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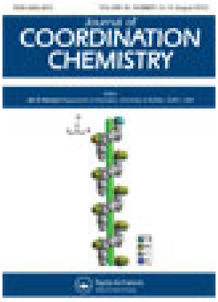

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Preparation, characterization, and properties of a Ag(I) coordination polymer $\{[Ag(H_3bptc)(bpe)]\cdot 2H_2O\}_n$

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Accepted author version posted online: 11 Jun 2012.Published online: 26 Jun 2012.

To cite this article: Ya-Nan Zhang , Xiao Hai , Yun-Tao Li , Lin Cui & Yao-Yu Wang (2012) Preparation, characterization, and properties of a Ag(I) coordination polymer $\{[Ag(H_3bptc)(bpe)]\cdot 2H_2O\}_n$, Journal of Coordination Chemistry, 65:15, 2724-2731, DOI: 10.1080/00958972.2012.701736

To link to this article: http://dx.doi.org/10.1080/00958972.2012.701736

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Journal of Coordination Chemistry
Vol. 65, No. 15, 10 August 2012, 2724–2731

Preparation, characterization, and properties of a Ag(I) coordination polymer $\{[Ag(H_3bptc)(bpe)]\cdot 2H_2O\}_n$

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(*Received 14 February 2012; in final form 1 May 2012*)

A new coordination polymer, $\{[Ag(H_3bptc)(bpe)]\cdot 2H_2O\}_n$ (**1**) ($H_4bptc = 3,3',4,4'$-benzophenonetetracarboxylic acid, bpe = 1,2-bis(4-pyridyl)ethene), has been synthesized through a hydrothermal technique and structurally characterized. The crystal structure of **1** exhibits a 2-D hydrogen-bonding sheet between H_3bptc^- and two free water molecules. Fluorescent property, TG analysis, and X-ray powder diffraction for **1** were also measured and discussed.

Keywords: Coordination polymer; Hydrogen-bond; Fluorescence spectrum; Hydrothermal reaction

1. Introduction

Design and synthesis of metal-organic frameworks (MOFs) have received attention to develop new functional materials with potential applications such as gas storage [1], magnetism [2], and optical properties [3, 4]. The molecular architecture is based on selection and utilization of suitable metal ions and multifunctional organic ligands. Multicarboxylates are often used as multifunctional organic ligands because of their various coordination modes and their ability to act as H-bond acceptors and donors assembling supramolecular structures [5]. H_4bptc ($H_4bptc = 3,3',4,4'$-benzophenonetetracarboxylic acid) can afford the possibility of connections between units for supramolecular assembly and is a good candidate for construction of coordination polymers [6].

Hydrothermal reactions can offer a synthetic route to better quality crystals than traditional solution techniques such as diffusion, evaporation, and cooling. Accordingly, we employ H_4bptc and Ag(I) to construct extended polymer networks

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2012.701736

through hydrothermal techniques. The silver(I) salt is used in crystal engineering for its metallophilic interaction, short M–M bond and variety of coordination geometries such as linear, bent, trigonal planar, T-shaped, tetrahedral, and trigonal pyramidal. Systematic investigation has been reported on structures of silver(I) polycarboxylates incorporating secondary ligands, revealing that weak interactions could play an important role in interlinking low-dimensional entities to high-dimensional supramolecular frameworks. Furthermore, weak silver–ligand bonds supposes that in the solid state, various weak interactions and crystal packing forces could have greater influence on structure than that for more rigid metal–ligand systems [7].

In previous work, two flexible rod-like N-donor coligands have been introduced into the Ag-H_4bptc system to bring fascinating architectures, $\{[Ag_3(Hbptc)(bpa)_2]\cdot H_2O\}_n$ and $[Ag_2(H_2bptc)(bpp)_2]_n$, in different pH values, which exhibit two ladder-like chains based on linear or T-shaped coordination environment of Ag(I) (bpa = 1,2-bi(4-pyridyl)ethane; bpp = 1,3-bis(4-pyridyl)propane). In this report, with rigid rod-like 1,2-bis(4-pyridyl)ethene (bpe), a new complex, $\{[Ag(H_3bptc)(bpe)]\cdot 2H_2O\}_n$ (**1**), was obtained to extend our previous research [8a]. The results show that these ligands exhibit special ability to formulate complex and play an important role in directing the final structures [8]. In addition, the fluorescence, TG analysis, and X-ray powder diffraction (XRPD) of **1** are discussed.

