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Structural characterization and luminescence behavior of a 2D silver (I) coordination polymer assembled from pyridine-2,6-dicarboxylic acid N-oxide

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Abstract

A 2D network complex $[Ag_2(pydco)]_n$ (1) (pydco = pyridine-2,6-dicarboxylic acid N-oxide) was synthesized and structurally characterized. Fluorescence spectrum of complex 1 and the free ligand indicates that the cooperative association of Ag–Ag contacts and the intraligand (π – π^*) interactions lead to the unusual intense fluorescent emission upon photoexcitation. © 2006 Elsevier B.V. All rights reserved.

Keywords: Coordination polymer; Ag-Ag contacts; Silver strings; Fluorescence spectrum; X-ray structure

Design and synthesis of inorganic-organic composite coordination polymers exhibiting novel structures and properties have provided exciting new prospects [1,2]. In principle, some control over network topology can be gained by judicious selection of reaction-influencing factors, such as the chemical structure of the organic spacers (ligands), the coordination geometry preference of the metal, the inorganic counterions, and the metal-to-ligand ratio [3].

Pyridine-2,6-dicarboxylic acid N-oxide (pydco) (Chart 1)a has limited steric hindrance and weak stacking interactions and can offer possibilities to form coordination polymers through a carboxylate and N-oxide bridge, which is a far better electron donor than the ring nitrogen atom of pyridine-2,6-dicarboxylic acid [4,5]. Although recently Meng and his co-workers have reported some d^{10} metalorganic framework structures assembled from it [5], its coordination chemistry has not been well explored [5–7]. Therefore, much more work is required to extend our knowledge of the ligand's coordination behavior and its

coordination polymers' properties. On the other hand, silver(I). Salts are often used in forming supramolecular architectures because silver(I) is a labile coordination center and can easily form complexes with coordination numbers of 2, 3, or 4 and even more as needed to form many different architectures [8]. Moreover, the potential Ag–Ag interactions can affect the structures and properties of the resulting coordination polymers [9]. Herein, we report the synthesis, X-ray single crystal structure and luminescent property of a strong fluorescent emission silver(I). Coordination polymeric complex $[Ag_2(pydco)]_n$ (1), containing 1D infinite silver strings constructed by Ag–Ag contacts in it.

Aqueous and CH₃OH mixed solution of Na₂(pydco) layered upon an aqueous solution of AgAc (Ac = CH₃COO⁻) at room temperature yielded colorless crystals [10]. The compound is stable in light and is insoluble in common solvents except water. The crystallographic studies revealed that complex 1 exists in the solid state as a 2D polymer [11]. Fig. 1 depicts the coordination environment around Ag(I). There are two kinds of Ag(I) atoms in 1. The first Ag(I) center (Ag2H) exhibits a distorted tetrahedral coordination environment formed by two oxygen atoms from two different pydco ligands' carboxylate and two oxygen donors from the third ligand that is a

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Chart 1. (a) Pydco; (b) coordination mode of pydco ligand in complex 1.



Fig. 1. View of Ag(I) coordination environment and 2D molecular structure of complex 1, H atoms are omitted for clarity.

carboxylate oxygen atom and the N-oxide. The Ag-O bond lengths range from 2.287(3) to 2.552(4) Å, and O-Ag–O bond angles range from 78.25(10) to 147.26(11)°. The second Ag(I) center (Ag1J) adopts a {AgO₅} coordination sphere, which consists of four carboxylate O-donor from four different ligands and one O-donor from a N-oxide group. Although similar coordination spheres $\{AgN_5\}, \{AgN_2O_3\}$ have been found in schiff-base complexes and others such as {AgN₄O}, {AgN₂S₃} [3a, 12, 13], to the best our knowledge, $\{AgO_5\}$ coordination fashion based on organic aromatic polycarboxylate ligands has not been reported, All the Ag-O bond lengths are close to the first one, excepting one that is Ag(1J)-O(2AE) (2.652(3) Å) is longer than the others but resembles those were found in other silver(I) complexes [3a,14], and O-Ag-O bond angles range from 74.25(10) to $160.28(7)^{\circ}$.

The N-oxide group of all pydco exhibit bridging coordination mode, while carboxylate group is coordinated to Ag atoms in an unprecedented coordination fashion, different from the monodentate mode in previous reports [5–7]. That is within a pydco ligand, an oxygen atom exhibiting $\mu_{1,1}$ -O mode bridging two Ag(I), while an oxygen atom of the sec-

ond carboxlate adopting $\mu_{1,1,1}$ -O mode bridging three Ag(I), the other two monodentates. So each ligand links seven silver ions (Chart 1)b. To this end, there are tetranuclear units in 1 and each unit contains a 12-membered metallorganic cycle which is composed of two pydco and two silver atoms, each cycle was linked through pyridyl N-oxide groups to form 1D chain (Fig. 2). Furthermore, bridging oxygen atoms of pydco extended adjacent chains through coordinating to the silver(I) of the tetranuclear units to generate a 2D coordination polymer (Fig. 2 and 3). However, the 3D supramolecular structure is formed via π - π interactions of the adjacent pyridine rings are 3.576 and 3.713 Å and angles are the same as 79.26°).

