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Ag coordination compounds of a bifunctional diaminotriazine–imidazole ligand with various anions and solvents: Synthesis, structures, photoluminescence, and thermal properties

Hong-Xin Mei, Hua-Qi Huang, Ting Zhang, Rong-Bin Huang*, Lan-Sun Zheng

State Key Laboratory of Physical Chemistry of Solid Surface, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

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Six coordination compounds of Ag(I) and 2,4-diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine (L, Ag:L = 1:2) with different anions and solvents, namely, $[Ag(L)_2]\cdot(NO_3)\cdot4(H_2O)$ (**1**), $[Ag(L)_2]\cdot1/2(nds)\cdot(MeOH)\cdot(H_2O)$ (**2**, H2nds = 1,5-naphthalenedisulfonic acid), $[Ag(L)_2]\cdot1/2(nds)\cdot(MeOH)\cdot5/2(H_2O)$ (**3**), $[Ag(L)_2]\cdot1/2(nds)\cdot(CH_3CN)$ (**4**), $[Ag(L)_2]\cdot(ClO_4)\cdot(MeOH)\cdot(H_2O)$ (**5**), and $[Ag(L)_2]\cdot(ClO_4)\cdot2(H_2O)$ (**6**), have been synthesized and characterized by elemental analysis, IR, PXRD and X-ray single-crystal diffraction. In these compounds, each Ag(I) ion is ligated by two imidazole nitrogens to form a $Ag(L)_2$ unit. The anions and solvents determine hydrogen-bonding between the DAT groups links the $Ag(L)_2$ units whether to form chains in **1** and **2** or layers in **3**–**6**. In addition, thermogravimetric analysis (TGA) and luminescent properties of these compounds were also investigated.

1. Introduction

An important goal of crystal engineering is to get control over the preparation of crystalline materials so that their structures and properties are, at least to some degree, predictable. Thus researchers dedicate to produce architectures by virtue of wide-ranging possible molecular and supramolecular interactions. Research in this field has been dominated to date by the utilization of hydrogen bonds in organic crystals [1,2] and the coordinative bonds for coordination polymers [3]. Recently, the use of bifunctional ligands which can both bind metal ions and engage in reliable hydrogen bonds to direct molecular assembly has also received attention [4–10].

Melamine derivatives have been widely used for their brilliant supramolecular interaction abilities to build remarkable architectures which may lead to applications in host-guest chemistry, sensoring, anion recognition, catalysis, electronics and magnetism [11–18]. Moreover, the excellent H-bonding ability of diaminotriazinyl (DAT) moiety has been successfully used in some DAT based bifunctional ligands for crystal engineering [19–23]. These bifunctional ligands incorporate coordination groups, such as pyridine and imidazole, to bind metal ions to form coordination units with established constitutions, in addition, they incorporate DAT groups to direct intermolecular association with reliable hydrogen bonds. However, these studies of bifunctional ligands are restricted to rigid ones.

The reports of DAT based flexible ligands are still rare. Our previous work of a flexible diaminotriazine-imidazole ligand, 2,4-diamino-6-[2-(2-methyl-1-imidazolyl)ethyl]-1,3,5-triazine (L), reveals that the combination of Ag(I) and L in 1:1 M ratio leads to metallocycle and helical chain in which a triazine nitrogen cooperate with the imidazole nitrogen to complete the coordination sphere of Ag(I) ion and the DAT group further direct intermolecular association through double-complementary hydrogen bonds. As a continuation of this work, we carried out systematic investigations on the combination of Ag(I) and L in 1:2 M ratio in the presence of diverse anions and solvents. Herein, we report the syntheses and structures of six coordination compounds, namely, $[Ag(L)_2].(NO_3).4(H_2O)$ (**1**), $[Ag(L)_2]\cdot1/2(nds)\cdot(MeOH)\cdot(H_2O)$ (**2**, H_2nds = 1,5-naphthalenedisulfonic acid), $[Ag(L)_2]\cdot1/2(nds)\cdot(MeOH)\cdot5/2(H_2O)$ (**3**), $[Ag(L)_2]\cdot1/2(nds)\cdot(CH_3CN)$ (**4**), $[Ag(L)_2].(ClO_4).(MeOH).(H_2O)$ (**5**), and $[Ag(L)_2].(ClO_4).2(H_2O)$ (**6**). In these compounds, each Ag(I) ion is ligated by two imidazole nitrogens to form a $Ag(L)_2$

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* Corresponding author.
E-mail address: rbhuang@xmu.edu.cn (R.-B. Huang).

