



A New Two-Dimensional Silver Coordination Polymer Constructed by 1,3-Bis(4-pyridyl)propane and 2,6-Dichlorophenylacetic Acid: Synthesis, Structure, Luminescence and Thermal Stable Properties†

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A novel complex **1** of $\{[Ag(bpp)(dcpa)]H_2O\}_n$ [Hdcpa: 2,6-dichlorophenylacetic acid; bpp: 1,3-bis(4-pyridyl)propane] was synthesized and characterized by elemental analysis, IR, TGA, X-ray single crystal diffraction. The carboxylate oxygens of the Hdcpa ligands connect one Ag(I) ion in bidentate chelating mode to form mononuclear silver building blocks, which are into a 1D infinite chain through *trans*-bpp ligands. A two-dimensional network consist of adjacent Ag-bpp chain through Ag-Ag interaction. Furthermore, the luminescent property of complex **1** was investigated at room temperature. CCDC: 996495.

Keywords: Ag(I) coordinated polymer, Crystal structure, Luminesce.

INTRODUCTION

Inorganic-organic hybrid materials constructed from organic ligands and metal ions have attracted considerable attention for their variety of interesting architectures and beneficial properties such as porosity, catalysis, magnetism, luminescence, non-linear optics, *etc.*¹⁻⁴. Currently, considerable efforts have been made to design and construct such compounds with desired structures and properties. Among them, tactical synthesis or selection of the organic ligand and controlling reaction condition are key factors for achieving expected hybrid materials⁵. Carboxylates can provide various coordination modes (monodentate and *bis*-monodentate), while pyridyl ligands can be used as a pillar or bridge to ligate metal nodes^{6,7}. It is well known that the flexible 1,3-*bis*(4-pyridyl)propane (bpp) is an excellent candidate for constructing novel structures as the auxiliary ligands⁸⁻¹¹. The aromatic carboxylate ligand of chlorophenylacetic acid to construct various coordination polymers may result in some tailorable structures^{12,13}. So far, work on the construction of metals coordination polymers involving 2,6-dichlorophenylacetic acid (Hdcpa) and N-containing auxiliary ligands is still scarce. In this study, we introduced Hdcpa with the bpp ligand in order to assemble Ag(I) coordination polymer. In addition, thermal stability and luminescent property of polymer were measured.

EXPERIMENTAL

All chemicals purchased should be of reagent grade and used without further purification. Elemental analysis were performed on a CARLO ERBA 1106 analyzer. FT-IR spectra were recorded on a BRUKER EQUINOX 55 FT-IR spectrometer using KBr pellet at a resolution of 0.5 cm⁻¹ (4000-400 cm⁻¹). Luminescence spectra for crystal solid samples were recorded at room temperature on a Perkin Elmer LS 55 phosphorimeter. Thermogravimetry analyses were performed on an automatic simultaneous thermal analyzer (PE TG/DTA 6300) under a flow of N₂ at a heating rate of 10 °C min⁻¹ between ambient temperature and 800 °C.

General procedure: Complex **1** was prepared by the addition of stoichiometric amounts of silver nitrate (0.069 g, 0.5 mmol), 2,6-dichlorophenylacetic acid (0.1025 g, 0.5 mmol) and 1,3-*bis*(4-pyridyl)propane (0.0991 g, 0.5 mmol) dissolved in 1:1 methanol/water solution and the pH was adjusted to 7 with 0.1 M potassium hydroxide solution. After the mixture was stirred for 0.5 h, the precipitate was dissolved in the aqueous solution of ammonia (14 M) which was added drop by drop. Colourless crystals of compound were obtained by evaporation of the solution for 10 days at room temperature. Analysis calculated for C₄₂H₄₀N₄O₅Cl₄Ag₂: C 53.89, H 4.15, N 5.60 %; found: C 51.09, H 3.90, N 5.42 %. IR (KBr pellet,

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TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENTS OF COMPLEX 1

Empirical formula	C ₄₂ H ₄₀ N ₄ O ₅ Cl ₄ Ag ₂	γ (°)	90
Formula weight	1038.32	V (Å ³)	4264.9(17)
Temperature (K)	296(2)	Z	4
Size (mm)	0.30 × 0.20 × 0.18	μ (mm ⁻¹)	1.217
θ range for data collection (°)	1.72– 25.00	D _c (g cm ⁻³)	1.617
Crystal system	Monoclinic	F ₍₀₀₀₎	2088
Space group	C2/c	Reflections collected	11265
a (Å)	25.477(6)	Independent reflections (R _{int})	3731 (0.0230)
b (Å)	8.583(2)	Goodness of fit on F ²	1.022
c (Å)	21.013(5)	R ₁ , wR ² (I > 2 σ (I))	0.0313, 0.0796
α (°)	90	R ₁ , wR ₂ (all data)	0.0382, 0.0853
β (°)	111.840(2)	($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / e Å ⁻³ (e nm ⁻³)	0.762, -0.728

cm⁻¹): 3403(w), 2940(w), 2373(w), 1610(s), 1584(s), 1556(m), 1527(w), 1496(w), 1435(m), 1364(m), 1266(w), 1215(w), 1156(w), 1156(w), 1140(w), 1078(w), 1007(w), 936(m), 904(w), 806(m), 771(m), 664(w), 509(w).

