

一对杂环异构体作为配体与 Ag(I)的配位化学研究: 合成、晶体结构和荧光表征

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摘要: 成功合成并分离了一对异构的杂环配体 L_1 和 L_2 ($L_1=1-((\text{吡啶-4-基})\text{甲基})-1\text{-H-苯并三唑}$, $L_2=2-((\text{吡啶-4-基})\text{甲基})-1\text{-H-苯并三唑}$)。这类配体在构筑复杂的金属有机框架方面,具有许多优点。把这对配体分别和高氯酸银作用,得到了 2 个新的化合物 **1** 和 **2** 并测定了结构,分别为 $[\text{Ag}(L_1)(\text{ClO}_4)]_n$ (**1**) 和 $[\text{Ag}(L_2)_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2**)。化合物 **1** 为一维双螺旋结构,而化合物 **2** 仅仅展现出零维结构。配体在结构上的细微差别可以导致所形成的配位化合物的结构的巨大差异。

关键词: 异构; 杂环配体; 双螺旋结构; 银配合物

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Coordination Chemistry of Two Structural Isomeric Heterocyclic Ligands towards Silver(I): Syntheses, Crystal Structures and Fluorescent Characterization

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Abstract: A pair of isomeric heterocyclic ligands ($L_1=1-((\text{pyridin-4-yl})\text{methyl})-1\text{-H-benzotriazole}$, $L_2=2-((\text{pyridin-4-yl})\text{methyl})-1\text{-H-benzotriazole}$) was synthesized and separated. The obtained ligands are with lots of advantages in constructing complicated metal-organic frameworks (MOFs). The interaction of both ligands was studied with silver perchlorate. Two new complexes, namely $[\text{Ag}(L_1)(\text{ClO}_4)]_n$ (**1**) and $[\text{Ag}(L_2)_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2**), were obtained as crystals suitable for single-crystal X-ray analysis. Complex **1** gives a 1D double helical conformation, whereas complex **2** only exhibits a zero-dimensional structure. It is revealed that a small difference of ligands would lead the complete diversity of ultimate coordinated compounds' geometrical structure. CCDC: 816547, **1**; 816548, **2**.

Key words: isomeric heterocyclic ligands; double helical conformation; silver complex

0 Introduction

In the research of supramolecular chemistry, a great interest has recently been focused on the crystal engineering of coordination frameworks due to their intriguing architectures, new topologies, intertwining

phenomena and potential applications in microelectronics, nonlinear optics, ion exchange, molecular selection, molecular separation and recognition^[1-8]. The structural motifs of coordination polymers rest on several factors, such as the central atom, the performance of the ligands, the coordinated and/or non-

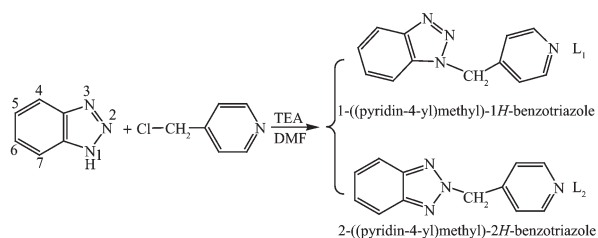
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coordinated counter ions, the solvent systems and the reaction conditions. The choice of appropriate ligands is no doubt the key factor because it has an obvious influence on the topologies of the coordination polymers and behavior of the molecules. Some flexible bidentate ligands, which can adopt various conformations, have been widely used to construct helices^[9-14]. So far, a number of metal complexes by utilizing flexible bis (triazole), bis (benzotriazole) or dipyridyl ligands have been reported^[15-19], but the symmetry of these ligands greatly limits the novelty and variety of the configuration.

Recently, by a radical nucleophilic substitution, we have got a pair of ligands L_1 and L_2 (L_1 =1-((pyridin-4-yl)methyl)-1*H*-benzotriazole, L_2 =2-((pyridin-4-yl)methyl)-1*H*-benzotriazole), which are versatile N-donor in transition metal chemistry (Scheme 1). From a structural point of view, it should be pointed out that (1) these ligands, unlike the rigidity of bipyridine, possess flexibility owing to the presence of a $-\text{CH}_2-$ spacer between the pyridyl ring and benzotriazole moiety; (2) if both N-donor sites can coordinate to the metal center, L_1 and L_2 can act as μ_2 -bridging ligands. Accordingly, a chain-like structure may be expected, and the flexibility may result in a novel framework; (3) due to their unsymmetrical nature, L_1 and L_2 can be considered as a potential link for the construction of acentric solids, which may be NLO materials^[20-22]. Furthermore, we quite wonder whether the positional isomerization of ligands would affect the polymers' structure and properties. In this paper, we have studied the interaction of both ligands with silver perchlorate. Among our attempts, two new complexes, namely $[\text{Ag}(L_1)(\text{ClO}_4)]_n$ (**1**) and $[\text{Ag}(L_2)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2**), were obtained as crystals suitable for single-crystal X-ray analysis.



