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Hydrogen Bonding and Water Networks in a 3-D Coordination Polymer $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ (bpp = 1,3-*Bis*(4-pyridyl)propane; BDC = Benzene-1,4-dicarboxylic acid)

CHONG-CHEN WANG* and PENG WANG

Key Laboratory of Urban Stormwater System and Water Environment (Beijing University of Civil Engineering and Architecture), Ministry of Education, No. 1, Zhanlanguan Road, Xicheng District, Beijing 100044, P.R. China

*Corresponding author: E-mail: chongchenwang@126.com

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A 3-D coordination polymer of silver, *i.e.*, $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ was obtained by evaporating the mixture of an ammonical solution containing $AgNO_3$, benzene-1,4-dicarboxylatic acid and an acetonic solution of 1,3-*bis*(4-pyridyl)propane at room temperature slowly for several weeks. The crystals should be protected by vaseline oil as soon as possible after taken from mother liquid because they were unstable when exposed under air. In asymmetric unit of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$, the Ag ions are coordinated in bent linear geometry by two N atoms from two different 1,3-*bis*(4-pyridyl)propane ligands. Benzene-1,4-dicarboxylic acid is uncoordinated to any Ag ions, playing the role of charge compensation of the cationic polymer coordination chains. The rich hydrogen bond interactions were formed by the O atoms from benzene-1,4-dicarboxylic acid ligands and the lattice water molecules, which form novel water networks. The crystal structure reveals that 3-D framework of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ is built up of 1-D $[Ag(bpp)]^{n+}_n$, BDC^{2-} counter-ions and lattice water molecules.

Key Words: 1,3-*Bis*(4-pyridyl)propane, Benzene-1,4-dicarboxylic acid, Hydrogen bond, Water network, Crystal structure.

INTRODUCTION

1,3-*Bis*(4-pyridyl)propane (bpp) as pyridyl-donor ligand similar to 4,4'-bipyridine is a flexible and versatile spacer to built novel coordination polymers and a few complexes of Ag(I) and bpp but different counterions have been reported[1-5]. Here we present a novel coordination polymer $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ with 3-D framework linked by rich hydrogen bonds.

EXPERIMENTAL

All commercially available chemicals and solvents are of reagent grade and used as received without further purification.

Synthesis: An ammonia solution (25 mL) containing 0.0085 g $AgNO_3$ (0.05 mmol) and 0.083 g benzene-1,4-dicarboxylic acid (0.05 mmol, H_2BDC) was added drop-wise to an acetonic solution (25 mL) of 0.01 g of 1,3-*bis*(4-pyridyl)-propane (0.05 mmol, bpp). The clear mixture was stirred for few minutes and then allowed to evaporate at room temperature slowly. Long needle-like colourless crystals of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ appeared after several weeks. The crystals must be protected by Vaseline oil as soon as possible after taken from mother liquid because they were unstable when exposed under air. The IR and TGA of the title compound were failed to be carried out because it is unstable.

Crystal structure determination: A crystal of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ suitable for single-crystal X-ray diffraction was selected for the experiment. The intensity data of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ were collected at room temperature (293 K) on a Rigaku R-axis rapid IP area detector diffractometer by ω oscillation scan technique using graphite-monochromatized MoK_α radiation (λ = 0.071073 nm). The total reflections of 60782 were measured, unique 7038 with R(int) = 0.0531 within the limits $1.20° < \theta < 27.48°$. The structure was solved using direct method with SHELXS-97[6] and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. All calculations were performed using SHELXTL-97 program package[6]. The final full-matrix least-squares refinement gave $R_1 = 0.046$, $wR_2 = 0.095$. The highest and lowest residual peaks in the final difference Fourier map are 1.184 and -0.623 e/nm^3, respectively. The crystal belongs to orthorhombic, crystal system, space group Pca2(1) with cell parameters a = 1.8712(4) nm, b = 1.6926(3) nm, c = 2.4627(5) nm, V = 7800(3) and Z = 4. The asymmetric unit of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ was shown in Fig. 1, selected bond lengths and angles were listed in Table-1.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters, the selected bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and hydrogen bonds are listed in Tables 1 and 2, respectively. The perspective view of the framework of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ along c axis, the coordination mode of 1,3-*bis*(4-pyridyl)propane and Ag ion are illustrated in Figs. 1-4, respectively.