Detection method: A single crystal with dimensions of 0.30 mm × 0.20 mm × 0.18 mm was mounted on a glass fiber for data collection which was performed on a Bruker SMART APEXII CCD diffractometer operating at 50 kV and 30 mA using a MoK α radiation (λ = 0.071 073 nm) at 295(2) K by using a ω scan mode. In the range $1.72^\circ \leq \theta \leq 25.00^\circ$, a total of 11265 reflections were collected, of which 3731 were unique (R_{int} = 0.0230) and 3195 observed ones (I > 2 σ (I)) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software¹⁴. Multi-scan absorption corrections were applied using the SAINT¹⁵. The structure was solved by direct methods and refined on F² by full-matrix least squares technique using the SHELX-97 program package^{16,17}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of O-H 0.0842 nm and HH 0.138 nm, with a standard deviation of 0.001 nm and with Uiso(H) = 1.5Ueq(O). R₁ = 0.0313 and wR₂ = 0.0796 (w = 1/[$\sigma^2(F_o^2) + (0.0432P)^2 + 8.2553P$], P = (F_o² + 2F_c²)/3 for 3731 observed reflections with I > 2 σ (I). S = 1.022, (Δ/σ)_{max} = 0.000, ($\Delta\rho$)_{max} = 0.762 e Å⁻³ and ($\Delta\rho$)_{min} = -0.728 e Å⁻³. Crystal parameters and details of the data collection and refinement are given in Table-1. Selected bond lengths and angles and H-bonding parameters are given in Tables 2 and 3, respectively.

TABLE-2

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Ag(1)-N(2)#1	2.202(3)	Ag(1)-N(1)	2.219(2)
Ag(1)-O(1)	2.561(2)	Ag(1)-O(2)	2.680(3)
Ag(1)-Ag(1)#2	2.9603(7)	—	—
N(2)#1-Ag(1)-N(1)	154.54(9)	N(2)#1-Ag(1)-O(1)	105.22(9)
N(1)-Ag(1)-O(1)	93.89(9)	N(2)#1-Ag(1)-Ag(1)#2	86.47(7)
N(1)-Ag(1)-Ag(1)#2	102.33(6)	O(1)-Ag(1)-Ag(1)#2	111.23(6)
Symmetry codes: #1 x-1/2, y+1/2, z-1/2 #2 -x+1, -y+1, -z.			

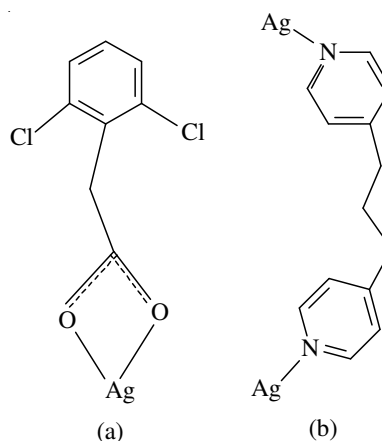
RESULTS AND DISCUSSION

Structure description: The X-Ray crystal structure of 1 contains silver atom, one 1,3-bis(4-pyridyl)-propane (bpp) and

TABLE-3
HYDROGEN BONDS FOR COMPLEX 1

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
C(2)-H(2B)...Cl(2)	0.97	2.65	3.131(5)	111.0
OW-H(1OW)...O(1)#4	0.842(10)	2.034(13)	2.868(4)	171(5)
C(10)-H(10)...O(2)#2	0.93	2.49	3.203(4)	133.7
Symmetry codes: #2 -x+1, -y+1, -z #4 -x + 1, y, -z + 1/2.				

one 2,6-dichlorophenylacetic acid (dcpa⁻) anions and one uncoordinated water molecule in the asymmetry unit, with the water molecule (OW) in special position. Each silver atom is coordinated to two nitrogens atom from two bpp ligand and two oxygen atom of the one dcpa⁻ anion in the four-coordinate distorted tetrahedral configuration. The Hdcpa ligands are terminal and shows bidentate chelating modes [Ag-O 2.561(2) and 2.680(3) Å] and the bpp ligand has adopted two end pyridyl N atoms that link to two Ag atoms [Ag-N 2.202(3) and 2.219(2) Å] (**Scheme-I**), the Ag1 and Ag1ⁱⁱ distance is 2.960 Å, much shorter than van der Waals radii of two silver ions (3.440 Å)¹⁸ (Fig. 1 and Table-1).



