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Metallacycles or coexistence of isomeric metallacycle and chain: Anion-dependent luminescent Ag complexes of a flexible diaminotriazine–imidazole ligand ☆

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HIGHLIGHTS

- Five Ag complexes were obtained using a flexible diaminotriazine–imidazole ligand.
- Cocrystal structures of ring-opening isomers were observed in 1 and 2.
- Both the diaminotriazine and the imidazole group participate in coordination.
- TGA and emission behaviors of the complexes were investigated.

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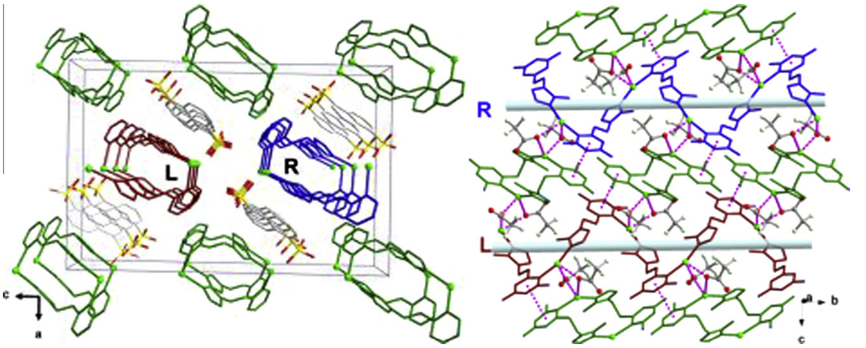
GRAPHICAL ABSTRACT



ABSTRACT

Reaction of a flexible ligand 2,4-diamino-6-[2-(2-methyl-1-imidazolyl) ethyl]-1,3,5-triazine (L) with Ag(I) in the presence of different counteranions afforded five complexes, namely, $2[Ag_n(L)_n(NH_3)_n]\cdot n[Ag_2(L)_2(NH_3)_2]\cdot 2n(nds)$ (**1**, $H_2nds = 1,5$-naphthalenedisulfonic acid), $2[Ag_n(L)_n]\cdot n[Ag_2(L)_2(CF_3CO_2)_2]\cdot nCF_3CO_2$ (**2**), $[Ag_2(L)_2(NH_3)_2]\cdot 2(ClO_4)$ (**3**), $[Ag_2(L)_2]\cdot 2(NO_3)$ (**4**), $[Ag_2(L)_2]\cdot 2(ClO_3)$ (**5**), which were characterized by element analysis, IR, PXRD and X-ray single-crystal diffraction. Structural analysis reveals that the L ligand take the same bidentate coordination mode in these complexes. The nds anion and the $CF_3CO_2^-$ anion lead to the coexistence of isomeric metallacycle and helical chain (ring-opening isomers) in the crystals of **1** and **2**, while ClO_4^-, NO_3^- and ClO_3^- anions afford dimeric metallacycles in complexes **3–5**. Moreover, thermal gravity analysis (TGA) and emissive behaviors of these complexes were investigated.

Introduction

In the recent decades, coordination complexes (CCs) have attracted considerable attention due to their intriguing structural features and their potential applications in many fields. Generally, the structures and properties of such complexes obtained from self-assembly greatly depends on the information stored on the metal centers and the organic ligands. On the other hand, the production of these complexes is also affected by other factors such as counteranions, solvents and temperature. Among the above factors, counteranions not only can serve as balance charges but also can act as true structure-directing agents [1–8]. Counteranions with different coordination abilities, sizes, and geometries may cause significant structural changes of the resultant complexes [9–15].

