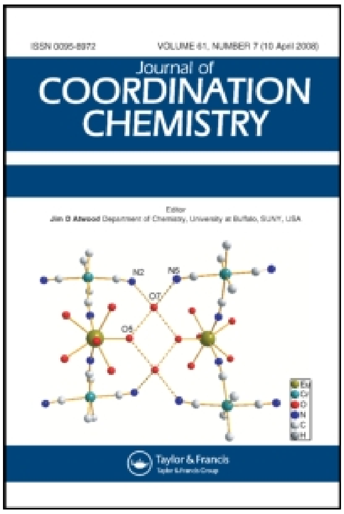

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Synthesis, structure, and characterization of a silver(I) coordination polymer with μ_6-bridging 2,2'-bipyridyl-3,3'-dicarboxylate

Xiao-Li Chen[ab]; Yue-Juan Yao[a]; Huai-Ming Hu[a]; Shuan-Hu Chen[a]; Feng Fu[b]
[a] Department of Chemistry, Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education/Shaanxi Key Laboratory of Physical-Inorganic Chemistry, Northwest University, Xi'an, 710069, China [b] Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yanan University, Yan'an, 716000, China

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Synthesis, structure, and characterization of a silver(I) coordination polymer with μ_6-bridging 2,2′-bipyridyl-3,3′-dicarboxylate

XIAO-LI CHEN†‡, YUE-JUAN YAO†, HUAI-MING HU*†,
SHUAN-HU CHEN† and FENG FU‡

†Department of Chemistry, Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education/Shaanxi Key Laboratory of Physical-Inorganic Chemistry, Northwest University, Xi'an, 710069, China
‡Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yanan University, Yan'an, 716000, China

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A silver(I) coordination polymer, $[Ag_2(bpdc)]_n$ (**1**) ($H_2bpdc = 2,2'$-bipyridyl-3,3′-dicarboxylic acid), has been synthesized and characterized. Compound **1** exhibits a 2-D network containing 1-D channels. Each $(bpdc)^{2-}$ is an octadentate μ_6-1igand coordinating with six Ag(I)'s in **1**. This coordination of $(bpdc)^{2-}$ ligand is first observed here. Neighboring networks are arranged in a [ABAB···] pattern to form 3-D supramolecular architecture by $\pi\cdots\pi$ stacking. Compound **1** shows intense photoluminescence at room temperature.

Keywords: 2,2′-Bipyridyl-3,3′-dicarboxylic acid; Silver; Coordination polymer; Crystal structure

1. Introduction

In construction of metal-organic frameworks (MOFs), Ag(I) is often used due to its high affinity to N and O donors, its flexible coordination number and geometry, and Ag···Ag weak interaction. Many Ag(I) complexes with different frameworks and topologies have been synthesized [1–10]. To construct metal-organic complexes, careful selection of a multifunction organic ligand is important with multidentate N or O donors employed as organic spacers in the construction of extended structures [11–17]. These building blocks contain multi-oxygens and nitrogens to coordinate with metal ions in different ways, resulting in the formations of various MOFs with specific topologies and properties [18–20]. We introduce a multidentate N and O donor ligand, 2,2′-bipyridyl-3,3′-dicarboxylic acid (H_2bpdc) for construction of MOFs.

H_2bpdc is a multifunctional bridging ligand containing one 2,2′-bipyridyl unit and two carboxyl groups, functioning as bis(monodentate) [21], tridentate [22–24], *bis*(bidentate) [23, 25, 26], pentadentate [27], and even hexadentate [28] bridging

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*Corresponding author. Email: chemhu1@nwu.edu.cn

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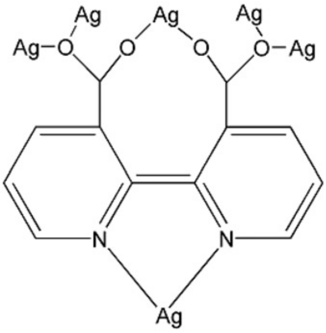

Scheme 1. The coordination of $(bpdc)^{2-}$ in **1**.

connecters in ligand-directed synthesis, owing to the strong chelating bipyridyl and adjacent carboxyl groups. The two pyridyl rings of $(bpdc)^{2-}$ are not coplanar in coordination, owing to the steric hindrance of 2,2′-positioned carboxylate groups [29–33]. The distortion of bipyridyl about the central C–C bond endows $(bpdc)^{2-}$ ability to link metal ions into chains [29–33].