TABLE-1
BOND LENGTHS AND ANGLES FOR $[Ag(bpp)]_2(BDC)\cdot 8H_2O$

Bond	Length (nm)	Bond	Angle (º)
Ag1-N1	0.2147(8)	Ag4-N8#5	0.2140(7)
Ag1-N4	0.2150(7)	N3-Ag2#2	0.2114(8)
Ag2-N3#1	0.2114(8)	N8-Ag4#4	0.2140(7)
Ag2-N2	0.2140(7)	Ag3-N6	0.2144(8)
Ag4-N7	0.2112(8)	Ag3-N5	0.2167(8)
		N1-Ag1-N4	168.1(3)
		N3#1-Ag2-N2	166.2(3)
		N6-Ag3-N5	163.4(3)
		N7-Ag4-N8#5	172.3(3)

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

TABLE-2
HYDROGEN BONDS FOR $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ (Å AND º)
HYDROGEN BONDS (nm AND º) IN THE CRYSTAL STRUCTURE OF $[Ag(bpp)]_2(BDC)\cdot 8H_2O$

D–H···A	D–H	H–A	D···A	∠DHA
O23–H23C···O4#7	0.85	2.12	2.971(11)	179
O23–H23B···O6#8	0.85	1.90	2.751(9)	180
O22–H22D···O9	0.86	2.10	2.816(9)	140
O22–H22C···O18	0.85	2.01	2.817(11)	158
O21–H21D···O1#9	0.86	1.95	2.802(13)	174
O21–H21C···O14	0.85	2.05	2.668 (12)	129
O20–H20F···O21#8	0.85	2.07	2.787 (11)	142
O20–H20C···O23	0.85	2.17	2.796 (10)	130
O19–H19D···O12	0.85	2.03	2.695 (9)	135
O19–H19C···O13	0.85	2.14	2.778 (9)	132
O18–H18C···O7	0.86	2.21	2.869 (12)	134
O18–H18B···O11	0.87	1.93	2.770 (12)	161
O17–H17C···O5#8	0.85	1.92	2.771 (7)	180
O17–H17B···O2	0.85	1.94	2.796 (12)	180
O16–H16D···O15	0.85	1.91	2.754 (10)	179
O16–H16A···O24	0.85	2.27	2.783 (9)	119
O15–H15D···O3#10	0.85	2.03	2.836 (11)	157
O15–H15C···O8#11	0.85	2.09	2.764 (7)	136
O14–H14C···O7xi	0.85	1.95	2.799 (8)	179
O14–H14B···O16	0.85	1.89	2.740 (13)	179
O13–H13D···O10	0.85	2.12	2.807 (9)	137
O13–H13C···O22#12	0.85	2.07	2.774 (13)	140
O12–H12D···O2#10	0.85	2.16	2.725 (8)	124
O12–H12C···O5	0.88	1.88	2.754(11)	170
O11–H11C···O1#5	0.85	1.94	2.794 (8)	180
O11–H11B···O19#7	0.85	2.34	3.146 (13)	157
O10–H10C···O8	0.85	1.98	2.830 (11)	180
O10–H10B···O3#13	0.85	1.92	2.748 (8)	165
O9–H9D···O6	0.85	2.22	2.886 (12)	136
O9–H9A···O4#9	0.85	1.88	2.731 (8)	179
O24–H24C···O17#10	0.86	1.85	2.697 (8)	169
O24–H24B···O20#10	0.85	2.09	2.873 (13)	153

Symmetry codes: #7: –x+1/2, y, z+1/2; #8: x–1/2, –y+1, z; #9: –x+1, –y+1, z+1/2; #10: x+1/2, –y+1, z; #11: x+1, y, z; #12: –x+1/2, y,z–1/2; #5: –x, –y+1, z+1/2.