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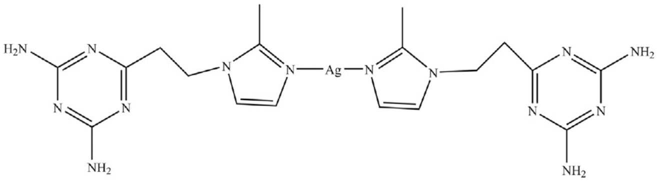

Scheme 1. The AgL_2 unit.

unit.(Scheme 1) The anions and solvents determine the hydrogen-bonding between the DAT groups links the $Ag(L)_2$ units whether to form chains in **1** and **2** or to form layers in **3**–**6**. In addition, photoluminescent properties of these compounds were also investigated.

2. Experimental

2.1. Materials and methods

All chemicals of analytical grade were purchased and used without further purification. Distilled H_2O was used in the reactions. Elemental analyses were carried out on a CE instrument EA 1110 elemental analyzer. IR spectra were recorded on a Nicolet 380 FTIR Spectrometer in the range of 4000– 400 cm^{-1} using KBr pellets. X-Ray single-crystal diffraction experiments were conducted on a Bruker-AXS CCD single-crystal diffractometer. X-Ray powder diffractions were collected on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. Thermogravimetric analyses were performed on SDT Q600 instrument from 20 to 800° C at the heating rate of 10° C/min under the N_2 atmosphere (100 mL/min). Photoluminescent properties were investigated on a Hitachi F-7000 Fluorescence Spectrophotometer with solid powder.

2.2. Preparation

2.2.1. [Ag(L)2].(NO3).4(H2O) (1)

A mixture of $AgNO_3$ (33.9 mg, 0.2 mmol), L (87.6 mg, 0.4 mmol) was stirred in methanol/water mixed solvent ($8\,mL, v/v{:}1/1$). Then, a aqueous NH_3 solution ($25\%, 2\,mL$) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was placed in darkness to evaporate slowly at room temperature for several days to afford colorless crystals of **1** (yield 62%, based on silver). Anal. Calc. (found) for $AgC_9H_13N_8O_3$: C 31.77 (31.98), H 5.04 (5.22), N 30.88 (30.96)%. Selected IR peaks (cm^{-1}): 3461 (s), 3346 (s, sh), 3112 (s), 1658 (s), 1550 (s), 1459 (s), 1415 (s), 1278 (m), 1135 (w), 1024 (w), 983 (w), 821(w), 676 (w).

2.2.2. $[Ag(L)_2]\cdot 1/2(nds)\cdot(MeOH)\cdot(H_2O)$ (2)

A mixture of Ag_2O (23.2 mg, 0.1 mmol), L (87.6 mg, 0.4 mmol) and $H_2nds.4H_2O$ (36.1 mg, 0.1 mmol) was stirred in methanol/water mixed solvent (8 mL, v/v: 1/1), and a aqueous NH_3 solution (25%, 2 mL) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was filtered and then placed in darkness to evaporate slowly at room temperature for several days to give colorless crystals of **2** (yield 41%, based on silver). Anal. Calc. (found) for $AgC_{24}H_{35}NO_5S$: C, 38.98 (38.76), H, 4.77 (4.65); N, 26.52 (26.71)%. Selected IR peaks (cm^{-1}): 3333 (s), 3112 (s), 1660 (s), 1634 (s), 1650 (s), 1498 (s), 1459 (s), 1417 (s), 1339 (m), 1279 (m), 1205 (s), 1160 (m), 1138 (m), 1047 (s), 982 (w), 941 (w), 820 (m), 769 (m), 692 (m).

