

Short communication

Ag(I)-triazolylcarboxylates: The role of hydrocarbon tails in the formation of “sitting-on-layer” supramolecular bowls

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ARTICLE INFO

Article history:

Received 16 September 2015

Received in revised form 12 October 2015

Accepted 13 October 2015

Available online 19 October 2015

Keywords:

Ag(I) coordination polymers
1,2,4-triazolyl carboxylic acids
Supramolecular containers
Host-guest interactions
Photoluminescence properties

ABSTRACT

Several α -amino acids, (*l,d*)-alanine and (*l,d*)-phenylalanine were utilized, as precursors for synthesis of 1,2,4-triazolyl carboxylic acids (*l,d*)-**trala-H** and (*l,d*)-**trphe-H**, which were explored as angular bifunctional building blocks for engineering Ag(I)-coordination polymers. Two complexes, [Ag(μ_4 -**trala**)]·H₂O (**1**) and [Ag(μ_4 -**trphe**)]·H₂O (**2**), were prepared under mild hydrothermal conditions and characterized. The organic ligands coordinate silver cations in a deprotonated form via a N₂O₂ donor set, where the *tr* group behaves in a [N–N] mode while the carboxylate function serves as a μ_2 - η^2 : η^0 bridge. Complexes **1** and **2** possess a layered structure consisting of [Ag([N–N](COO))]_n chains which are interlinked through ligand spacers. Being oriented toward the neighboring layers, the hydrocarbon side “tails” display a peculiar role in the supramolecular organization of “sitting-on-layer” three-dimensional baskets. Each container is pleasantly suitable for binding a water molecule via an H-bonding acceptor portal of carboxylate fragments.

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Multifunctional organic ligands bearing N-heterocyclic and carboxylic acid donor groups exhibit unique chemical versatility enabling them to be in the mainstream of metal-organic frameworks (MOFs) and supramolecular chemistry [1]. In this concern the ligand family containing 1,2,4-triazole (*tr*) and –COOH moieties displays special attention. For multiple purposes, 1,2,4-triazoles offer short and quite stable [–N–N–] staple-bridges between two metal ions resulting in a variety of well-recognized coordination clusters [2]. Among the compounds Ag–*tr* structures demonstrate the most striking motifs that span from discrete di-, tri-, tetra- and hexanuclear to oligonuclear polymeric types [3–13], despite inherently low coordination numbers of Ag(I) ion, typically ranging between 2 and 4. These structural features are of fundamental importance for practical applications [14–15]. For instance, the investigation of photoluminescence properties of Ag(I)-MOFs involving triazolyl heterocyclic ligands has received a substantial interest in the field of coordination polymers [3b,5,16].

1,2,4-Triazolyl carboxylic acids derived from natural amino acids offer a unique possibility to explore the concept of angular linkers and the role of side chains for the designing MOFs. This makes the ligand class especially important for interdisciplinary researches [17]. In this context, 1,2,4-triazolyl-carboxylate building blocks represent a special

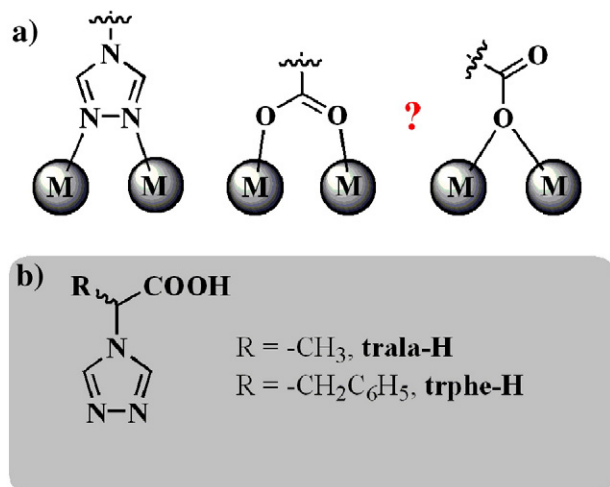
example for establishing the competing role of different donor functions as well as their influence on the local coordination cluster geometry and resulting topology of coordination networks. Based on a close isosteric relationship, the [–N–N–]*tr* linkage resembles carboxylate bridges in a μ_2 - η^1 : η^1 coordination mode (Scheme 1, a). Thus, both groups can interact with metal cations in a tandem fashion supporting the formation of various heteroleptic *tr*/COO[–] clusters.