Scheme-I: Coordination mode of Hdcpa and bpp in complex 1

All the Ag(I) ions are surrounded by two nitrogen atoms from two bpp ligands form an infinite [Ag(bpp)]_n, adjacent Ag-bpp chains are linked into interesting two-dimensional, β -sheetlike layers by weak ligand-unsupported Ag...Ag contacts¹⁹. The Ag1...Ag1b distance separated by bpp ligand is 13.335 Å and the bpp ligand has TG conformation (the two pyridyl groups of bpp ligand show different trans (T) and gauche (G) orientations)²⁰ (Fig. 2).

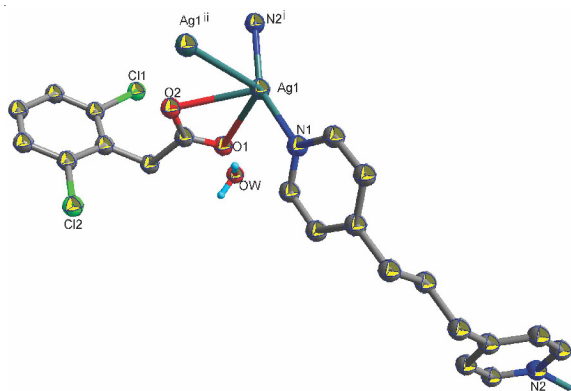


Fig. 1. View of the asymmetric unit of **1** with 30 % probability ellipsoids. Symmetry codesⁱ $x-1/2, -y+1/2, z-1/2$;ⁱⁱ $-x+1, -y+1, -z$

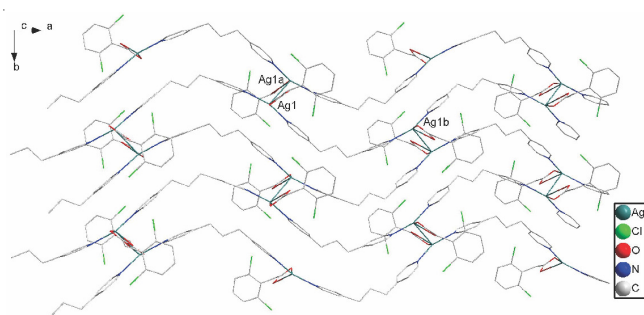


Fig. 2. β -Sheet like layers of the complex **1**

The reverse arrangement of 2,6-dichlorophenylacetate (dcpa) ligand layers on both sides. With the help of hydrogen-bonded interactions between adjacent 2D sheet [O^v-H(1OW)...O(1)^{iv} = 2.034 Å, symmetry codes^{iv} $-x+1, y, -z+1/2$], the polymeric sheet are assembled to form a supramolecular 3-D network structure (Fig. 3 and Table-2).

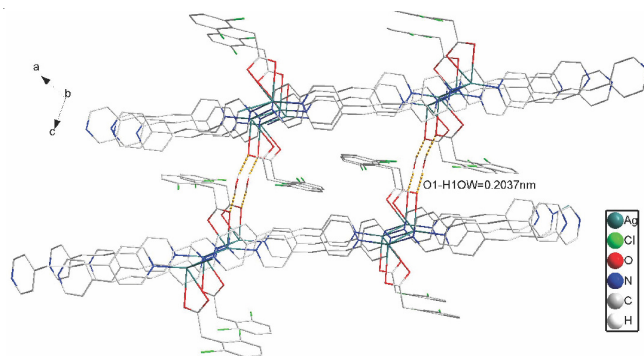


Fig. 3. A packing diagram for complex **1**

IR spectrum: The IR spectrum of **1** clearly shows the presence of the Hdcpa and bbbp. The absence of the absorption at 1691 cm^{-1} in the free Hdcpa in **1** illustrates the complete deprotonation of the ligands in the reaction with Ag(I) ion. The strong bands at 1610 and 1435 cm^{-1} correspond to asymmetric $\nu_{\text{as}}(\text{COO})$ and symmetrical $\nu_{\text{s}}(\text{COO})$ stretching vibrations, respectively of the coordinated carboxylate groups. In the compound **1**, The $\Delta\nu[\nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO})]$ value is 175 cm^{-1} . According to Nakamoto²¹, the carboxylate groups show bidentate-chelating coordination mode. Meanwhile, characteristic bands nearby 1527 cm^{-1} (1496 cm^{-1} in **1**) belong to the stretching vibration of $-\text{N}=\text{C}-$ of bbbp ligands. The results of the IR

spectra analyses of the complexes are in consistent with that of single-crystal X-ray analyses.

