms were refined anisotropically. The alkyl hydrogen atoms were generated geometrically (C−H = 0.96 Å), while the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[18] The crystallographic data for both complexes are listed in Table 1. The selected interatomic distances and angles are given in Table 2. Drawings were produced with ORTEP-3[19] and SHELXTL-PC.[20]

Results and Discussion

Compounds **1** and **2** were synthesized by self-assembly of AgX (X = NO_3^-, ClO_4^-) salts with 2,4′-bpy ligands. The elemental C, H, and N analysis and NMR spectra confirmed the chemical formulation for both complexes. They are air- and light-stable.

Table 1. Crystallographic and Experimental Data for **1** and **2**

	1	**2**
formula	$C_{10}H_8AgN_3O_3$	$C_{10}H_8AgClN_2O_4$
fw	326.06	363.50
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a (Å)	11.2884(7)	10.6361(4)
b (Å)	11.3981(10)	9.9896(4)
c (Å)	16.5299(13)	11.2661(6)
β (deg)		98.527(4)
V (Å^3)	2126.8(3)	1183.80(9)
Z	8	4
ρ_{calc} (g cm^{-3})	2.037	2.040
T (°C)	25(2)	20(2)
λ(Mo Kα) (Å)	0.710 73	0.710 73
μ(Mo Kα) (cm^{-1})	1.894	1.935
R1($I > 2\sigma(I)$)[a]	0.0327	0.0414
wR2(all data)[a]	0.0625	0.1145

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (0.1(\max(0,F_o^2) + 2F_c^2)/3)^2$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	[Ag(2,4′-bpy)]NO$_3$ (**1**)		
Ag(1)−N(2a)[a]	2.192(2)	Ag(1)−O(2)	2.801(3)
Ag(1)−N(1)	2.199(2)	Ag(1)−O(2b)	2.903(2)
Ag(1)−O(1)	2.660(2)		
N(2a)−Ag(1)−N(1)	169.03(8)	C(1)−N(1)−Ag(1)	114.9(2)
N(2a)−Ag(1)−O(1)	92.49(8)	C(5)−N(1)−Ag(1)	126.9(2)
N(1)−Ag(1)−O(1)	96.81(7)	C(10)−N(2)−Ag(1c)	121.9(2)
N(2a)−Ag(1)−O(2)	95.99(8)	C(6)−N(2)−Ag(1c)	121.0(2)
N(1)−Ag(1)−O(2)	94.66(8)	O(2b)−Ag(1)−Ag(1b)	44.61(5)
O(1)−Ag(1)−O(2)	45.99(6)	N(2a)−Ag(1)−Ag(1c)	80.95(6)
N(2a)−Ag(1)−O(2b)	78.56(8)	N(1)−Ag(1)−Ag(1c)	88.13(5)
N(1)−Ag(1)−O(2b)	98.58(7)	O(1)−Ag(1)−Ag(1c)	142.38(4)
O(1)−Ag(1)−O(2b)	135.62(6)	O(2)−Ag(1)−Ag(1c)	170.82(5)
O(2)−Ag(1)−O(2b)	91.33(7)	O(2b)−Ag(1)−Ag(1c)	79.59(5)
N(2a)−Ag(1)−Ag(1b)	85.92(6)	Ag(1b)−Ag(1)−Ag(1c)	124.190(10)
N(1)−Ag(1)−Ag(1b)	99.54(6)	N(3)−O(1)−Ag(1)	98.7(2)
O(1)−Ag(1)−Ag(1b)	91.85(4)	N(3)−O(2)−Ag(1)	92.0(2)
O(2)−Ag(1)−Ag(1b)	46.72(5)		
	[Ag(2,4′-bpy)]ClO$_4$ (**2**)		
Ag(1)−N(1a)	2.165(2)	Ag(1)−Ag(1b)	3.1526(6)
Ag(1)−N(2)	2.184(2)	Ag(1)−O(1)	2.692(2)
N(1a)−Ag(1)−N(2)	169.63(9)	C(1)−N(1)−Ag(1c)	122.9(2)
N(1a)−Ag(1)−Ag(1b)	72.88(7)	C(5)−N(1)−Ag(1c)	118.1(2)
N(2)−Ag(1)−Ag(1b)	113.84(7)	C(10)−N(2)−Ag(1)	117.5(2)
C(6)−N(2)−Ag(1)	124.5(2)		

[a] Symmetry codes: (a) $x - {}^1/_2, -y + {}^1/_2, -z$; (b) $-x, -y, -z$; (c) $x + {}^1/_2, -y + {}^1/_2, -z$ for **1**; (a) $-x + 1, y + {}^1/_2, -z + {}^1/_2$; (b) $-x + 1, -y + 1, -z + 1$; (c) $-x + 1, y - {}^1/_2, -z + {}^1/_2$ for **2**.

