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Synthesis, characterization and antibacterial activity of a new silver(I) complex based on a flexible dicarboxylic acid ligand

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A novel silver(I) complex sustained by a flexible dicarboxylic acid ligand, $[Ag_2(L)]_n$ (**1**, H_2L = 2,2′-{[1,2-phenylenebis(methylene)]-bis(sulfanediyl)}dibenzoic acid), has been synthesized and structurally characterized. In **1**, four *anti* conformation L^{2-} ligands bind three silver(I) ions to form a trinuclear subunit through S···Ag and Ag···Ag interactions, and then those trinuclear subunits are further extended to an infinite 1D silver(I) chain through the *anti* L^{2-} ligands. Thus, the thermal stability, luminescent behavior and antibacterial activity of **1** were also discussed.

1. Introduction

The past decade have witnessed the boom of metal-organic coordination complexes(MOCCs), due to their intriguing topologies and potential functional applications in the fields of storage and separation, magnetism, catalysis, luminescence and membrane [1–6]. As we know that much attention has been focused on the assembly of MOCCs based on a rigid carboxylate and N-containing ligands, however, the systemic research of flexible carboxylate ligand in the construction of metal–organic coordination systems is somewhat rare [7]. Flexible counterparts can transform their conformations to match the coordination requirements of the metal center. This can give a richer variety of structures than found for a rigid-ligand equivalent. Among various flexible ligands, multicarboxylates containing $-CH_2-O-$ or $-CH_2-S-$ arms have attracted great interests [8]. Recently, Sun's group have reported four metal–organic complexes based on three flexible dicarboxylic acid ligands and copper paddlewheel SBU [9], our group have also reported a mononuclear copper complex $Cu(NH_3)_3(L_6)]\cdot(H_2O)_{0.66}$ (**1**) (H_2L_6 = 2,2′-(1,2-phenylenebis(methylene))bis(sulfanediyl)-dibenzoic acid) and the complex could be dimerized to form a binuclear complex with an altered copper coordination geometry through thermal SCSC transformation or solid state reaction under dry grinding conditions [10].

On the other hand, compared to wildly used Zn, Cd, Cu transition and rare earth element during construction of MOCCs, silver-centered metal-organic coordination systems are also rarely investigated. Silver-containing complex appeared as antimicrobial agents since the middle age [11]. Because of their multi-targeting mechanism, silver-based antimicrobial agents are often applied to overcome bacterial resistance [12]. Silver(I) has shown to be able to inactivate proteins, bind to thiol groups and form stable Ag–S bonds. Silver ions are also able to change the structure of the bacteria cell wall, leading to changes in its mobility and stability and to a subsequent bacterial death, the mechanisms of action and resistance of silver ions have been intensively study by recent reviews [13]. It is reported that silver-centered complexes show higher antibacterial activity than silver ions, because of their synergistic effects between silver ions and organic ligands. Based on the considerations above, herein we reported a silver(I) complex based on a flexible dicarboxylic acid ligand(H_2L), and studied the photo- and biological properties of final complex.

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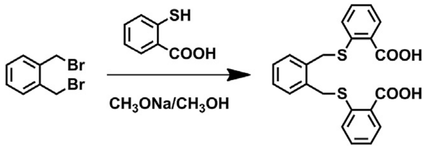

Scheme 1. The synthesis procedures of the H_2L in complex **1**.

2. Experimental procedure

2.1. Materials and methods

All the reagents and solvents employed were commercially available and used as received without further purification. H_2L was synthesized according to the procedure of Dai et al. [9] (Scheme 1). Infrared spectra were recorded on a Bruker VERTEX-70 spectrometer as KBr pellets in the frequency range 4000–400 cm^{-1}. The elemental analyses (C, H contents) were determined on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate with a dewar flask apparatus. TG curves were measured from 30 to 600 °C on a SDT Q600 instrument at a heating rate 10 °C/min under the N_2 atmosphere (100 mL/min).

2.2. Synthesis of $[Ag_2(L)]_n$

Three drops of NaOH (0.1 mL, 0.8 M) was added to a suspension of H_2L (0.015 g, 0.037 mmol) in H_2O (1 mL) to give a clear solution. $AgNO_3$ (0.030 g, 0.170 mmol) in MeOH (9 mL) was added to the clear solution, upon which lots of brown precipitate formed immediately. After three drops of $NH_3 \cdot H_2O$ (0.1 mL, 25–28%) was added, a colorless solution was generated after 10 min stirring, which was filtered and transferred to a test tube. After slow evaporation at room temperature for two months, large stick colorless crystals of **1** were formed (yield: 45%). Elemental analysis calcd (%) for **1**: C 42.30, H 2.56, N 10.25; found: C 42.02, H 2.52, N 10.11%. Selected IR peaks (cm^{-1}): 3395 (m), 2963 (m), 1590 (s), 1546 (s), 1399 (s), 1361 (m), 854 (w), 788 (m), 725 (w), 713 (m).

Table 1
Crystal data and structure refinement for complex 1.