Melamine derivatives are well known for their brilliant supramolecular interaction abilities to construct remarkable

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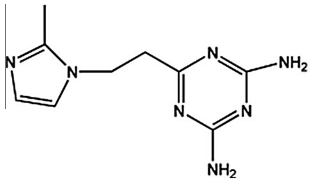
architectures which may have applications in host–guest chemistry, catalysis, anion recognition, sensoring, electronics and magnetism [16–23]. Furthermore, the excellent H-bonding ability of diaminotriazinyl (DAT) group has been successfully used in combination with coordination bonds in some DAT based rigid ligands for crystal engineering [24–28]. However, there are still no reports of flexible ligands incorporating the DAT group, and in this work, we selected a flexible ligand 2,4-diamino-6-[2-(2-methyl-1-imidazolyl) ethyl]-1,3,5-triazine (L) based on the following reasons. Firstly, the coordination behavior of the DAT group in flexible ligands is still to be explored. It has been shown that both the endocyclic and exocyclic nitrogen atoms can ligate metal ions and the DAT group can ligate up to five metal atoms in ligands containing the DAT and other noncoordinating groups [29,8,30–34]. However, the electron-deficient character of the triazine ring determines that the coordination involving the DAT group must be weaker than the coordination involving other groups, such as pyridine and imidazole. In rigid ligands incorporating the DAT and other coordinating groups, the DAT group generally does not engage in coordination [35]. Thus, it is interesting to explore whether the flexibility of the L ligand allow the DAT group to coordinate together with the imidazole group. Secondly, the L ligand can provide multiple supramolecular interaction sites. In the L ligand, the DAT group can donate up to three H-bonding acceptors and four H-bonding donors, also, both the triazine ring and the imidazole ring have the π-interaction abilities. It is expected that the L ligand could involve in strong supramolecular interactions with other components, such as counteranions and solvents, which may exert profound effects in the self-assembly process and the architectures of the final products, especially in the Ag(I) system due to the modest stereochemical preferences of the Ag(I) ion [36–40].



L

Sparked by the above-mentioned points, and as a continuation of our work in Ag(I) CCs with melamine-based ligands [30–32,41], herein, we present five Ag(I) complexes of 2,4-diamino-6-[2-(2-methyl-1-imidazolyl) ethyl]-1,3,5-triazine, with different anions, namely, $2[Ag_n(L)_n(NH_3)_n]\cdot n[Ag_2(L)_2(NH_3)_2]\cdot 2n(nds)$ (**1**, H_2nds = 1,5-naphthalenedisulfonic acid), $2[Ag_n(L)_n]\cdot n[Ag_2(L)_2(CF_3CO_2)_2]\cdot nCF_3CO_2$ (**2**), $[Ag_2(L)_2(NH_3)_2]\cdot 2(ClO_4)$ (**3**), $[Ag_2(L)_2]\cdot 2(NO_3)$ (**4**), $[Ag_2(L)_2]\cdot 2(ClO_3)$ (**5**). Out of these complexes, both **1** and **2** contain isomeric metallacycle and helical chain (ring-opening isomers), while complexes **3–5** display three dimeric metallacycles. Furthermore, emissive behaviors of these complexes are discussed.

Experimental

Materials and methods

All chemicals of analytical grade were obtained from commercial sources and used without further purification. Distilled H_2O was used in the reactions. Elemental analyses was performed on a CE instruments EA 1110 elemental analyzer. IR spectrum was recorded on a Nicolet 330 FTIR Spectrometer in the range of 4000–400 cm^{-1} using KBr pellets. X-ray powder diffractions were collected on a Panalytical X-Pert pro diffractometer with Cu Kα radiation. Thermogravimetric analyses was performed on SDT Q600 instrument from 30 to 900 °C at the heating rate of 10 °C/min under the N_2 atmosphere (20 mL/min).