Thermal analysis: The thermal stability and thermal decomposition behavior of compound were studied by thermal analysis in a static N_2 atmosphere in the temperature range 30-800 $^{\circ}\text{C}$ (Fig. 4). The first corresponding to the escape of one free water molecule is observed from 105-181 $^{\circ}\text{C}$ (Obsd. 4.20 %, calcd. 3.46 %). The second corresponding to the escape of dcpa⁻ and bbbp ligands is observed from 181-274 $^{\circ}\text{C}$ (Obsd. 70.09 %, calcd. 69.80 %). Thermogravimetric curve displays the most weight loss of 7.49 % from 274-408 $^{\circ}\text{C}$, corresponding to the decomposition of the complex on the cards to form silver oxide. On further heating, the final decomposition product is metallic silver, with a total weight loss of 20.59 %.

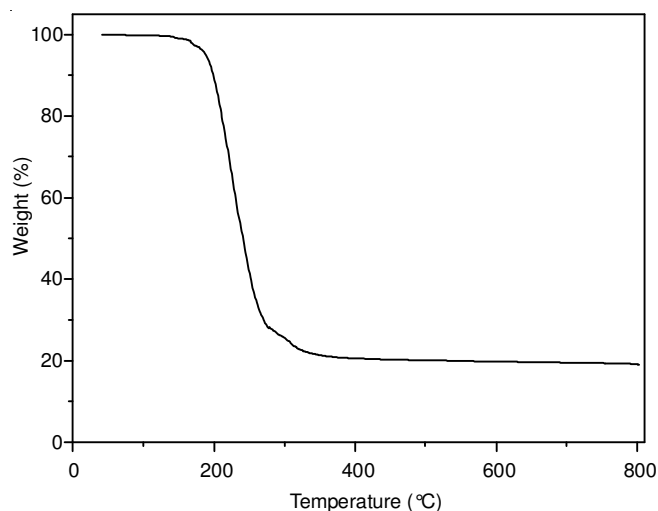


Fig. 4. Thermogravimetric curve of the complex **1**

Photoluminescence properties: Coordination polymers based on d^{10} metal centers and organic ligands are promising candidates for photoactive materials with potential applications²². In this study, fluorescent property of compound has been investigated in the solid state. The emission peaks were not observed for free Hdcpa ligands. The emission peaks at ca. 455 nm ($\lambda_{\text{ex}} = 372 \text{ nm}$)²³ were observed for free bbbp ligands. The emission bands for free ligands are probably attributed to the $\pi \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions. In the complex, strong fluorescence with emission peak at about 503 nm ($\lambda_{\text{ex}} = 289 \text{ nm}$) was observed at room temperature (Fig. 5) and the emissions arising from the free ligands are not observed. This feature is due to energy transfer from the ligands to the Ag(I) atoms during photoluminescence. Therefore, the photoluminescence can probably be assigned to the ligand-to-metal charge-transfer transitions²⁴.

Conclusion

A new 2D silver (I) complex based on Hdcpa and bbbp ligands, $\{[\text{Ag}(\text{bbbp})(\text{dcpa})]\text{H}_2\text{O}\}_n$, has been synthesized and structurally characterized. This successful preparation of the title compound indicates that the bbbp can be an excellent candidate for the construction of supramolecular complexes. Complex **1** emits the intensely luminescence with the fluorescence of 503 nm in the solid state at room temperature.

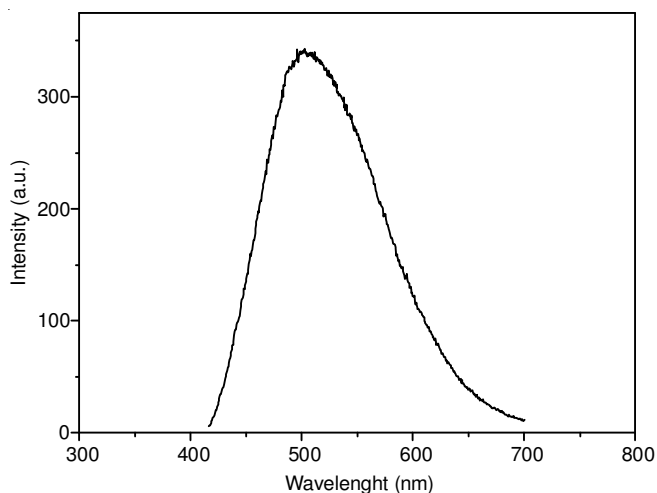


Fig. 5. Solid-state photoluminescent spectrum of complex 1

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