In this paper we describe the syntheses, crystal structures, photoluminescence properties of Ag(I) coordination polymers with representative 1,2,4-triazolyl-carboxylic acid based ligands, (*l,d*)-2-(1,2,4-triazol-4-yl)propionic acid (**trala-H**) and (*l,d*)-3-phenyl-2-(1,2,4-triazol-4-yl)propionic acid (**trphe-H**) derived from alanine (*ala*) and phenylalanine (*phe*), respectively (Scheme 1, b) [18].

Since **trala-H** and **trphe-H** were employed as racemic mixtures, [Ag(μ_4 -**trala**)]·H₂O (**1**) and [Ag(μ_4 -**trphe**)]·H₂O (**2**) crystallize in centrosymmetric space groups (*P2*₁/*c* and *Pbcm*). In **1** and **2**, the silver ions are aligned in a linear chain of O,O-vertex-sharing AgN₂O₂ seesaw arrangement with two short Ag–N (2.175 (3)–2.196 (7) Å) and two long Ag–O (2.595 (10)–2.644 (3) Å) bond lengths. The column motifs are assembled via mutual coordinations of μ_2 -*tr* and μ_2 - η^2 : η^0 -carboxylate fragments from the deprotonated organic ligands (Fig. 1). Because of the presence of tetrahedral carbon atoms between *tr* – and –CO₂[–] in **trala-H** and **trphe-H**, the hydrocarbon side arm and functional donor groups have inherently angular orientation at the α -position. This suggests similar multiple interlinks between parallel [AgN₂O₂] chains

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Scheme 1. a) $[-\text{N}-\text{N}-\text{tr}]$ linkage is isosteric with $\mu_2-\eta^1:\eta^1$ carboxylate bridge; b) 1,2,4-triazolyl carboxylic acids bearing two donor functions disposed angularly are utilized in this paper.

through a ligand spacer. As a consequence the side hydrocarbon tails are positioned up and down from the metal-organic layers leading to their boat-like conformation. The coordination ensembles can be imagined as “sitting-on-layer” supramolecular containers each of which consists of four silver ions coordinated by four triazolyl carboxylate tectons (Figs. 2, 3). Two silver atoms and a triazole unit reside approximately in a plane creating the unsymmetrical bottom of a bowl (“lower rim”, similarly to calixarenes). The other pair of silver ions sitting on the upper level is bound to the bottom silver-pair through two ligands, which visually cover the inclined cone surface, and one ligand connecting with the ground level. The fourth ligand connects a silver basic pair by $-\text{CO}_2^-$ group above the plane thus, completing the whole construction. In this way, hydrophobic side chains of three ligands ($-\text{CH}_3$ and $-\text{CH}_2\text{C}_6\text{H}_5$) are guided to reach the highest position of the bowl that determines height (ca. 8.5 and 13.0 Å for **1** and **2**, respectively) and diameter of the “upper rim”.

Four coordinated carboxylate functions form a hydrophilic pocket around a quasi-planar $\{\text{Ag}_2(\text{tr})\}$ bottom and their disposition seems to be especially suitable for a guest water molecule incorporated inside. In such a case the guest–host interactions are preferably stabilized by characteristic two-point H-bonded synthons involving two acceptor

sites from opposite carboxylate groups and a water molecule acting as a double H-donor ($\text{O}-(\text{H})\dots\text{O}$: 2.830(8), 2.800(8) for **1** and 2.761(6), 2.834(6) Å for **2**). Thus, the overall structures of **1** and **2** can be regarded as a linear sequence of directed “up and down” molecular containers which are arranged in 2D layered motifs.

Our recent studies around triazole-based coordination polymers revealed that they were very prone to undergo temperature-induced crystal structure transformation confirming their substantial structural flexibility in comparison with polycarboxylate-based MOFs. Employing two independent physical methods, temperature-dependent PXRD as well as thermogravimetry/mass spectrometry (TG-MS), provides important information for examination of further functional properties. The temperature-dependent PXRD patterns of compound **2** reveal three temperature intervals, rt–130 °C, 130–210 °C and >210 °C attributed to three different phases: original (**2**), unknown composition, and metallic silver. The thermogravimetric analysis (TGA) profile shows a gradual weight loss of 4.9% in the temperature range of ~100–160 °C that corresponds to the release of a water molecule ($m/z = 18$, calculated weight loss 5.27%).