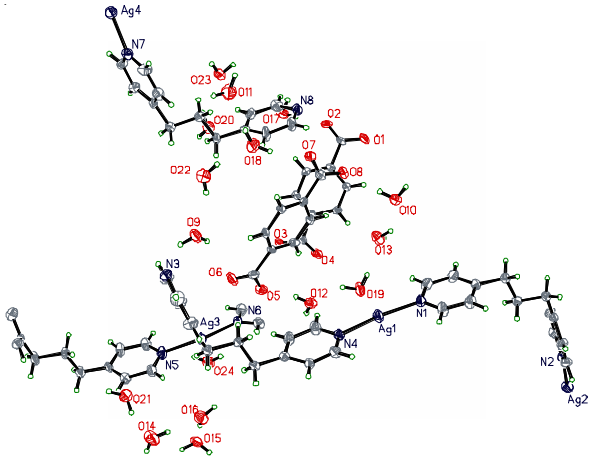

Fig. 1. Ortep view of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$

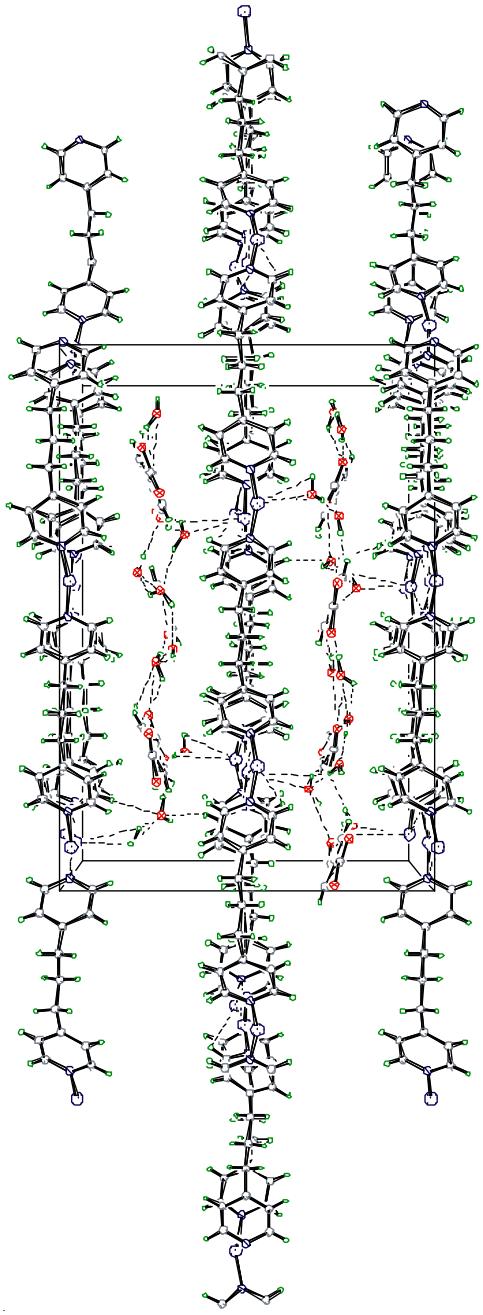

Fig. 2. Packing view of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ along c axis, showing the rich hydrogen bonds