Scheme 1 Synthesis and structure of ligands L_1 and L_2

1 Experimental

1.1 Materials and methods

Benzotriazole was purchased from Acros Ltd. and used without further purification, the other reagents were commercially available and used as purchased. The IR spectra as KBr discs were recorded on a Magna 750 FTIR spectrophotometer. C, H, and N analyses were determined on an Elementary Vario EL III elemental analyzer. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FL920.

1.2 Synthesis of the ligands

The desired ligands L_1 and L_2 were prepared by condensation of 1*H*-benzotriazole with the 4-picolyl chloride in DMF at reflux for 4 h in the presence of triethylamine as a basic catalyst^[23]. Separation of the isomeric mixtures was performed by chromatography on silica gel column (eluent: ethyl acetate-light petroleum 40:60, V/V).

1.3 Synthesis of $[\text{Ag}(L_1)(\text{ClO}_4)]_n$ (**1**)

A solution of L_1 (0.021 g, 0.10 mmol) in MeOH (5 mL) was carefully layered on a solution of AgClO_4 (0.021 g, 0.10 mmol) in H_2O (5 mL). Diffusion between the two phases over a period of two weeks produced colorless block crystals. Yield: 0.016 g (38% based on L_1); Elementary analysis calcd. for $\text{AgClC}_{12}\text{H}_{10}\text{N}_4\text{O}_4$ (%): C, 34.52; H, 2.41; N, 13.42; found (%): C, 34.63; H, 2.28; N, 13.71. IR (KBr, cm^{-1}): 3 700~3 500 (w), 2 924 (w), 1 615 (s), 1 600 (m), 1 561 (w), 1 498 (w), 1 458 (w), 1 384 (s), 1 224 (s), 1 166 (m), 1 120 (m), 782 (m), 764 (m), 743 (s), 727 (m), 626 (w), 563 (w), 482 (w).

1.4 Synthesis of $[\text{Ag}(L_2)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2**)

The procedure for synthesis **2** was similar to that of **1** except that L_2 was used instead of L_1 . Yield: 0.011 g (48% based on L_2); Elementary analysis: calcd. for $\text{AgClC}_{12}\text{H}_{10}\text{N}_4\text{O}_4$ (%): C, 44.64; H, 3.43; N, 17.35; found (%): C, 46.00; H, 3.23; N, 17.70. IR (KBr, cm^{-1}): 3 600~3 400 (s), 2 973 (s), 1 593 (s), 1 573 (s), 1 451 (w), 1 417 (s), 1 326 (s), 1 227 (s), 1 140 (s), 1 093 (w), 1 050 (m), 993 (w), 940 (w), 802 (s), 761 (s), 709 (m), 633 (w), 574 (m), 531 (w), 439 (w).

1.5 X-ray crystallography

The single crystal X-ray diffraction measurement

was carried out on a Mercury CCD area detector. Intensities of reflections were measured using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$), with ω scan mode at 293(2) K in the range of $3.18^\circ < \theta < 27.49^\circ$ for **1** and $2.56^\circ < \theta < 27.48^\circ$ for **2**, respectively. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied to the diffraction data for all structures^[24]. The structure was solved by direct method^[25] and non-

hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on F^2 by SHELXL-97 program package^[26]. For both **1** and **2**, hydrogen atoms were generated geometrically and treated as riding. The crystallographic data for **1**, **2** are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

CCDC: 816547, **1**; 816548, **2**.