Preparation

*$2[Ag_n(L)_n(NH_3)_n]\cdot n[Ag_2(L)_2(NH_3)_2]\cdot 2n(nds)$ (**1**)*

A mixture of Ag_2O (23.2 mg, 0.1 mmol), L (43.8 mg, 0.2 mmol) and $H_2nds\cdot 4H_2O$ (36.1 mg, 0.1 mmol) was stirred in ethanol/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 afford colorless crystals of **1** (yield 43%, based on silver). Anal. Calc. (found) for $Ag_2C_{28}H_{38}N_{16}O_6S_2$: C, 34.51 (34.32), H, 3.93 (3.89); N, 23.00 (23.05)%. Selected IR peaks (cm^{-1}): 3458 (s), 3310 (s), 3110 (s, sh), 1674 (s), 1632 (s), 1541 (s), 1449 (s), 1405 (s, sh), 1202 (s, SO), 1189 (s, SO), 1159 (s, SO), 1019 (m, SO), 757 (m), 618 (m).

*$2[Ag_n(L)_n]\cdot n[Ag_2(L)_2(CF_3CO_2)_2]\cdot nCF_3CO_2$ (**2**)*

Crystals of complex **2** were obtained in a method similar to that of complex **1**, except the replacement of $H_2nds\cdot 4H_2O$ by $CF_3COONa\cdot 3H_2O$ (27.2 mg, 0.2 mmol). (yield 52% based on silver). Elemental analysis: Anal. Calc. (found) for $Ag_2C_{22}H_{26}F_6N_{14}O_4$: C 30.02 (29.85), H 2.98 (2.99), N 22.28 (22.38)%. Selected IR peaks (cm-1): 3377 (s), 3213 (s), 3140 (s, sh), 1676 (vs), 1633 (vs), 1581 (vs CO), 1540 (vs CO), 1468 (s), 1445 (s), 1431 (s), 1120 (s, sh), 716 (s, CF).

*$[Ag_2(L)_2(NH_3)_2]\cdot 2(ClO_4)$ (**3**)*

Crystals of complex **3** were obtained in a method similar to that of complex **1**, except the replacement of $H_2nds\cdot 4H_2O$ by $NaClO_4$ (28.1 mg, 0.2 mmol). (yield 45%, based on silver). Anal. Calc. (found) for $Ag_2C_{18}H_{32}Cl_2N_{16}O_8$: C 24.37 (24.25), H 3.64 (3.13), N 25.26 (25.03)%. Selected IR peaks (cm^{-1}): 3462 (s), 3427 (s), 3219 (s), 1639 (s), 1540 (s, sh), 1460 (s), 1404 (s, sh), 1120 (s, sh, ClO).

*$[Ag_2(L)_2]\cdot 2(NO_3)$ (**4**)*

A mixture of $AgNO_3$ (33.9 mg, 0.2 mmol), L (43.8 mg, 0.2 mmol) was stirred in ethanol/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 **4** (yield 62%, based on silver). Anal. Calc. (found) for $Ag_2C_{18}H_{26}N_{16}O_6$: C 27.78 (27.58), H 3.37 (3.32), N 28.80 (28.24)%. Selected IR peaks (cm^{-1}): 3462 (s), 3363 (s, sh), 3155 (s), 1647 (s), 1581 (s), 1532 (s), 1460 (m), 1381 (s, NO).

*$[Ag_2(L)_2]\cdot 2(ClO_3)$ (**5**)*

A mixture of Ag_2O (23.2 mg, 0.1 mmol), L (43.8 mg, 0.2 mmol) and $NaClO_3$ (21.2 mg, 0.2 mmol) was stirred in ethanol/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 **5** (yield 53%, based on silver). Anal. Calc. (found) for $Ag_2C_{18}H_{26}Cl_2N_{14}O_6$: C 26.33 (26.53), H 3.19 (3.29), N 23.88 (23.68)%. Selected IR peaks (cm^{-1}): 3470 (s), 3313 (s), 3110 (s, br), 1675 (s), 1636 (s), 1538 (s), 1453 (s), 1401 (s), 975 (s, sh, ClO).

X-ray crystallography

Suitable single crystals of the complexes **1–5** with appropriate sizes were chosen under an optical microscope and then mounted