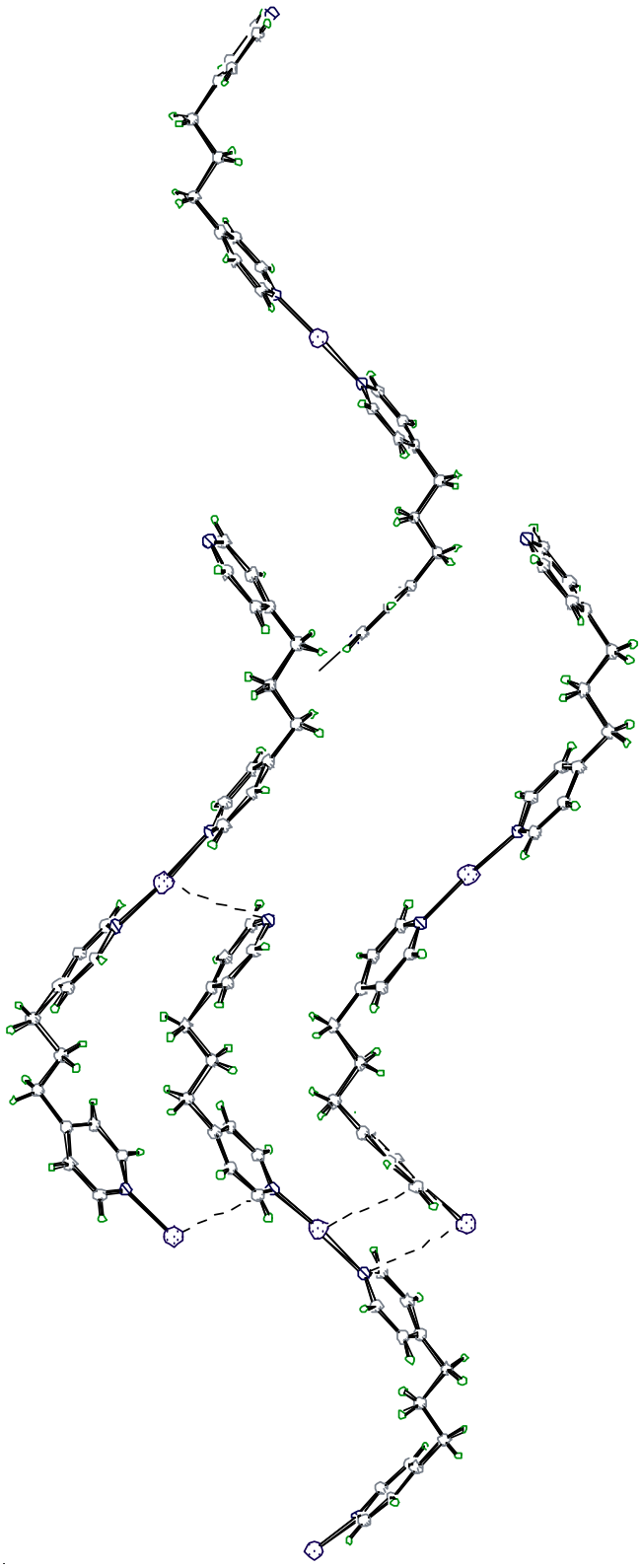

Fig. 3. Ag···N interactions between the $[Ag(bpp)]_\infty$ chains in the crystal

In asymmetric unit of present compound, the Ag ions are coordinated in bent linear geometry by two N atoms from two different bpp ligands, with Ag1-N1 = 0.2147 nm, Ag1-N4 = 0.2150 nm and N1-Ag1-N4 = 168.1°. Each bent bpp ligand bridges two Ag ions, with Ag2-$N3^{\#1}$ = 0.2144 nm, Ag2-N2 = 0.2140 nm and $N3^{\#1}$-Ag2-N2 = 166.2°, as shown in Fig. 1. Benzene 1,4-dicarboxylic acid is uncoordinated to any Ag^+