Table 1 Crystallographic data for complexes **1** and **2**

Complex	1	2
Empirical formula	C ₁₂ H ₁₀ N ₄ O ₄ AgCl	C ₂₄ H ₂₂ N ₈ O ₅ AgCl
Formula mass	417.56	645.8
Colour, habit	Colorless, prism	Yellow, prism
Crystal dimensions / mm	0.55×0.30×0.25	0.60×0.10×0.10
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Fdd2</i>	<i>Fdd2</i>
<i>Z</i>	16	16
<i>a</i> / nm	2.060 400(10)	2.673 7(2)
<i>b</i> / nm	2.808 85(6)	4.900 7(6)
<i>c</i> / nm	0.969 200(10)	0.848 71(6)
Volume / nm ³	5.609 10(14)	11.12 05(18)
<i>D_c</i> / (Mg·m ⁻³)	1.987	1.5
Absorption coeff. μ / mm ⁻¹	1.652	0.865
Absorption correction	Intergration	Intergration
<i>F</i> (000)	3 296	5 056
θ range for data collection / (°)	3.18~27.49	3.05~27.46
Observed reflections	2 594	4 673
Independent reflections	2 705	6 217
Data / restraints / parameters	199	347
Maximum shift / error	0	0
Goodness-of-fit on F^2	1.006	0.956
Final <i>R</i> indices ($I > 2\sigma(I)$)	<i>R</i> ₁ =0.021 6, <i>wR</i> ₂ =0.057 2	<i>R</i> ₁ =0.054 8, <i>wR</i> ₂ =0.157 1
<i>R</i> indices (all data)	<i>R</i> ₁ =0.022 6, <i>wR</i> ₂ =0.057 9	<i>R</i> ₁ =0.075 5, <i>wR</i> ₂ =0.175 6

Table 2 Selected bond lengths (nm) and angles (°) for complexes **1** and **2**

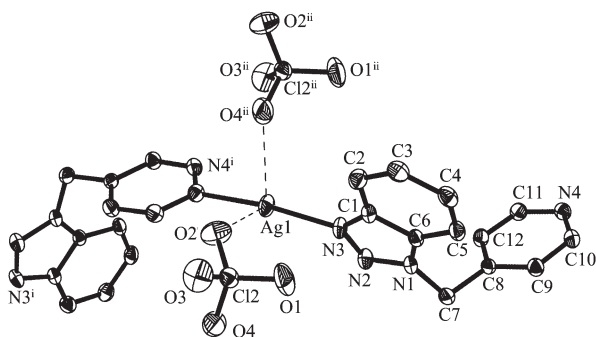
1					
Ag(1)-N(3)	0.212 6(2)	Ag(1)-N(4 ⁱ)	0.216 0(2)	Ag(1)-O(2)	0.279 4(3)
Ag(1)-O(4 ⁱⁱ)	0.285 7(4)				
N(3)-Ag(1)-N(4 ⁱ)	169.17(9)	N(1)-C(7)-C(8)	111.7(2)		
2					
Ag(1)-N(4)	0.216 8(5)	Ag(1)-N(8)	0.215 5(5)		
N(4)-Ag(1)-N(8)	178.0(2)	N(2)-C(7)-C(8)	113.1(5)		

Symmetry codes: **1**: ⁱ $-x+2, -y, z-1$; ⁱⁱ $x+1/4, -y+1/4, z+1/4$.

2 Result and discussion

2.1 Structure description

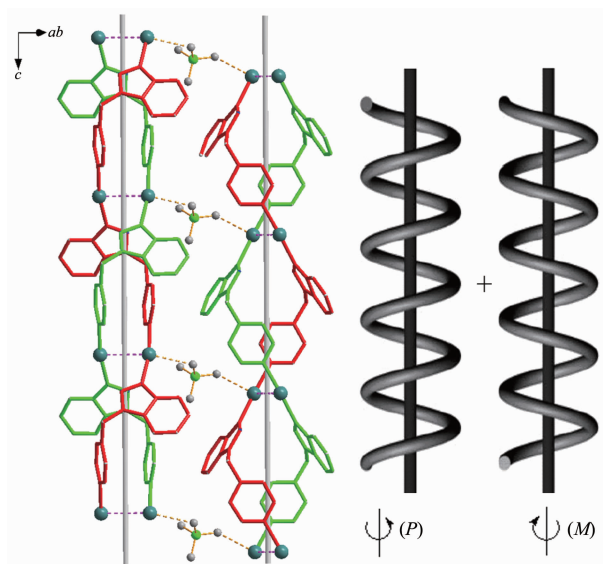
X-ray diffraction reveals that complex **1** crystallizes in the orthorhombic space group $Fdd2$ and possesses a 1D infinite double helix. The crystallographically independent silver(I) center is four-coordinated with a tetrahedral geometry, as shown in Fig.1. Besides being coordinated by two L_1 ligands via the N_{py} ($Ag(1)-N(4^i)$ 0.216 0 nm) and N_{pta} ($Ag(1)-N(3)$ 0.212 6 nm) nitrogen donor atoms, Ag (1) center also displays an outward weak contact to the perchlorate group with O(2) and O(4) ($Ag-O$ 0.279 4 and 0.285 7 nm, respectively). Interior of each L_1 molecule, sufficient flexibility makes it twisted to meet the requirement of coordination geometries of Ag (I) center with the $N(1)-C(7)-C(8)$ angle of $111.7(2)^\circ$ and the dihedral angle for the benzotriazole to pyridyl rings of $78.595(70)^\circ$.