Our aim is to synthesize high-dimensional coordination polymers through combining $(bpdc)^{2-}$ and silver(I) and studying the influence on the framework structure of their compounds. A metal coordination polymer was synthesized, $[Ag_2(bpdc)]_n$, as a 2-D network containing 1-D channels. Each $(bpdc)^{2-}$ is μ_6-1igand as an octadentate ligand (scheme 1) to coordinate six silver(I)'s in **1**. We report the synthesis, characterization, crystal structure, and photoluminescence of $[Ag_2(bpdc)]_n$ (**1**).

2. Experimental

2.1. *Reagents and physical measurements*

H_2bpdc was prepared according to the literature method [34]. Other chemicals and reagents were used as received from commercial sources. Elemental analyses (C, H, and N) were determined with a Elementar Vario EL elemental analyzer; IR spectra were recorded as KBr pellets on a Bruker EQUINOX55 spectrophotometer from 4000 to $400\,cm^{-1}$. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Syntheses of complex (1)*

A solution of $AgNO_3$ (0.0338 g, 0.2 mmol) in MeOH (10 mL) was slowly added to a stirring solution of H_2bpdc (0.0488 g, 0.2 mmol) in H_2O (10 mL), and then $0.5\,mol\,L^{-1}$ NaOH aqueous solution was added dropwise to the reaction mixture to give a transparent solution. The solution was allowed to stand at room temperature for one month giving colorless quadrate-like crystals. Yield: 83.8% (based on H_2bpdc). Anal. Calcd for $C_{12}H_6Ag_2N_2O_4$: C, 31.47; H, 1.32; N, 6.12%. Found: C, 31.41; H, 1.38; N, 6.15%. FT-IR ($KBr\,cm^{-1}$): 1597(s), 1378(s), 1062(m), 843(m), 768(w), 691(m), 595(w).

2.3. *X-ray crystallography*

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied using SADABS. The structures were solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 [35]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1** are summarized in table 1. Selected bond distances and angles are listed in table 2.

Table 1. Crystal data and structure refinement parameters for **1**.

Compound	**1**
Empirical formula	$C_{12}H_6Ag_2N_2O_4$
Formula weight	457.93
Crystal system	Monoclinic
Space group	*C2/c*
Units of cell dimensions (Å, °)	
a	13.649(10)
b	12.022(9)
c	6.813(5)
α	90
β	91.539(9)
γ	90
V (Å^3)	1117.6(14)
Z	4
D Anal. Calcd (Mg^{-1} m^{-3})	2.722
μ (mm$^{-1)}$	3.519
F (000)	872
λ (Mo-Kα)/Å	0.71073
Reflections collected	2698
Unique reflections	998
Parameters	93
S on F^2	1.074
R_1, wR_2 [$I > 2\sigma(I)$]	0.0207, 0.0494
R_1, wR_2 (all data)	0.0238, 0.0516
$\Delta\rho$ max and min (e Å^{-3})	0.551 and −0.633

$R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ for $F_o \geq 4\sigma(F_o)$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Ag(1)–O(1)#2	2.386(2)	Ag(2)–O(1)	2.365(2)
Ag(1)–O(1)#3	2.386(2)	Ag(2)–O(1)#4	2.365(2)
Ag(1)–O(2)	2.373(2)	Ag(2)–N(1)#5	2.372(3)
Ag(1)–O(2)#1	2.373(2)	Ag(2)–N(1)#6	2.372(3)
O(2)#1–Ag(1)–O(2)	86.13(11)	O(1)–Ag(2)–O(1)#4	73.49(11)
O(2)#1–Ag(1)–O(1)#2	119.39(9)	O(1)–Ag(2)–N(1)#5	148.47(8)
O(2)–Ag(1)–O(1)#2	133.31(8)	O(1)#4–Ag(2)–N(1)#5	116.19(9)
O(2)#1–Ag(1)–O(1)#3	133.31(8)	O(1)–Ag(2)–N(1)#6	116.19(9)
O(2)–Ag(1)–O(1)#3	119.39(9)	O(1)#4–Ag(2)–N(1)#6	148.47(8)

Symmetry transformations used to generate equivalent atoms: #1: $-x, y, -z+1/2$; #2: $x, -y+2, z+1/2$; #3: $-x, -y+2, -z$; #4: $-x, y, -z-1/2$; #5: $-x, -y+1, -z$; #6: $x, -y+1, z-1/2$.