2. Experimental

2.1. *Materials and measurements*

Reagents were used as commercially supplied without purification. Elemental analyses (C, H, and N) were determined with a Perkin-Elmer model 240C automatic instrument. Infrared spectra on KBr pellets were recorded on a Bruker Equinox-55 spectrometer from 4000–400 cm^{-1}. Luminescence spectra for solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer. The XRPD pattern was recorded with a Pigaku D/Max 3III diffractometer. Thermal analysis was determined with a Netzsch STA 449C microanalyzer under flowing N_2 at a heating rate of 10°C min^{-1}.

2.2. *Preparation of $\{[Ag(H_3bptc)(bpe)]\cdot 2H_2O\}_n$ (1)*

Compound **1** was obtained by reaction of $AgNO_3$ (0.2 mmol), bpe (0.05 mmol) and H_4bptc (0.05 mmol) in 4 : 1 : 1 molar ratio in 15 mL of water and 1 mL of triethylamine under hydrothermal conditions (at 150°C for 6 days and cooled to room temperature with a 5°C h^{-1} rate). Then the pH of the resulting solution was adjusted to two. Colorless crystals of **1** were collected in 55% yield. Anal. Calcd for $C_{29}H_{23}AgN_2O_{11}$: C, 50.97; H, 3.39; N, 4.10. Found: C, 51.04; H, 3.61; N, 4.36%. IR (KBr, cm^{-1}): 3441(w), 3078(w), 2459(w), 1708(s), 1664(s), 1608(s), 1544(w), 1487(m), 1430(m), 1360(s), 1313(s), 1230(m), 1132(w), 1069(m), 1005(w), 828(m), 767(m), 736(m), 650(m), 547(m).

2.3. *Crystallographic data collection and structure determination*

Single-crystal X-ray diffraction analysis of **1** was carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ϕ/ω scan technique at room temperature. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [9a], and refined using full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [9]. The crystallographic data and selected bond lengths and angles for **1** are listed in tables 1 and 2, respectively. Possible hydrogen bond geometries are listed in table 3. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center.

Table 1. Selected crystallographic data for **1**.[a]

Empirical formula	$C_{29}H_{23}AgN_2O_{11}$
Formula weight	683.36
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.0032(18)
b	11.788(2)
c	12.707(2)
α	104.65(2)
β	106.929(2)
γ	97.968(2)
Volume (Å^3), Z	1349.9(4), 2
Calculated density (g cm^{-3})	1.681
Absorption coefficient (mm^{-1})	0.816
$F(000)$	692
θ range for data collection (°)	1.83–25.10
Reflections collected	5880
Goodness-of-fit on F^2	1.007
Final R^a indices [$I > 2\sigma(I)$]	$R_1 = 0.0478$, $wR_2 = 0.1151$

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.[a]

Ag(1)–N(1)	2.153(4)	Ag(1)–N(2)[a]	2.160(4)
N(1)–Ag(1)–N(2)[a]	176.58(16)		

[a] Symmetry code: $x-1$, y, $z-1$.

Table 3. Hydrogen-bonding geometries for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(1)–H(1A)···O(3)#1	0.82	1.88	2.65	166
O(4)–H(14A)···O(5)#2	0.90	1.59	2.48	167
O(7)–H(7A)···O(6)#3	0.73	1.89	2.60	164
O(10)–H(10A)···O(11)	0.85	1.82	2.67	180
O(11)–H(11B)···O(5)#4	0.89	2.08	2.97	177

Symmetry codes: #1: $-x$, $1-y$, $-z$; #2: $-1+x$, y, $-1+z$; #3: $2-x$, $-y$, $1-z$; #4: $1-x$, $1-y$, $1-z$.