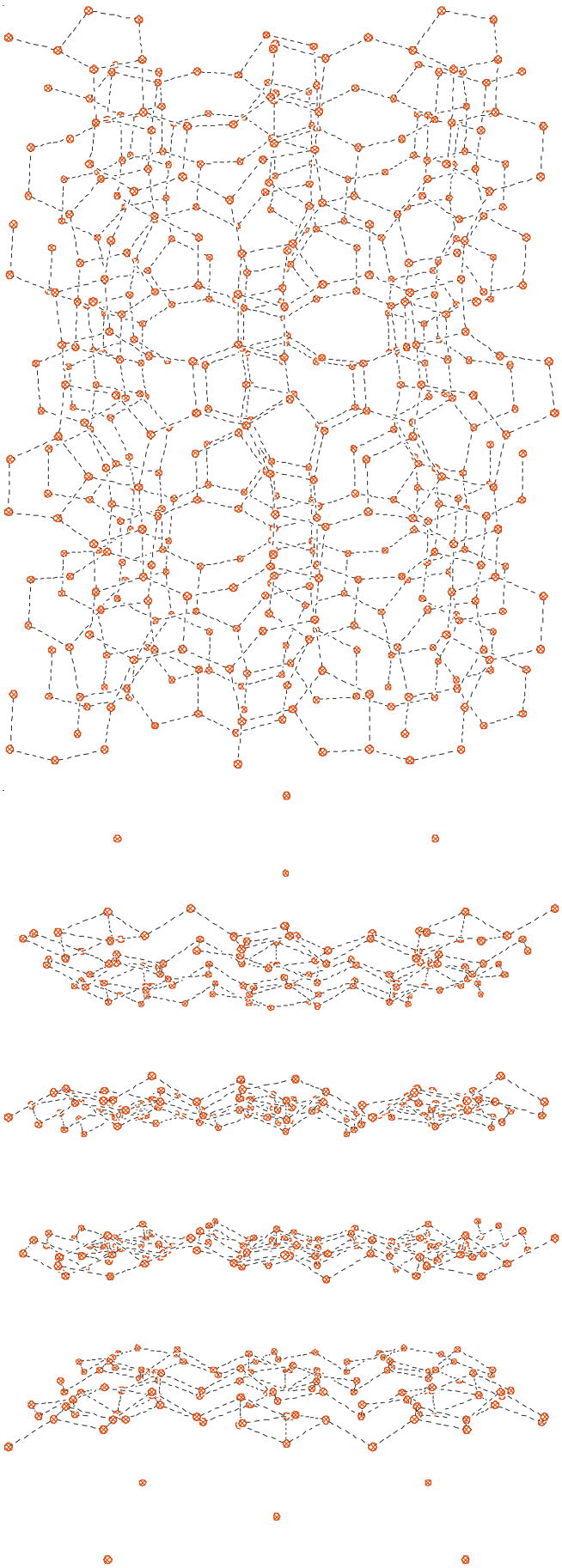

Fig. 4. Water sheet formed *via* hydrogen bonding interaction in the title compound

ion, playing the role of charge compensation of the cationic polymer coordination chains. And rich hydrogen bond interactions were formed by the O atoms from benzene 1,4-dicarboxylic acid ligands and the lattice water molecules.

The crystal structure reveals that 3-D framework of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ is built up of 1-D $[Ag(bpp)]^{n+}{}_n$, BDC^{2n-} counter-ions and lattice water molecules. The 2-D cationic layers, $[Ag(bpp)]^{n+}{}_n$, were formed by adjacent 1-D sinusoidal chains by Ag-N interaction, as illustrated in Fig. 2, where Ag-N distances are *ca.* 0.355 nm. The 2-D counter-ion organic layers were formed with BDC^{2-} and water molecules *via* rich hydrogen bonding interaction, as listed in Table-2 and Fig. 4. In the other words, the sandwich 3-D crystal framework of the title compound is build up of 2-D cationic organic-inorganic layers and organic counterion layers *via* weak Ag-N interactions, as depicted in Fig. 3.

Conclusion

The coordination polymer $[Ag(bpp)]_2(BDC)\cdot 8H_2O$ with novel 3-D framework built from rich hydrogen bonds was synthesized by slow evaporating the mixture of an ammonia solution containing $AgNO_3$, benzene-1,4-dicarboxylic acid and an acetonic solution 1,3-*bis*(4-pyridyl)propane at room temperature slowly for several weeks. The rich hydrogen bonds contribute to form 3-D framework of $[Ag(bpp)]_2(BDC)\cdot 8H_2O$.

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