3. Results and discussion

3.1. *Structural description of [Ag$_2$(bpdc)]$_n$ (1)*

Compound **1** is a 2-D network containing 1-D channels, stable in air and insoluble in common organic solvents. As shown in figure 1, the asymmetric unit consists of two crystallographically independent Ag(I) atoms. Ag1 is tetrahedral *via* binding with two oxygens (O1A and O1B) from two different carboxylates of two different (bpdc)$^{2-}$ ligands and the other two oxygens (O2 and O2C) from two different carboxylates of the same (bpdc)$^{2-}$. The Ag1–O bond lengths are 2.373(2) and 2.386(2) Å, similar to those observed previously [36]. Ag2C is chelated by two pyridyl nitrogens (N1 and N1C) from a (bpdc)$^{2-}$ ligand and two oxygens (O1E and O1F) from two carboxylates of two (bpdc)$^{2-}$ ligands. The Ag2–N and Ag2–O bond lengths are 2.372(3) and 2.365(2) Å, respectively. The O–Ag2–O bond angle is 73.49(1)°, N–Ag2–N is 72.34(1)° and N–Ag2–O are in range 116.19(9)–148.47(8)°.

The most striking feature of **1** is that each (bpdc)$^{2-}$ ligand is simultaneously bound to three Ag1 (Ag1, Ag1A, and Ag1B) and three Ag2 (Ag2, Ag2B, and Ag2C) atoms as a μ_6-bridging connecter. It is different from reported examples based on (bpdc)$^{2-}$ ligand and Ag(I) [25, 28], in which it is a μ_3-ligand in a hexadentate fashion (N, N′; O, O′; and O, O′) coordinating with three Ag(I) centers through three chelate bonds. In **1**, each carboxylate binds with three Ag(I)'s tridentately, while the bipyridyl chelates Ag(I) with bidentate coordination; the six-connecting octadentate coordination pattern in **1** is unique. Also in **1**, each carboxylate of (bpdc)$^{2-}$ exhibits a μ_3–η^1–η^2 bridging mode, very rare in complexes of (bpdc)$^{2-}$.

The pyridyl rings of (bpdc)$^{2-}$ are twisted with an angle of 42.96°, indicating they are not coplanar, perhaps reducing mutual repulsion between carboxylate groups. The carboxylate is dramatically out of the plane of pyridyl ring with dihedral angle of 42.55°. A slight twisting is observed between carboxylate groups in (bpdc)$^{2-}$ with dihedral angle of 11.78°. The combination of these twists and bonds of (bpdc)$^{2-}$ ligands make Ag(I) centers into a 2-D network (figure 2) with all sliver(I)'s in the same plane. The Ag1···Ag2 distance is 3.817 Å; Ag1···Ag1 and Ag2···Ag2 distances are 4.709 Å and 3.591 Å, respectively, significantly longer than the van der Waals distance of 3.40 Å, illustrating lack of direct Ag···Ag interaction.

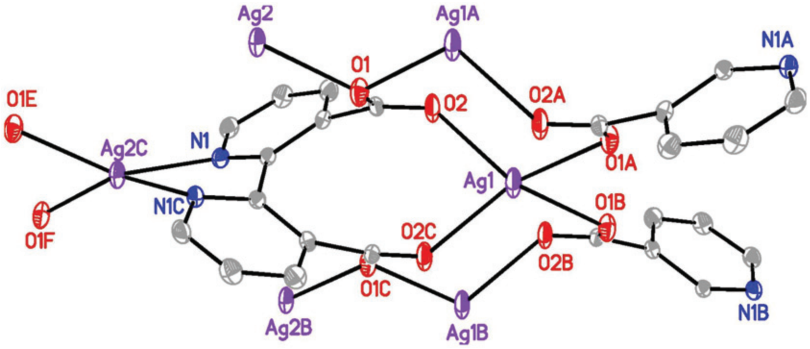

Figure 1. ORTEP drawing of [Ag$_2$(bpdc)]$_n$, drawn with displacement ellipsoids at the 30% probability; hydrogen atoms have been omitted for clarity.