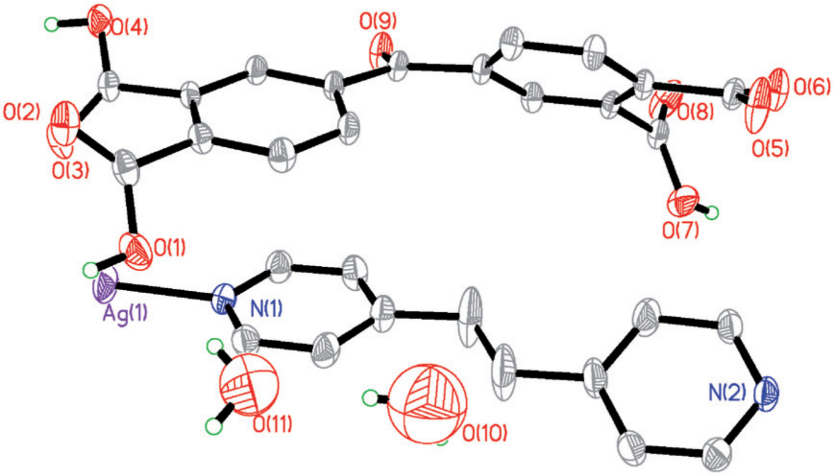

Figure 1. Local coordination environment of Ag(I) in **1**.

3. Results and discussion

3.1. *Crystal structure*

X-ray crystallography shows that **1** contains one $[Ag(bpe)]^+$, one $[H_3bptc]^-$, and two lattice water molecules (figure 1). Ag1 is two-coordinate with a linear coordination geometry binding two nitrogen atoms from two different bpe ligands (Ag–N 2.153(4) and 2.160(4)). The MOF in **1** consists of an infinite 1-D chain arrangement with $[Ag(bpe)]^+$. Due to partial deprotonation of H_4bptc, $[H_3bptc]^-$ acts as H-bond acceptors and donors in the framework of **1**. Thus, there exist hydrogen bonding interactions between $[H_3bptc]^-$ and free water forming a discrete unit which contains a six-membered ring (O···O 2.48–2.97 Å) (figure 2).

In **1**, $[H_3bptc]^-$ is a counter-anion to balance the polymeric host charge, while not participating in the primary coordination of Ag(I). The coordination ability of nitrogen ligands is stronger than that of the carboxylate of H_4bptc in this case can be explained by the Pearson HSAB theory [10] and is similar to previous research about mixed-ligand Ag(I) coordination polymers [7d, 7f, 8a, 8d]. The structural difference between mixed-ligand Ag(I) coordination polymers is attributed to the degree of deprotonation of carboxylic groups and various weak interactions. In **1**, the carboxylic groups of H_4bptc show hydrophilicity and are expected to facilitate formation of water aggregates. Thus, $[H_3bptc]^-$ anion is a bridge to connect free water molecules to afford a 2-D supramolecular layer in the *ac*-plane (figure 3). The average O···O separation of 2.67 Å approaches those observed in liquid water (2.80 Å) and comparable to the corresponding value in ice (2.77–2.84 Å) [11, 12]. In **1**, the 2-D supramolecular sheet and 1-D linear-like chain are alternating with a sequence of –ABAB– in the crystal (figure 4a), in which there are no interactions to support a channel (figure 4b). From the structural analysis of **1**, the presence of strong hydrogen-bonds is essential to construct water clusters and 2-D or 3-D polymer networks. In our previous work, comparing **1** with the same bptc ligand resulted in significant and distinguishable