The crystal structure of **1** consists of helical $[Ag(2,4'\text{-bpy})]_\infty$ chains that are interlocked by nitrate counterions, with pairs of racemic chains running parallel to the *a*-axis. As illustrated in Figure 1, the Ag^I atom is linked to two nitrogen atoms of the 2-pyridyl and 4′-pyridyl groups from two different 2,4′-bpy ligands (Ag−N = 2.192(2), 2.199(2) Å) as well as to the oxygen atom of the counterion [Ag−O = 2.660(2) Å]. The Ag^I atom, as has been observed in a number of polymeric silver(I) complexes,[8b,21] shows distorted T-shaped coordination (N−Ag−N = 169.03(8)°, N−Ag−O = 95.50(8)°, 96.80(8)°; $\sum_{Ag}$ = 361.3(2)°); the distortion is believed to be caused by the proximity of another nitrate oxygen atom (Ag···O = 2.801(3) Å). This nitrate oxygen atom is also linked to a Ag^I atom from an adjacent chain (Ag···O = 2.903(3) Å), the weaker link furnishing a wavy 2-D network structure[22] for **1**. In other words,

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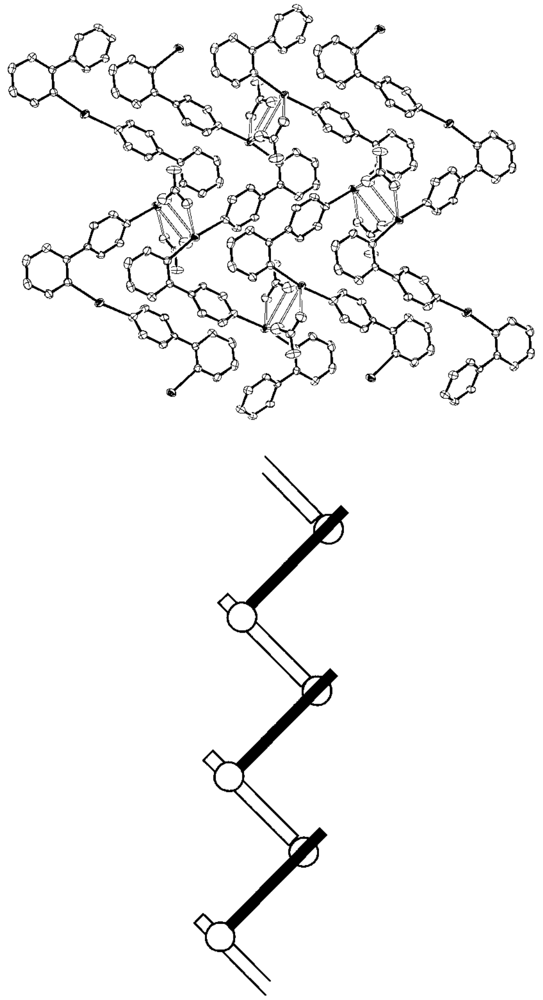

Figure 1. (a) Top view of the 2-D network consisting of helical chains linked through the NO_3^- ions in **1**. (b) Schematic view of the singly helical conformation of **1**.

the nitrate groups behave as linkages to bring the helical [Ag-(2,4′-bpy)]$_\infty$ chains together and result in the 2-D network structure.

In the crystal structure of **2**, each Ag^I atom is also ligated by two nitrogen atoms of the 2-pyridyl and 4′-pyridyl groups belonging to two different 2,4′-bpy ligands; the [Ag(2,4′-bpy)]$_\infty$ chains are surrounded by the ClO_4^- counterions, which bind through only one oxygen end (Ag−N = 2.165(2), 2.184(2) Å, Ag−O = 2.692(2) Å; N−Ag−N = 169.63(9)°). A 2-D network with compressed hexagons as building units (Figure 2) results from the weak ligand-unsupported metal−metal interactions (Ag···Ag = 3.1526(6) Å), a feature documented in several polynuclear silver(I) complexes.[8,23] The pyridyl rings of the 2,4′-bpy ligand are twisted by 45.51(8)°, a magnitude that minimizes steric effects in favor of the Ag−N interactions. Adjacent helical chains are racemic, and the 2-D network is open, as illustrated in Figure 3. On the other hand, the reported helical-chain complexes generally consist of double or triple helices,[1] and only two other examples of single-helical chains been documented.[24] The construction of a non-interpenetrating 2-D network in which helical chains are linked by metal−metal interactions is unprecedented, and **2** represents the first structural example of a non-interpenetrating network having asymmetric cavities.