Compound **1** possesses a 2-D framework with four grids, parallelogram, quadrangle, rhombus, and hexagon (figure 3). Two triangular $(\text{bpdc})^{2-}$ ligands coordinate to two Ag1's to form a distorted hexagon, producing a grid pore of 5.505 × 3.591 Å based on the Ag1···Ag1 and O1···O1. Two oxygens of carboxylate bridge Ag1 and Ag2 to form a regular rhombus and further connecting to Ag(I) nodes of adjacent hexagons with 2,2′-bipyridyl, resulting in an extended sheet in the *bc*-plane.

Neighboring 2-D layers are arranged in a [ABAB···] pattern to form a 3-D framework through $\pi\cdots\pi$ stacking in an offset edge-to-edge fashion with a distance of 3.389 Å between pyridyl rings of the neighboring 2-D layers, creating 1-D channels with a diameter of about 11 Å propagating infinitely along the *b*-axis (figure 4). Obviously, the $\pi\cdots\pi$ stacking interaction plays an important role in stabilization of the lattice.

Ligand conformation is a key factor in the coordination structures; $(\text{bpdc})^{2-}$ possesses oxygen and nitrogen donors on opposite sides, enabling the ligand to bridge. The conformation of free bipyridyl is controlled by repulsion between lone electron pairs of nitrogens. Thus, *trans*-conformation is energetically preferred, but the carboxyl groups in 3,3′-positions has an additional influence on the angle of the pyridyl planes

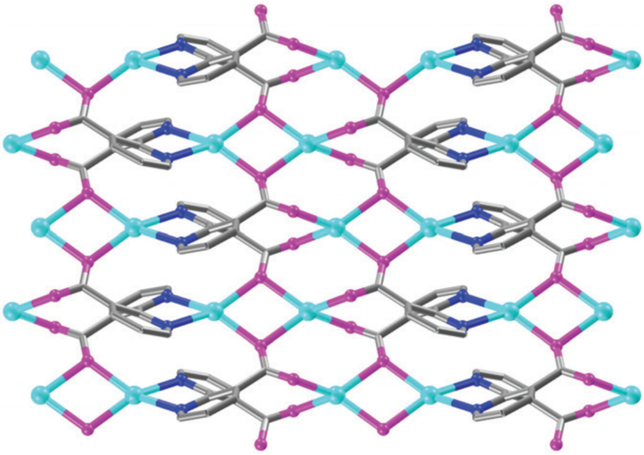

Figure 2. The 2-D layer in **1;** hydrogen atoms omitted for clarity.

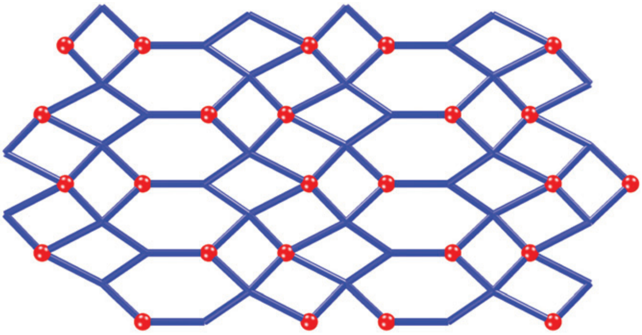

Figure 3. A simplified scheme of 2-D network with four grids along *a*-axis.

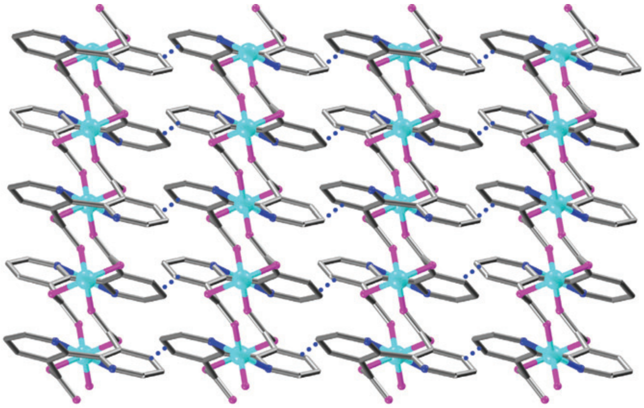

Figure 4. View of 3-D structure containing 1-D channels through $\pi\cdots$ packing interaction along *b*-axis.

owing to (i) conjugative effect between pyridyl ring and carboxylate and (ii) steric factors such as size and spatial arrangement of carboxyl group. The twists of $(bpdc)^{2-}$ are responsible for formation of the network.