Symmetry code: $i: -x+2, -y, z-1$; $ii: x+1/4, -y+1/4, z+1/4$

Fig.1 Local coordination environment around Ag(I) center in **1**

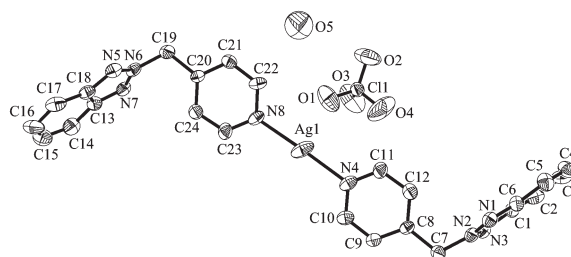
Each L_1 group behaves as an exo-bidentate linker, bridging adjacent Ag (I) cations to give rise to the infinite $[-Ag(L_1)]_n$ helix along the $[001]$ direction, and each strand is interwind compactly by another strand through the strong $Ag \cdots Ag$ (0.316 3 nm) aurophilic $d^{10}-d^{10}$ interactions^[13], to form a tubular double helix (Fig.2). Within each chain the two strands run in the same direction, while adjacent chains run in opposite chirality, to afford an internal racemate. Each chiral double helical chain links to its adjacent symmetric-related equivalents via the weak attraction of perchlorate anions, to generate a quasi 3D supramolecular architecture.



Balanced packing of P and M chirality affords an internal racemate

Fig.2 View of the adjacent double helical chains in **1**

Compound **2** crystallizes in the orthorhombic space group $Fdd2$ too, but completely different from **1**, **2** only possesses a zero-dimension structure. As shown in Fig. 3, Ag(I) center is coordinated by two N atoms, both from pyridyl ring of L_2 with a bond length of 0.215 5 and 0.216 8 nm. The angle of $N(4)-Ag(1)-N(8)$ is $178.0(2)^\circ$, nearly forming an ideal beeline. In complex **1**, each L_1 acts as a bidentate joiner, bridging adjacent Ag (I) cations to give rise to an infinite 2^1 helix. However, each L_2 only serves as a monodentate ligand in complex **2**. Inside of each L_2 ligand, the benzotriazole links the picoyl with $2^\#$ N atom, thereupon steric hindrance prevents the $1^\#$ N and $3^\#$ N atoms from N-donor function. The metal center is unable to extent through the L_2 ligands, so complex **2** merely exhibits a zero-dimension structure. The mononuclear crystal cell exists another aqua molecule which does not participate



H-atoms have been omitted for clarity

Fig.3 Mononuclear structure of the complex **2**

in the coordination.

2.2 Fluorescent properties

Metal-organic polymer compounds with a d^{10} configuration have been found to exhibit photoluminescent properties^[31-33]. Here, we want to examine the photoluminescence of **1** and **2**. The solid-state emission spectra of L_1 and L_2 ligands, complexes **1** and **2** at room temperature are shown in Fig.4. It can be observed that the intense emissions occur in the same range for the two complexes ($\lambda_{ex}=350$ nm, $\lambda_{em}=420$ nm for **1**; $\lambda_{ex}=338$ nm, $\lambda_{em}=414.5$ nm for **2**), which show a very light red-shift to that observed from two ligands (L_1 : $\lambda_{ex}=340$ nm, $\lambda_{em}=403$ nm; L_2 : $\lambda_{ex}=345$ nm, $\lambda_{em}=404$ nm). In d^{10} -metal ions with one or two positive charges, the d-orbitals are contracted and therefore the electrons in these orbitals are much less accessible for back bonding to p-acceptor ligands, and silver cations have a weak electro-accepting nature with respect to electrons from L, so these emissions can be assigned to ligand-to-metal charge transfer (LMCT) bands.

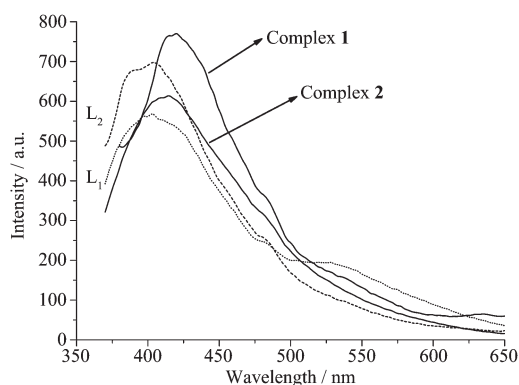


Fig.4 Fluorescent spectra of ligands L_1 and L_2 (dashed line), complex **1** and **2** (solid line) at room temperature

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