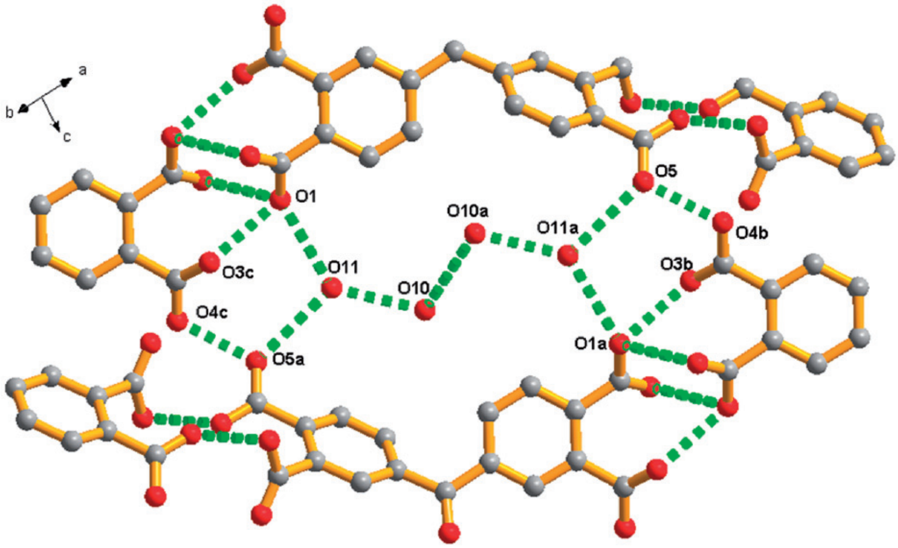

Figure 2. The discrete unit connected by hydrogen bonding interactions.

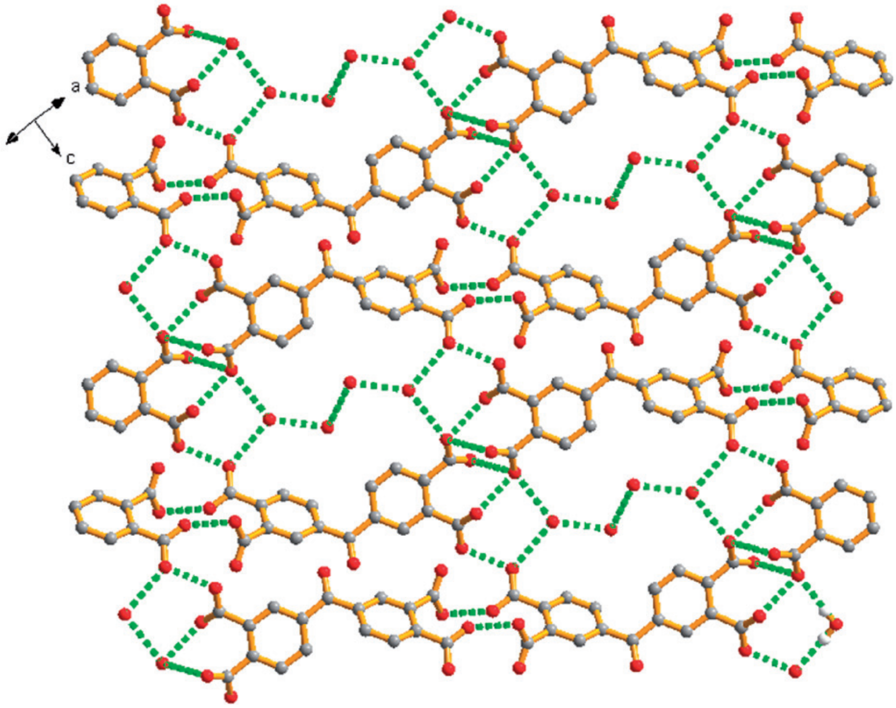

Figure 3. The 2-D supramolecular layer constructed by $[H_3bptc]^-$ and free water in **1**.

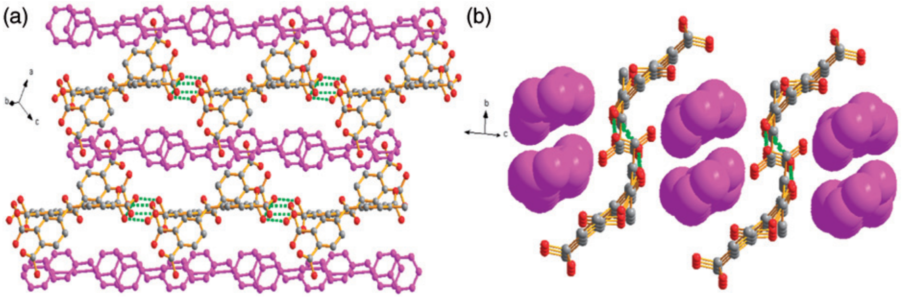

Figure 4 (a), (b) The 3-D supramolecular network showing the 2-D sheets and 1-D chain packed in an ABAB fashion in different directions.

