Zigzag Double-Strands Consisting of "Coordination-Gallery, $[Ag_3(NO_3)_3(Py_2S)_2{\bullet}2H_2O]$"

Ok-Sang Jung,* Sung Ho Park, Chul Hee Park, and Jong Ku Park†
Materials Chemistry Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
†Ceramic Processing Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

(Received May 31, 1999; CL-990458)

Zigzag silver(I) single-strands connected by 4,4'-dipyridyl sulfide are bridged via weak π–π and Ag^I-Ag^I interactions to generate subtle double-strands that exhibit the most plentiful and characteristic coordination modes. The compound gives an intense and broad emission (λ_{max} at 561 nm) which is yellow luminescence.

Interest in coordination polymers from multifunctional spacers and transition metals has stimulated by the possibility that desirable molecular materials such as electrical conductors,[1] molecular magnets,[2] host-guest molecules,[3] and crystal bending materials[4] may be engineered. Weak intra- or intermolecular interactions such as hydrogen bondings, π–π, and metal-metal interactions can often give rise to unusual supramolecular aggregates.[5] Though the discovery of unprecedented molecular structures is usually serendipitous, a number of intriguing motifs have been constructed by rational strategy based on designed building blocks.[6] A noninnocent 4,4'-dipyridyl sulfide (Py_2S)[7] possesses a magic angle (C-S-C, ~100°), conformational nonrigidity, and potential tridentate donating atoms (N,N',S-). We now describe a "coordination-gallery" double-strand which is obtained by the self-assembly of $AgNO_3$ (**1**) and Py_2S (**2**).

Careful layering of **1** in methanol and **2** in chloroform affords beige-colored crystals at the interface.[8] The product is air-, light-stable, and insoluble solids in water and common organic solvents. A coordination polymer of the building block $[Ag_3(NO_3)_3(Py_2S)_2{\cdot}2H_2O]$ (**3**) was established by X-ray characterization[9] (Figure 1). Each **2** ligand connects two silver(I) ions to give zigzag single-strands. The two strands are bridged via weak Ag-Ag[10] and π–π interactions[5] to generate zigzag double-strands. The Ag(1)···Ag(2) distance (3.436(2) Å) is similar to that (3.493(1) Å) of $[Ag(imid)_2]_6{\cdot}6ClO_4$,[11] but much longer than general Ag^I-Ag^I interactions (2.50 - 3.00 Å).[10] Such weak interactions seems to be partially due to Coulomb repulsion between two formal cations induced by the migration of their counteranions to the Ag(3) ion. The Ag(1)···Ag(2) distance is much shorter than the S···S (4.26 Å), N···N, and C(3)···C(13) distances, which is indirect evidence of the interactions. Within the double-strand, two pyridine groups concomitantly interact via face-to-face (π–π) interactions (plane-plane angles 11.17°, 27.96°; N···N, 3.65 Å, 3.83 Å; C(3)···C(13), 4.03 Å). The N(1)-Ag(1)-N(2) angle is linear (175.9(4)°) while the N(3)-Ag(2)-N(4) angle is severely bent (156.4(4)°). Thus, the Ag(2) geometry is distorted toward tetrahedron in contrast to the T-shape Ag(1): a water molecule occupies the fourth site of Ag(2) (Ag(2)···O(w2), 3.20 Å). The Ag(3) geometry is a distorted octahedral arrangement with one sulfur, isobidentate nitrate (Ag(3)-O(7), 2.63(1) Å; Ag(3)-O(8), 2.62(1) Å), anisobidentate nitrate (Ag(3)-O(2), 2.44(1) Å; Ag(3)-O(3), 2.63(1) Å), and monodentate nitrate (Ag(3)-O(6), 2.46(1); Ag(3)···O(4), 2.97(1) Å). The coexistence of three nitrate bonding modes around a silver ion is very rare. More surprising feature is that one **2** is coordinated to the Ag(2) and Ag(1)' atoms in an N,N'-bidentate while the other **2** is bonded to the Ag(1), Ag(2)', and Ag(3) atoms in an N,N',S-tridentate, (Ag(3)-S(1) 2.564(3) Å; Ag(3)···S(2), 3.49 Å). Thus, the bent

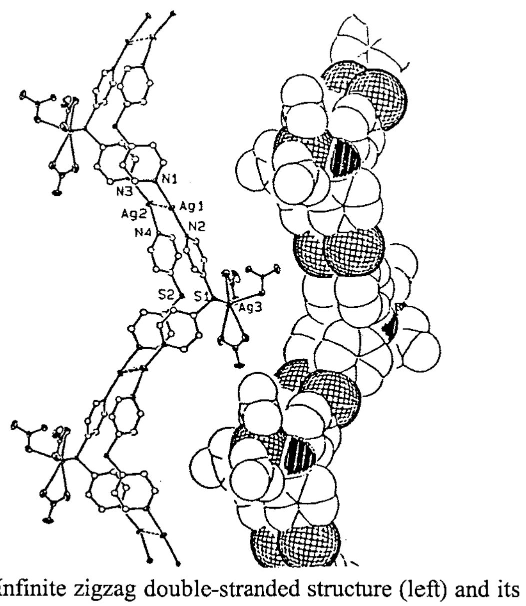

Figure 1. Infinite zigzag double-stranded structure (left) and its space-filling view (right) of **3**. Solvate water molecules and hydrogen atoms are omitted for clarity.

