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Short communication

Synthesis, crystal structures and photoluminescences of silver(I) complexes with chelating carboxylic and pyrazine derivatives

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ABSTRACT

Four mixed-ligand silver(I) coordination polymers (CPs) $\{Ag_2(tpyz)(L)\}_n$ (**1**), $\{Ag_4(tpyz)_2(L)_2\}_n$ (**2**), $\{Ag_2(mpyz)(L)\}_n$ (**3**) as well as its isomer (**4**), (tpyz-2,3,5-trimethylpyrazine, mpyz = 2,3,5,6-tetramethylpyrazine, H2L = (+)-camphoric acid), were synthesized with reactions of L and pyrazine derivatives with silver nitrate in different solvent systems. Systematic characterizations with single-crystal X-ray diffraction indicate that, **1** and **3** show a 3D framework which constructed by silver(I) and L anion, the pyrazine derivatives only give one N to connect to metal, which may be due to the disorder of the methyl which shares the same carbon with carboxylate; **2** and **4** demonstrate a 2D 4^4–sql network. The difference between two: one structure is single layer and the other is double layer. Furthermore, **4** contains a 1D helical chains which connected by Ag(I) and mpyz ligand. Meanwhile, the L anion exhibits different coordination modes in **1**–**4**. **1**–**4** spanning from two-dimensional network to three-dimensional framework suggest that the kinds of pyrazine derivatives and solvents play significant roles in the formation of such coordination architectures. The thermogravimetric analyses (TGA), IR, and photoluminescence were also measured.

1. Introduction

In recent years, the research in metal-directed coordination polymers (CPs) has been rapidly expanding. One aspect is their fascinating structural diversity. So far, one to three-dimensional CPs have been found, like *T*-shaped [1], ladder [2], zigzag [3], helicities [4], brick wall [5], square [6], honeycomb [7], octa-hedral [8] and other uncommon CPs. Another aspect is their potential application properties, such as catalysis [9–11], non-linear optics (NLO) [12,13], luminescence [14–16], gas storage [17–19], magnetism [20–22] and ferroelectricity [23–25]. A successful strategy in constructing such framework is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more new materials. Considering various organic linkers, we select (+)-camphoric acid as auxiliary ligand, which possesses two carboxyl groups. Carboxyl group can be completely deprotonated and can coordinate with Ag(I) in diversified coordination modes, such as monodentate, bridging, chelating and so on.

Multi-dentate ligands like rode-like rigid spacers are usually employed to bridge between metal centers to form polymeric structures by covalent bonds such as 4,4′-bipyridine [26,27], thiocyanate [28,29] and so on. Here, we introduce two linear *N*-donor ligands, 2,3,5-trimethylpyrazine, and 2,3,5,6-tetramethylpyrazine, into the Ag(I) system to explore the influence of *N*-donor ligand on the structural topologies.

On the other hand, solvent [30–33] systems may also play a critical role in the structural direction of CPs in the assembly processes, especially for those with metal and neutral ligand. Here we synthesized four new CPs: $\{Ag_2(tpyz)(L)\}_n$ (**1**), $\{Ag_4(tpyz)_2(L)_2\}_n$ (**2**), $\{Ag_2(mpyz)(L)\}_n$ (**3**) and its isomer (**4**), (tpyz-2,3,5-trimethylpyrazine, mpyz = 2,3,5,6-tetramethylpyrazine, H2L = (+)-camphoric acid). The crystal structures of the four new CPs were determined by single crystal and powder X-ray diffractions. The results reveal that these complexes exhibit unique frameworks, in which L ligand displays different binding modes, influenced by the nature of *N*-donor ligand and the effect of mixed-solvent systems. Infrared spectra(IR), elemental analyses, thermogravimetry, photoluminescences of all compounds were measured.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were commercially available and used as purchase without further purification. The FT-IR spectra were recorded on a Nicolet AVATAT FT-IR 360 spectrometer as KBr pellets in the frequency range 4000–400 cm $^{-1}$. Elemental analyses of C, H, O and N were performed on a CE instruments EA 1110 analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a SDT Q600 instrument in room temperature to 800 °C at a heating rate of 10 °C min $^{-1}$

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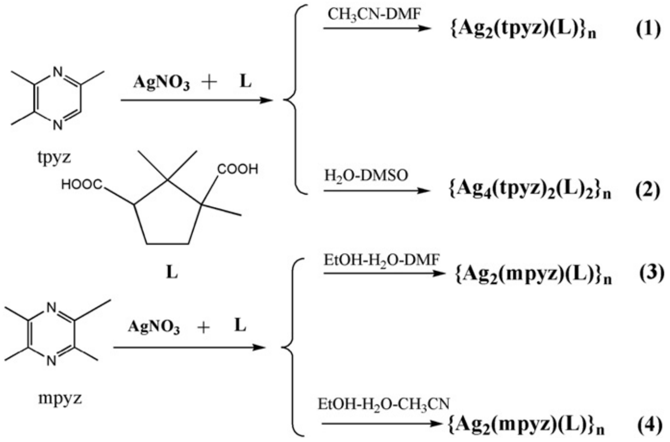

Fig. 1. The synthetical route of Ag(I) complexes with *N*-donor ligands and carboxylates in different mixed solvents.

under N2 atmosphere. All fluorescence data were collected on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

All diffraction data were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer using graphite monochromated Mo—K $_\alpha$ radiation source (λ = 0.71073 Å) operating at 50 kV and 90 mA in ω scan mode. In the process, the crystal was protected by liquid nitrogen at 173 K. Absorption corrections were applied using the multi-scan with the ABSCOR program [34]. The powder X-ray diffractions (PXRD) data of the samples were measured on a Panalytical X-Pert pro diffractometer with Cu—K $_\alpha$ radiation. The calculated PXRD patterns were obtained from the single-crystal diffraction data.

