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Structural variation in silver(I) complexes with pyridazine ligand and aromatic polycarboxylic acids: Structural analysis with silver chains

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ABSTRACT

To systematically explore the influence of pyridazine ligands and aromatic polycarboxylate on the existence of argentophilicity, four inorganic–organic hybrid Ag(I) complexes were obtained by one-pot ultrasonic reaction. Four complexes were named $[Ag_6(pdz)_2(btc)_2]_n$ (**1**), $[Ag_2(pdz)(npt)]_n$ (**2**), $[Ag_2(pdz)(pma)_{1/2}]_n$ (**3**), and $[Ag_2(pdz)(npa)\cdot H_2O]_n$ (**4**) (pdz = pyridazine, H_3btc = 1,3,5-benzene tricarboxylic, H_2npt = 3-nitrophthalic acid, H_4pma = pyromellitic acid, H_2npa = 1,4-naphthalenedicarboxylic acid). Structural analyses reveal that complexes **1**–**4** display diverse 2D or 3D frameworks, which all of the N-donor pdz ligands exhibit the same coordination mode but the distances of the silver atoms which link to the pdz ligands are different to each other. Complex **1** shows Ag_6 clusters and the cluster is comprised by two distorted tetrahedron silver units. And the clusters are shared by two silver ions to form 1D silver chains. Complex **2** features 1D silver chains which are formed by the Ag_4 units and the four Ag(I) ions are in the vertices of parallelogram. Complex **3** is an interpenetrating architecture with the pdz ligands alternately repeating up and down in *ac* plane. The structure of complex **4** is a 2D layer structure which the pdz and npt ligands alternately repeat along *a* axis. Moreover, complexes **1**–**4** indicate different photoluminescence behaviors in the solid state.

1. Introduction

The past two decades have witnessed unprecedented progress in the synthesis of crystals with different sizes, shapes and compositions [1–4]. For the synthesis of coordination compounds (CCs), d^{10} metals are widely used because their flexible coordination sphere allows the generation of different kinds of supramolecular networks with ligands containing nitrogen or oxygen [5–9]. Silver(I) has a very flexible coordination sphere, which enables it to adopt coordination numbers from 2 to 6, resulting in its coordination sphere ranging from linear to octahedral, respectively. Polynuclear silver clusters are of special importance because of their novel structural motifs and various potential applications in catalysis, conduction, and luminescence [10–14]. Among these complexes, polynuclear clusters have attracted unparalleled attention because of their aesthetic appeal as well as properties [15–19], but the silver clusters predominate this family and the synthesis of 1D infinite chain containing the silver clusters remains highly demanding. However, how to construct appropriate crystal structures with infinite silver chains with silver clusters is the primary issue and using mixed ligands to create CCs with silver clusters is an important tactics these years [20–23]. From the previous studies, it seems that the rigid ligands are easier to generate distinctive structures than the flexible ones. Rigid ligands containing carboxyl group were studied intensely recently [24–28]. The rigid ligands with benzene ring often have fluorescence properties for $\pi\cdots\pi$ conjugation effect, and also have other unexpected nature after proper modification with mental ions [29–32]. In recent years, we have been interested in the construction of silver(I) complexes with infinite silver chains [33,34]. In the course of our research on the assembly of silver chains with clusters, our synthetic attempt under basic conditions led accidentally to the isolation of two novel complexes with polynuclear silver clusters which are containing 1D silver chains and two complexes with no silver chain, namely $[Ag_6(pdz)_2(btc)_2]_n$ (**1**), $[Ag_2(pdz)(npt)]_n$ (**2**), $[Ag_2(pdz)(pma)_{1/2}]_n$ (**3**), and $[Ag_2(pdz)(npa)\cdot H_2O]_n$ (**4**), assembled from the reaction of $AgNO_3$ and pdz and coligands which is represented in Scheme 1. Four complexes are characterized by elemental analysis, infrared spectroscopy, and X-ray powder diffraction. Furthermore, the crystal structures and photoluminescent spectra are investigated in detail.

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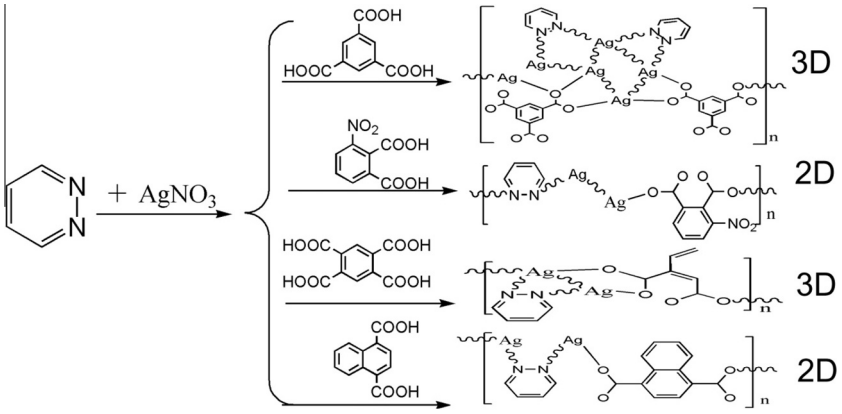

Scheme 1. The preparation route of Ag(I), pdz and coligands.

2. Experimental

2.1. Materials and methods

All chemicals and solvents which were used in the syntheses were of analytical grade and they were used without further purification. IR spectra were carried out on a Nicolet Avatar 330 FITR Spectrometer in the range of 4000–400 cm^{-1}. Elemental analyses (C, H, N contents) were measured on a CE instruments EA 1110 elemental analyzer. The solid-state photoluminescence measurements were carried out on a Hitachi F-7000 Fluorescence Spectrophotometer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu Kα radiation.