Complex **2** was selected to study photoluminescence properties. The solid state PL and PLE spectra recorded at 298 K for the complex and for the protonated ligand **trphe-H** are shown in Fig. 4a. Both the emission and excitation bands are very similar for the protonated ligand **trphe-H** and complex **2**, however, a shift of the band positions toward shorter wavelengths can be noticed for the latter. The maximum of the excitation band is observed at 407 nm for **trphe-H** and at 365 nm for **2**. The emission maxima are observed at 458 nm and at 433 nm for **trphe-H** and compound **2**, respectively. The inset in Fig. 4a shows the emission decay curves recorded at 298 K for **trphe-H** and complex **2**. In both cases the decay curves are biexponential and the determined time constants are: $t_1 = 2.7$ ns, $t_2 = 8.5$ ns for **trphe-H**, and $t_1 = 3.1$ ns, $t_2 = 9.6$ ns for **2**. There is only a small increase in the decay times observed for the complex as compared to the protonated ligand, which may suggest that the efficiency of non-radiative relaxation processes is reduced insignificantly after incorporation of the ligand into the coordination framework.

The emission bands of **trphe-H** should be assigned as $n-\pi^*$ or $\pi-\pi^*$ transitions. Based on the observed similarity of excitation and emission bands of the protonated ligand and the Ag-complex, the emission of **2** should be assigned to intraligand transitions. The reflectance spectra presented in Fig. 4b are very similar for the protonated ligand and complex **2**. In the spectrum recorded for **trala-H** the absorption band at about 260 nm, observed for **trphe-H** and **2**, is missing, which indicates that it should be assigned to a phenyl ring of the phenylalanine

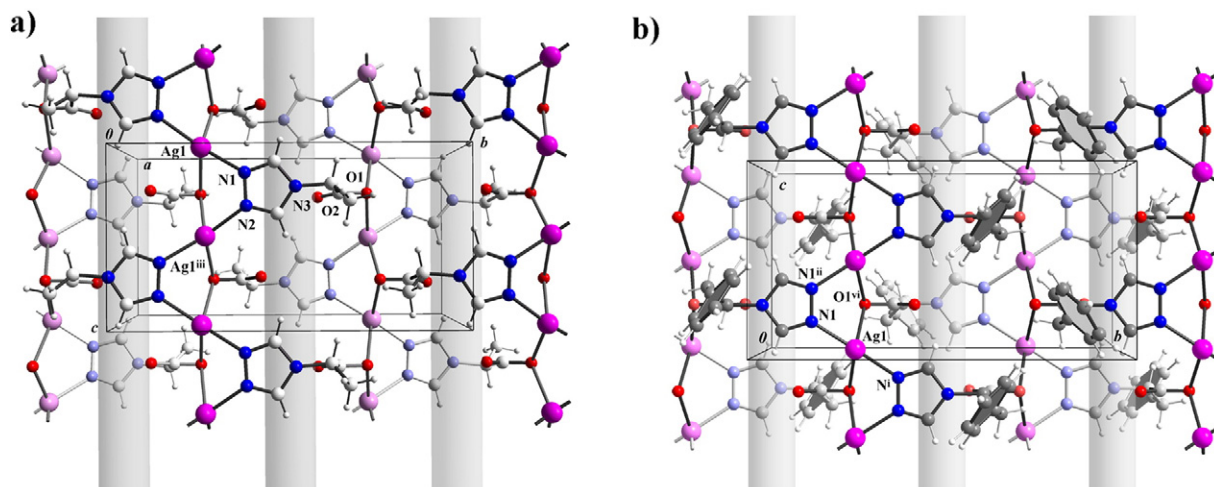


Fig. 1. Formation of layered structural motifs in $[\text{Ag}(\mu_4\text{-trala})]\cdot\text{H}_2\text{O}$ (a); and $[\text{Ag}(\mu_4\text{-trphe})]\cdot\text{H}_2\text{O}$ (b).

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