The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2, using SHELXS-97 [35]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on carbon and nitrogen atoms were positioned geometrically and refined using a riding mode (C—H 0.96 Å). Addsym subroutine of PLATON [36] to assure that no additional symmetry could be applied to the models. The phase purity of the synthesized **1**–**4** was confirmed by powder X-ray diffraction (PXRD) measurements. As shown in Figure S1, each PXRD pattern of the as-synthesized sample is consistent with the simulated one, which is indicative of phase purity of the products(Figure S1).

The synthetical route of the compounds is shown in Fig. 1.

2.2. Synthesis of complex {Ag2(tpyz)(L)}_n (1)

AgNO3 (34.2 mg, 0.2 mmol), tpyz (38 ml, 0.2 mmol) and H2L (313.6 mg, 0.2 mmol) were took place in CH_3CN-DMF (*N*,*N*-dimethylformamide) mixed solvent (6 ml, *v*/*v*: 3/3) under stirring. Then, ammonia (14 M, 10 d) was dropped into the mixture to give a clear solution under ultrasonic treatment (160 W, 40 KHz, 30 min) at room temperature. The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to give irregular-yellow crystals of **1** (Yield: 32%, based on Ag). Anal. Calc. (found) for Ag2C17H23N2O4: C, 38.10 (38.16); H, 4.50 (4.33); O, 11.86 (11.96); N, 5.32 (5.24) %. IR (KBr): ν(cm $^{-1}$) = 3425 (s), 2977 (m), 2887 (w), 2175 (w), 1653 (m), 1545 (s), 1463 (m), 1392 (s), 1363 (s), 1322 (m), 1288 (m), 1207(w), 1170 (w), 1126 (w), 1085 (w), 997 (w), 919 (w), 804 (m), 628 (s).

2.3. Synthesis of complex {Ag4(tpyz)2(L)2}_n (2)

The synthesis of **2** was similar to that of **1**, but with H2O-DMSO (Dimethyl sulfoxide) in place of CH3CN-DMF. Block-orange crystals of **2** were obtained in 26% yield (based on Ag). Anal. Calc. (found) for Ag4C34H48N4O8: C, 37.94 (38.09); H, 4.61 (4.51); O, 11.90 (11.94); N, 5.31 (5.23) %. IR (KBr): ν(cm $^{-1}$) = 3401 (s), 2973 (m), 2879 (w), 2177 (w), 1646 (m), 1542 (s), 1463 (m), 1392 (s), 1365 (s), 1319 (m), 1288 (w), 1214 (w), 1170 (w), 1128 (w), 1083 (w), 995 (w), 919 (w), 798 (m), 620 (s).

2.4. Synthesis of complex {Ag2(mpyz)(L)}_n (3)

The synthesis of **3** was nearly similar to that of **1**, but with mpyz (274.8 mg, 0.2 mmol) in place of tpyz in H2O-DMF-EtOH mixed solvent.

Table 1
Crystallographic data for **1**–**4.**

Complexes	1	2	3	4
Formula	Ag2C17H23N2O4	Ag4C34H48N4O8	Ag2C18H25N2O4	Ag2C18H26N2O4
Formula weight	535.12	1024.36	549.15	550.15
Temperature/K	173(2)	173(2)	173(2)	173(2)
Crystal system	Tetragonal	Monoclinic	Tetragonal	Monoclinic
Space group	$I4_1/a$	$P2_1$	$I4_1/a$	$P2_1$
a /Å	19.435(2)	9.9997(5)	19.9320(5)	6.7631(5)
b /Å	19.435(2)	10.9527(5)	19.9320(5)	15.5414(5)
c /Å	20.2563(12)	17.698(3)	19.996(3)	9.858(3)
α / °	90	90	90	90
β / °	90	103.05	90	104.626
γ / °	90	90	90	90
Z	16	2	16	2
V /Å ^{3}	7651.2(12)	1888.3(3)	7944.1(12)	1002.6(3)
ρ_{calc}/mg·mm $^{-3}$	1.8581	1.802	1.8365	1.8223
μ /mm $^{-1}$	16.626	16.839	16.031	15.879
F(000)	4255	969	4383.8	550
No. of unique reflns	36,812	18,130	36,820	9833
No. of obsd reflns [I>2σ(I)]	4354	8159	4531	4503
Parameters	241	433	249	163
GOF	0.887	1.055	1.024	1.004
Final R indices [I>2σ(I)]	$R_1 = 0.0664$ $wR_2 = 0.1513$	$R_1 = 0.0861$ $wR_2 = 0.1834$	$R_1 = 0.0656$ $wR_2 = 0.1377$	$R_1 = 0.0559$ $wR_2 = 0.1258$
R indices (all data)	$R_1 = 0.0686$ $wR_2 = 0.1523$	$R_1 = 0.1495$ $wR_2 = 0.2348$	$R_1 = 0.0809$ $wR_2 = 0.1526$	$R_1 = 0.0822$ $wR_2 = 0.1597$
Largest diff. peak and hole (eÅ $^{-3}$)	0.97 and −1.07	1.08 and −1.85	1.26 and −2.21	1.88 and −1.77