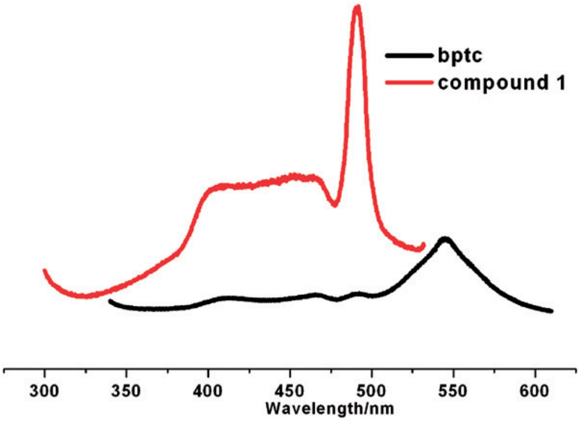

Figure 5. The solid-state photoluminescence spectrum of **1** and the free H_4bptc.

role that bptc as a connector can play in the assembly of hydrogen-bonding polymer networks [13].

3.2. *Solid-state fluorescent properties*

The photoluminescence of **1** in the solid-state is depicted in figure 5. Complex **1** shows pale fluorescence with the emission band at 490 nm by exciting the crystal sample at 320 nm. The emission peak exhibits very small blue-shift in contrast to free H_4bptc with a broad emission peak ($\lambda_{max} = 547$ nm) upon excitation at 320 nm. According to the literature, the luminescent property of **1** can be attributed to ligand-to-metal charge transfer [14]. The observation indicates that **1** may be an excellent candidate for photoactive material.

3.3. *XRPD Pattern and thermal stability analysis*

In order to confirm the phase purity of the bulk materials, XRPD was carried out on **1**. The XRPD experimental and computer-simulated patterns of **1** are shown in figure 6.

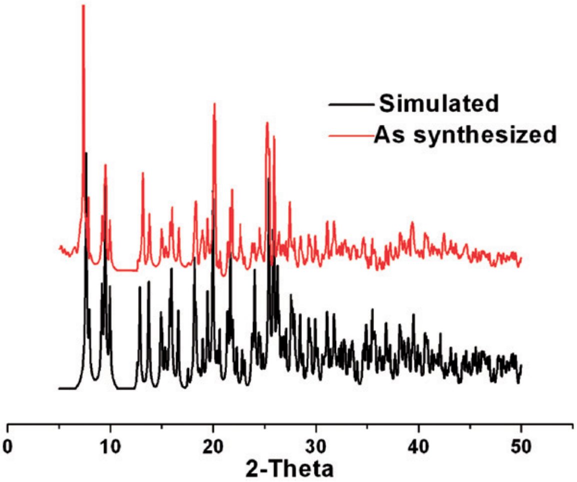

Figure 6. Comparison of XRPD patterns of the simulated pattern and the as-synthesized in **1**.

Although minor differences can be seen in the positions, intensities, and widths of some peaks, it can also be considered that the as-synthesized material is homogeneous.

To identify the thermal stability of **1**, the TGA measurement was carried out (figure S1). In **1**, a first major weight loss equal to 4.86% before 200°C is ascribed to release all free water molecules (Calcd 5.27%). Accordingly, the framework is stable to 200°C, at which point removal of organic ligands can ensue. Finally, the residual weight of 16.12% may be attributed to Ag (expected 17.17%).

4. Conclusion

This research focuses on the synthesis, structural characterization, and properties of a Ag-containing coordination polymer based on 3,3′,4,4′-benzophenonetetracarboxylic acid (H_4bptc) and 1,2-bis(4-pyridyl)ethene (bpe). The complex exhibits a 2-D hydrogen-bonding sheet between H_3bptc^- and two free water molecules, in which hydrogen bonds play important roles in formation of the resulting structures. The complex may be a candidate for photoactive materials. Further investigations on such interesting systems connected by mixed-ligand Ag(I) coordination polymers will occur in our future work.

Supplementary material

Crystallographic data for **1** has been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC: 861522). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 91022004/B01), Scientific Research Projects of Shaanxi Education Department (12JK0627), and Specialized Research Found for the Doctoral Program of Shaanxi University of Science & Technology (No. BJ11-22).

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