2.2.3. $[Ag(L)_2]\cdot 1/2(nds)\cdot(MeOH)\cdot 5/2(H_2O)$ (3)

A mixture of Ag_2O (23.2 mg, 0.1 mmol), L (87.6 mg, 0.4 mmol), $NaClO_4$ (24.5 mg, 0.2 mmol) and $H_2nds.4H_2O$ (36.1 mg, 0.1 mmol) was stirred in methanol/water mixed solvent (8 mL, v/v: 1/1), and a aqueous NH_3 solution (25%, 2 mL) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was filtered and then placed in darkness to evaporate slowly at room temperature for several days to give colorless crystals of **3** (yield 45%, based on silver). Anal. Calc. (found) for $AgC_{24}H_{37}N_{14}O_{6.5}S$: C, 37.65 (37.44), H, 4.87 (4.65); N, 25.61 (25.50)%. Selected IR peaks (cm^{-1}): 3463 (s), 3413 (s), 3336 (s), 3150 (s), 1654 (s), 1550 (s), 1457 (s), 1405 (s), 1363 (m), 1279 (m), 1193 (s), 1159 (s), 1029 (s), 995 (m), 819 (m), 797 (m), 769 (m).

2.2.4. $[Ag(L)_2]\cdot 1/2(nds)\cdot(CH_3CN)$ (4)

Colorless crystals of **4** were prepared in a method similar to that of **2** with the replacement of methanol/water mixed solvent by Ref. CH_3CN/water mixed solvent (8 mL, v/v: 1/1). The preparation procedure had a yield of 45% based on silver. Anal. Calc. (found) for $AgC_{25}H_{32}N_{15}O_3S$: C, 41.10 (40.92), H, 4.41 (4.21); N, 28.76 (28.59)%. Selected IR peaks (cm^{-1}): 3432 (s), 3336 (s), 3127 (s, sh), 1636 (s), 1554 (s), 1459 (s), 1429 (m), 1376 (m), 1281 (m), 1204 (s), 1166 (m), 1038 (m), 988 (w), 815 (m), 767 (m), 745 (m).

2.2.5. [Ag(L)2].(ClO4).(MeOH).(H2O) (5)

Colorless crystals of **5** were prepared in a method similar to that of **2** with the replacement of $H_2nds\cdot 4H_2O$ by Ref. $NaClO_4$ (24.5 mg, 0.2 mmol). The preparation procedure had a yield of 52% based on silver. Anal. Calc. (found) for $AgC_{19}H_{32}ClN_{14}O_6$: C, 32.79 (32.57), H, 4.64 (4.35); N, 28.18 (28.37)%. Selected IR peaks (cm^{-1}): 3317 (s), 3111 (s), 1660 (s), 1540 (s), 1459 (s), 1416 (s), 1388 9s), 1339 (s), 1279 (s), 1148 (s), 1119 (s), 1073 (s), 1024 (s), 981 (m), 941 (w), 821 (m), 736 (w), 693 (w).

2.2.6. [Ag(L)2].(ClO4).2(H2O) (6)

A mixture of Ag_2O (23.2 mg, 0.1 mmol), L (87.6 mg, 0.4 mmol) and $NaClO_4$ (24.5 mg, 0.2 mmol) was stirred in Ref. CH_3CN/water mixed solvent (8 mL, v/v: 1/1), and a aqueous NH_3 solution (25%, 2 mL) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was filtered and then placed in darkness to evaporate slowly at room temperature for several days to give colorless crystals of **6** (yield 53%, based on silver). Anal. Calc. (found) for $AgC_{18}H_{30}ClN_{14}O_6$: C, 31.71 (31.98), H, 4.43 (4.25); N, 28.76 (28.87)%. Selected IR peaks (cm^{-1}): 3348 (m), 3161 (m), 1645 (s), 1557 (s), 1533 (s), 144 (m), 1384 (s), 1330 (m), 1293 (m), 1193 (m), 1147 (m), 1108 (m), 1023 (m), 813 (m).

2.3. X-Ray crystallography

Single crystals of **1**–**6** with appropriate sizes were chosen under an optical microscope and then mounted on a glass fiber. Intensity data were collected at 173 K on a Bruker-AXS CCD single-crystal diffractometer with a graphite-monochromated Mo Ka radiation source ($\lambda = 0.71073$ Å). Data were reduced by SAINT and absorption corrections were applied using the SADABS program [24]. In all cases, the highest possible space group was chosen. Using OLEX2 [25], all structures were solved with the ShelXS [26] structure solution program using Direct Methods and refined with the XL[26] refinement package using Least Squares minimization. Atoms were located from iterative examination of difference F maps following least-squares refinements of the earlier models. Hydrogen atoms were placed at calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times Ueq of the attached C or N atoms. All structures were examined by the Addsym subroutine of PLATON [27] to assure that no additional