3.2. *IR spectra*

The IR spectra show features attributable to carboxylate stretching of the complex. In infrared spectra of **1**, no band was observed from 3600 to 3300 cm^{-1}, indicating absence of O–H stretch of carboxylic acids and complete deprotonation of the ligand. The $\nu_{as}(COO)$ is identified by the strong band at 1597 cm^{-1} and $\nu_s(COO)$ at 1378 cm^{-1}. The separation between the $\nu_{as}(COO)$ and $\nu_s(COO)$ band in **1** is 219 cm^{-1}, confirming the bridging of carboxylate groups in **1** [37].

3.3. *Luminescence properties*

Because of the excellent luminescent properties of d^{10} metal complexes, the luminescence of **1** and free ligand were investigated. The emission spectrum of **1** in the solid state at room temperature is shown in figure 5. Compound **1** exhibits one strong emission band at 390 nm upon excitation at 245 nm, which can be tentatively assigned to the π–π* electronic transition of ligand [38, 39], since a similar emission at 392 nm was observed for free ligand at the same excitation condition.

3.4. *Thermogravimetric analyses*

Thermal stability of the supramolecular framework constructed from Ag(I) and H_2bpdc was investigated by TGA. There is only one mass loss in the TGA curve of **1** (Supplemental Material), which is stable to 245°C. The weight loss of 51.2% (Anal. Calcd 49.4%) observed from 245 to 540°C corresponds to the release of ligands. The remaining weight of 48.4% corresponds to the final product Ag_2O (Anal. Calcd 50.6%).

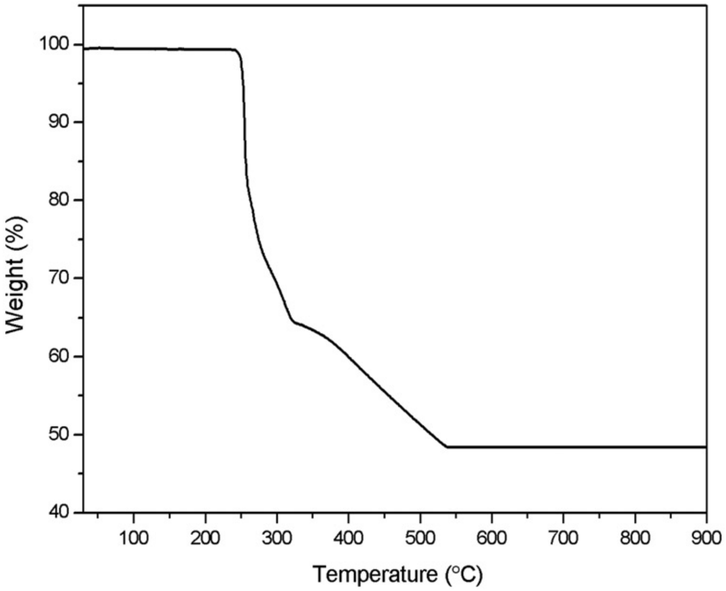

Figure 5. The emission spectrum of **1** in the solid state at room temperature.

4. Conclusion

A 2-D Ag(I) coordination polymer with 2,2′-bipyridyl-3,3′-dicarboxylate was structurally characterized. Each $(bpdc)^{2-}$ is μ_6-octadentate coordinating with six silvers in **1**. This coordination of $(bpdc)^{2-}$ has not been found in other complexes with $(bpdc)^{2-}$. Each carboxylate of $(bpdc)^{2-}$ is μ_3–η^1–η^2 bridging, also very rare. Ligand conformation plays a key role in the coordination structure. Compound **1** displays intense emission and may be a candidate for blue luminescent material.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 654624 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internet) +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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