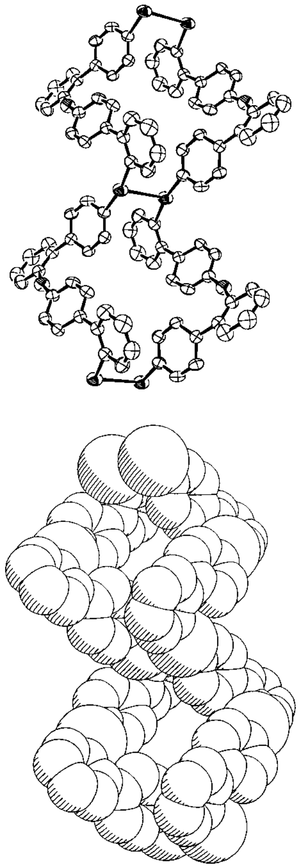

Figure 2. Pair of helical chains in **2**: (a) *ORTEP* representation; (b) space-filling representation.

It is noteworthy that the structures of **1** and **2** imply the role that counterions may play in the framework construction. Indeed, in the related silver(I) coordination polymers,[25] diverse conformations can be achieved by subtle changes in the nature of the counterions. In our cases, perchloric acid is a stronger acid than nitric acid, so that the perchlorate ion is not expected to use more than one oxygen end to bind to the metal atom. The Ag^I−ClO_4^- bond is a relatively weak bond, but its weak nature probably contributes to the strength of the Ag···Ag interaction, which presumably stabilizes the crystal structure of **2**.

Conclusions

Two two-dimensional coordination polymers have been prepared and characterized. Both complexes consist of helical [Ag(2,4′-bpy)]$_\infty$ chains which are surrounded by nitrate and perchlorate counterions, respectively. Adjacent helical chains are racemic. The Ag^I atom is linked to two nitrogen atoms of the 2-pyridyl and 4′-pyridyl groups from two different 2,4′-bpy ligands as well as to the oxygen atom of the counterion. In **1**, adjacent chains are linked into a wavy 2-D network by the weaker linkages between the silver(I) atoms and nitrate anions, whereas in **2**, adjacent helical chains are linked into a 2-D open network with compressed hexagons as building units by metal−

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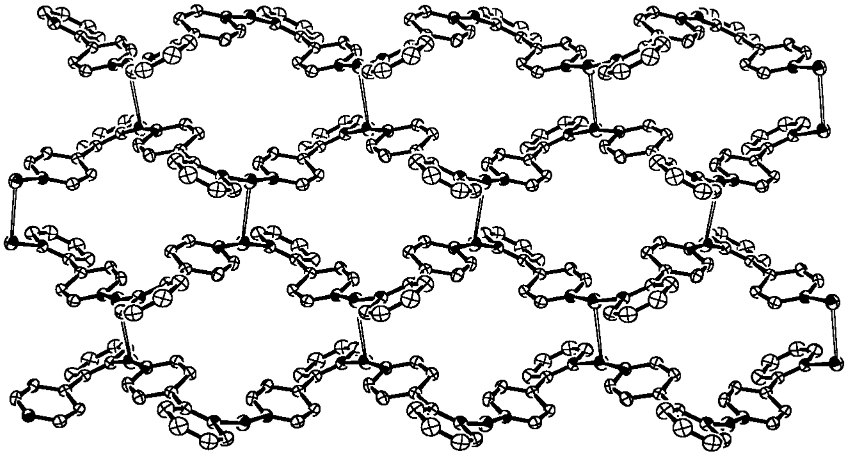

Figure 3. Top view of the 2-D network consisting of helical chains linked by Ag−Ag bonds in **2**.

metal interactions. The results described here can be related and suggest a potential route to extending the 1-D infinite chains to 2-D frameworks with asymmetric cavities in the self-assembly strategies. This work also provides nice examples for the role that counterions may play in the framework construction.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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