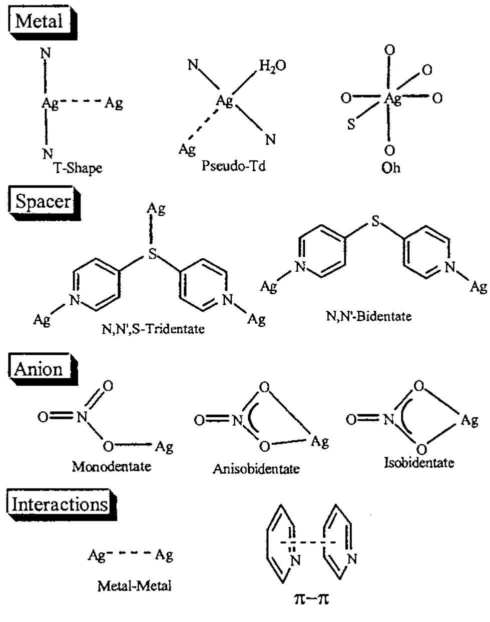

Figure 2. The most plentiful coordination features of **3**.

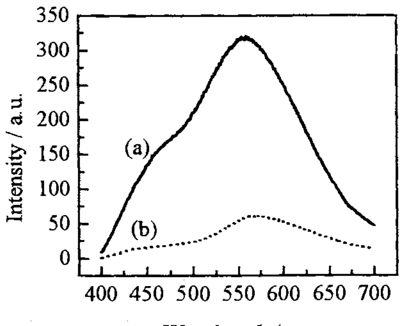

Figure 3. The solid-state emission spectra of **3** (a) and **2** (b).

angle of the S(1) atom (C-S-C, 104.4(4)°) is slightly contracted compared with the corresponding angle of the S(2) atom (C-S-C, 107.8(5)°) which is shielded by the three nitrate groups bonded to the Ag(3) ion. This may contribute to the slightly unsymmetrical zigzag structure. The silver-silver separation through a **2** ligand is 11.543 Å. There are no significant interactions between adjacent double-strands (Ag···Ag, 11.142 Å; S···S, 10.274 Å). To our knowledge, the most abundant and subtle features of **3** are displayed in Figure 2.

The emission spectra of **3** along with **2** for comparison were measured in the solid state (Figure 3). Excitation at 366 nm gives an intense and broad emission (λ_{max} at 562 nm; shoulder at 469 nm) which is clearly yellow luminescence to the human eye. The emission is much more intense than that of **2**, but the shape is similar to that (λ_{max} at 568 nm) of **2**. The process of the intense emission may be triggered by the conformational changes of the **2** unit via the face-to-face interactions relative to free **2** that obstructs the delocalization between the π-electrons of the sulfur atom and the π-system of both pyridine rings.[12] The Ag-Ag interactions[13] and metal-mediated interligand delocalizations also may enhance the luminescent properties. Considering various factors including anions and solvate molecules, further experiments aimed at rational synthesis, structure-properties relationships, and pervasive applications are in progress.

In conclusion, we have prepared an unprecedented "coordination gallery" double-strand that provides the most plentiful coordination modes. Understanding the key factors may be devoted to the development of rational strategies of materials that exhibit desirable photophysical properties.

Notes and References

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8 **3**: a methanolic solution (15 ml) of **1** (128 mg, 0.75 mmol) was slowly layered into a chloroform solution (10 ml) of **2** (94 mg, 0.50 mmol). Beige-colored crystals, **3**, began to form at the interface, and were obtained in 3 days in 75% yield. Anal. found: C, 27.60; H, 2.28; N, 11.42%. Calcd. for $C_{20}H_{20}N_7O_8S_2Ag_3$: C, 27.48; H, 2.31; N, 11.22%. The TGA and DSC traces suggest that the water molecules were evaporated in the wide range of 60 - 140 °C. Abrupt weight loss corresponding to **2** (obsd 41.7%, calc. 40.9%) was observed at 256 °C.
9 Crystal data for $C_{20}H_{20}N_7O_8S_2Ag_3$ **3**: M = 918.13, monoclinic, a = 9.345(1) Å, b = 22.190(6) Å, c = 14.243(3) Å, β = 107.399(1)°, U = 2818(1) Å^3, T = 293(2) K, space group $P2_1/c$, Z = 4, D = 2.164 g/cm^3, μ (Mo-K) = 2.282 mm^{-1}, 3215 reflections measured, 3031 unique (R = 0.0247) which were used in all calculations. $R1$ = 0.0603 ($wR2$ = 0.1683), GOF = 0.812 for 388 parameters.
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