It is worthwhile to point out that in this 2D coordination polymer, there are two kinds of short ligand-supported Ag-Ag contacts (Ag1H-Ag1H = 2.981 Å, Ag1J-Ag2H = 3.314 Å) as they all below the van der Waals diameter of silver (3.44 Å) [15]. Interestingly, silver ions are linked into 1D infinite silver strings (Ag1H-Ag2H-Ag1J-Ag2J) via two kinds of alterative Ag-Ag interactions. These silver strings probably intensify the links from 1D chain to 2D network. Ag \cdots Ag distances of adjacent silver strings (3.597 and 3.625 Å) are slightly longer than the van der Waals diameter of silver, so they lack inter-string Ag-Ag interactions.

2D fluorescence spectroscopy of complex 1 in the solid state at room temperature was investigated as shown in Fig. 4. There is a very strong emission band in range of



Fig. 2. View of the 1D chain in 2D network of 1 in ab plane.



Fig. 3. Packing view of 1 along the *b*-axis. Green = Ag, blue = N, red = O, gray = C.



Fig. 4. 2D fluorescence spectrum of complex 1 in the solid state at room temperature.

374–421 nm upon photoexcitation from about 230 to 255 nm. There are also relatively weak emission at about 454 and 473 nm (excitation wavelength: 211 nm). According to the literatures, complexes with Ag–Ag interactions show emission in similar energy [3a,16–18]. Experimental and theoretical results have proved that Ag–Ag interaction is significant for the formation of luminescent species [16,19]. Interestingly, similar emissions are observed for the free pydco at 398 nm ($\lambda_{Ex} = 260$ nm) (Fig. 5) and other d^{10} metal-organic framework structures from pydco [5]. Complex 1 significantly intensifies the emission intensity of the free pydco (almost decuple), and displays a very strong fluorescent emission bands. The unusual strong emission of 1 maybe indicate that the cooperative associa-



Fig. 5. Photoinduced emission spectrum of pydco in the solid state at room temperature ($\lambda_{Ex} = 260$ nm).

tion of the intraligand $(\pi - \pi^*)$ fluorescent emission and the existence of Ag–Ag interactions.

In conclusion, we have demonstrated here a luminescent silver(I) complexes with fluorescent pydco. Both pydco and silver ions display an interesting coordination fashion, and two kinds of alterative Ag–Ag interactions link Ag(I) ions into 1D infinite silver strings in the 2D network.

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Appendix A. Supplementary material

Crystallographic data for the complex 1 have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-294847). These data can be obtained free of charge at www.ccdc.cam.a-c.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.03.019.

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- [10] 10 mL aqueous and CH₃OH (1:1) mixed solution of Na₂(pydco) (0.1 mmol) was carefully layered upon an aqueous solution (10 mL) of AgAc (Ac = CH₃COO⁻) (0.1 mmol). The resulting solution was

allowed to stand undisturbed at room temperature for several weeks, yielding colorless crystal. Yield: 50%. Anal. Calc. for $C_7H_3Ag_2NO_5$: C, 21.19; H, 0.76; N, 3.53. Found: C, 21.04; H, 0.74; N, 3.46%. IR data (KBr, cm⁻¹): ν (aryl-H)3675(w), 3424(vs); ν (C=C)2921(w), 2850(w); $\nu_{asym}(CO_2)1630(s)$, 1594(s); $\nu_{sym}(CO_2)$ 1467(m), 1396(m), 1351(s); ν (N=O)1174(m). 1 was decomposed at about 250 °C.

- [11] Diffraction measurement for 1 were made on a Rigaku AFC7R X-ray diffractometer, Crystal data for $C_7H_3Ag_2NO_5$ ($M_r = 396.84$): 296(2) K, monoclinic, space group P2₁/c, a = 8.4081(10) Å, b = 5.2424(6) Å, c = 18.337(2) Å, $\beta = 90.91(2)^\circ$, V = 808.19(16) Å³, Z = 4, $F(000) = 744 \rho_{calcd} = 3.261 \text{ mg/m}^3$, $\mu = 4.843 \text{ mm}^{-1}$, GOF on $F^2 = 1.069$, $R_{int} = 0.0185$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0257$, w $R_2 = 0.0613$ (*R* for all data: $R_1 = 0.0289$, w $R_2 = 0.0624$).
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