2.2. Syntheses

It is well-known that the reactions of Ag(I) with carboxylates and/or neutral ligands in aqueous solution often result in the formation of good crystals of complexes in ammoniacal conditions to slowdown of the reaction rate and enhancing solubility. In this paper, ultrasonic synthesis under the ammoniacal conditions has been used to synthesize these complexes, and good crystals of **1**–**4** for structural data collection can be obtained within 2 weeks.

2.2.1. Synthesis of complex $[Ag_6(pdz)_2(btc)_2]_n$ (**1**)

Reaction of $AgNO_3$ (33.4 mg, 0.2 mmol), pyridazine (pdz) (16.0 mg, 0.2 mmol) and 1,3,5-benzene tricarboxylic (H_3btc) (44.2 mg, 0.2 mmol) took place in H_2O–DMF (*N*,*N*-Dimethylformamide) solvents (6 ml, v/v = 1:1) in the presence of ammonia (0.5 mL, 14 M) under ultrasonic treatment (160 W, 40 kHz, 30 min) at 40 °C. The resultant colourless solution was allowed slowly to evaporate at room temperature in the dark. The yellow crystals of complex **1** were obtained after several days.

The crystals were isolated by filtration and washed by deionized water and ethanol and dried in the air. Yield based on Ag is 88%. Elemental analysis: *Anal.* Calc. for $Ag_6C_{26}H_{14}N_4O_{12}$: C, 25.563; H, 1.155; N, 4.586. Found: C, 25.37; H, 1.19; N, 4.65%. Selected IR peaks (cm^{-1}): 3283 (s), 2264 (w), 1863 (w), 1614 (s), 1557 (s), 1417 (s), 1360 (s), 1099 (m), 1060 (w), 972 (w), 920 (w), 767 (s), 716 (s), 660 (w), 514 (m), 455 (w).

2.2.2. Synthesis of complex $[Ag_2(pdz)(npt)]_n$ (**2**)

The synthesis of **2** was similar to that of complex **1**, but 3-nitrophthalic acid (H_2npt) was used instead of H_3btc. And light yellow crystals of **2** were obtained in 78% yield based on Ag. Elemental analysis: *Anal.* Calc. for $Ag_2C_{12}H_7N_3O_6$: C, 28.545; H, 1.397; N, 8.322. Found: C, 28.65; H, 1.41; N, 8.36%. Selected IR peaks (cm^{-1}): 3410 (m), 3085 (m), 2970 (w), 2849 (w), 1964 (w), 1595 (s), 1519 (s), 1455 (s), 1372 (s), 1290 (s), 1156 (m), 1060 (m), 965 (m), 920 (s), 819 (s), 787 (m), 748 (s), 710 (s), 684 (s), 583 (w), 545 (w), 424(m).

2.2.3. Synthesis of complex $[Ag_2(pdz)(pma)_{1/2}]_n$ (**3**)

The synthesis of **3** was similar to that of complex **1**, but pyromellitic acid (H_4pma) was used instead of H_3btc. And clear yellowish crystals of **3** were obtained in 81% yield based on Ag. Elemental analysis: *Anal.* Calc. for $Ag_2C_9H_5N_2O_4$: C, 25.684; H, 1.197; N, 6.656. Found: C, 25.59; H, 1.28; N, 7.06%. Selected IR peaks (cm^{-1}): 3410 (m), 3072 (w), 3010 (w), 1576 (s), 1481 (m), 1411 (s), 1315 (m), 1264 (m), 1131 (m), 1054 (w), 972 (m), 920 (w), 857 (m), 805 (m), 767 (m), 670 (m), 576 (w), 525 (m), 435(m).

2.2.4. Synthesis of complex $[Ag_2(pdz)(npa)\cdot H_2O]_n$ (**4**)

The synthesis of **4** was similar to that of complex **1**, but 1,4-naphthalenedicarboxylic acid (H_2npa) was used instead of H_3btc. And clear light brown crystals of **4** were obtained in 78% yield based on Ag. Elemental analysis: *Anal.* Calc. for $Ag_2C_{16}H_{12}N_2O_5$: C, 36.396; H, 2.291; N, 5.305. Found: C, 36.33; H, 2.44; N, 5.42%. Selected IR peaks (cm^{-1}): 3423 (m), 3066 (w), 1654 (w), 1551 (s), 1455 (m), 1404 (s), 1360 (s), 1251 (m), 1207 (w), 1163 (w), 1054 (w), 1028 (w), 972 (w), 869 (w), 819 (m), 799 (m), 658 (w), 570 (m), 427(w).

2.3. X-ray crystallography

Crystals of the complexes **1**–**4** with appropriate dimensions were sticked to a glass fiber and used for data collection. Data were collected on a Rigaku R-AXIS RAPID Imaging Plate single-crystal diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å) operating at 50 kV and 90 mA in ω scan mode for **1**–**4**. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program [35]. In all cases, the highest possible space group was chosen. The crystal structures were solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 [36] and SHELXL-97 [37] within OLEX2 [38].

Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. The hydrogen atoms attached to oxygen were refined with O–H = 0.85 Å, and $U_{iso}(H) = 1.2U_{eq}(O)$. Non-hydrogen atoms were refined with anisotropic thermal parameters. The crystallographic details of **1**–**4** are provided in Table 1. Selected bond lengths and angles for **1**–**4** are collected in Table S1.