Identification code	Complex 1
Empirical formula	$C_{22}H_{16}Ag_2O_4S_2$
Formula weight	624.21
Temperature/K	273.15
Crystal system	Monoclinic
Space group	C2/c
a/Å	20.2580(16)
b/Å	15.6777(13)
c/Å	13.6916(11)
α/°	90.00
β/°	106.7530(10)
γ/°	90.00
Volume/Å^3	4163.9(6)
Z	8
ρ_{calc}g/cm^3	1.991
μ/mm^{-1}	2.109
F(000)	2448.0
Crystal size/mm^3	0.2 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71000)
2Θ range for data collection/°	4.96 to 55.1
Index ranges	$-25 \le h \le 26$, $-20 \le k \le 20$, $-17 \le l \le 17$
Reflections collected	17457
Independent reflections	4806 [$R_{int} = 0.0276$, $R_{sigma} = 0.0280$]
Data/restraints/parameters	4806/0/273
Goodness-of-fit on F^2	1.021
Final R indexes [I ≥ 2σ (I)]	$R_1 = 0.0317$, $wR_2 = 0.0664$
Final R indexes [all data]	$R_1 = 0.0453$, $wR_2 = 0.0716$
Largest diff. peak/hole/e Å^{-3}	0.65/-0.60

Table 2
Selected bond distances (Å) and angles (°) for 1.

Ag1–O1	2.393 (2)	Ag2–O2^{i}	2.280 (2)
Ag1–O1^{i}	2.393 (2)	Ag3–S1	2.9161 (8)
Ag1–O3^{ii}	2.238 (3)	Ag3–S1^{iii}	2.9161 (8)
Ag1–O3^{iii}	2.238 (3)	Ag3–O1	2.501(2)
Ag2–S1	2.5333 (8)	Ag3–O1^{iii}	2.501(2)
Ag2–S2^{ii}	2.5428 (8)	Ag3–O1^{iv}	2.244(2)
O1^{i}–Ag1–O1	82.18 (10)	O3^{iii}–Ag1–O1	119.91 (9)
O3^{iii}–Ag1–O1^{i}	106.65 (9)	O3^{iii}–Ag1–O1^{i}	119.91 (9)
O3^{iii}–Ag1–O1	106.65 (9)	O3^{ii}–Ag1–O3^{iii}	117.22 (18)
S1–Ag2–S2^{ii}	135.84 (3)	O2^{i}–Ag2–S1	120.02 (9)
O2^{i}–Ag2–S2^{ii}	101.21 (8)	S1–Ag3–S1^{iii}	180.0
O4^{ii}–Ag3–O1	97.89 (9)	O4^{iv}–Ag3–O1^{iii}	97.89 (9)
O4^{iv}–Ag3–O1	82.11 (9)	O4^{ii}–Ag3–O4^{iv}	180.000 (1)

Symmetry codes: (i) −x + 1, y, −z + 1/2; (ii) x, −y + 2, z − 1/2; (iii) −x + 1, −y + 2, −z + 1; (iv) −x + 1, y, −z + 3/2; (v) x, −y + 2, z + 1/2.

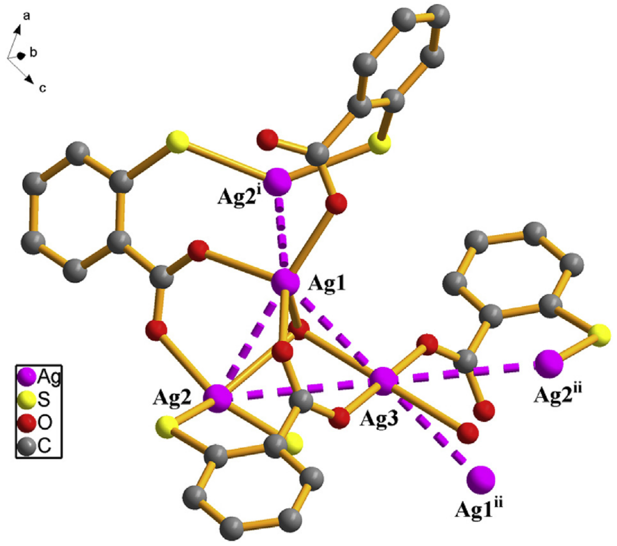

Fig. 1. The coordination environment around Ag(I) ions in **1**, all hydrogen atoms are omitted for clarity and Ag···Ag interactions highlighted by purple dashed lines][symmetry code: (i) 1−x, y, 0.5−z; (ii) 1−x, 2−y, 1−z].

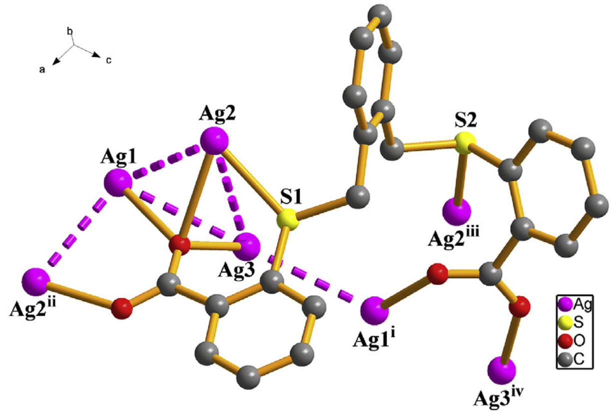

Fig. 2. The coordination environment H_2L ligand in **1**, all hydrogen atoms are omitted for clarity and Ag···Ag interactions highlighted by purple dashed lines] [symmetry code: (i) 1−x, 2−y, 1−z; (ii) 1−x, y, 0.5−z; (iii) x, 2−y, 0.5 + z; (iv) 1−x, y, 1.5−z].