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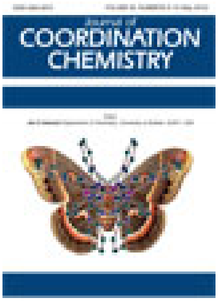

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Supramolecular isomerism of Cu(I) and 3,5-di-2-pyridyl-1,2,4-triazolate via in situ solvothermal ligand reaction: meso-helix and luminescence

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Supramolecular isomerism of Cu(I) and 3,5-di-2-pyridyl-1,2,4-triazolate *via in situ* solvothermal ligand reaction: meso-helix and luminescence

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The sixth supramolecular isomer of Cu(I) and 3,5-di-2-pyridyl-1,2,4-triazolate (2-pytz), $[Cu_2(2\text{-pytz})_2]_n$ (**1**), *via in situ* solvothermal ligand reaction, has been synthesized and characterized as a rare meso-helical chain. Complex **1** exhibits high thermal stability (until 400°C) confirmed by thermogravimetric analysis and has potential applications as an optical material. This research makes the maximum number of genuine supramolecular isomers with structural characterization, found for coordination polymers, six.

Keywords: Supramolecular isomerism; 3,5-Di-2-pyridyl-1,2,4-triazolate; Meso-helix; Luminescence

1. Introduction

Since Zaworotko and his coworkers introduced the term ‘‘supramolecular isomers’’ in 2001 [1], this area has been of intense interest in supramolecular chemistry and crystal engineering, providing an opportunity for new functional materials and better understanding of the factors that influence crystal growth [2–4]. However, most reported examples in coordination networks can be categorized as being supramolecular pseudo-isomers because of the co-existence of different guest/solvent molecules in the frameworks, and only a few are genuine supramolecular isomers with identical chemical compositions for all components [5–22]. Supramolecular isomerism of coordination polymers is usually generated by varied metal coordination geometry, as well as different coordination, stereo configuration, and spatial conformation of multifunctional ligands, which can introduce more elements of complexity and additional difficulty in the prediction and construction of coordination polymers [5–10, 19]. Though it is easy to predict the possible superstructure, especially for the simple and low dimensional system, controlled synthesis of such supramolecular isomerism is still a formidable task. 3,5-Di-2-pyridyl-1,2,4-triazolate (2-pytz), as a bischelating ligand, is a good candidate for constructing supramolecular isomers

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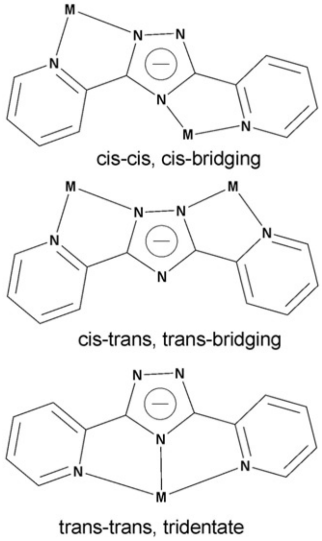
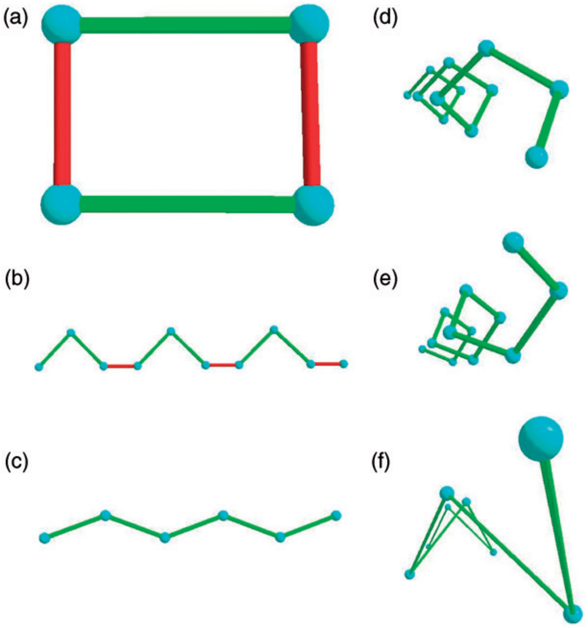


Scheme 1. Possible coordination modes of 2-pytz.

because: (a) it bears five potential coordination sites and easily adopts relatively stable bischelating coordination; (b) it has three kinds of possible coordination modes, favorable to assemble different supramolecular isomers (scheme 1); (c) the ligand is a derivative of 1,2,4-triazoles and always ligated to Cu(I) or Ag(I) in a monovalent form to build the simplest 1 : 1 binary coordination polymers, which helps to reduce the influence of counterions on the corresponding isomers; (d) lack of strong hydrogen bonding donor/acceptor of 2-pytz ligand can reduce additional guest/solvent components.

In situ solvothermal reactions are promising as a bridge between coordination and synthetic organic chemistry, in which relatively high temperatures and pressures, as well as the presence of metal ions, may facilitate new reactions or provide facile one-pot syntheses for compounds that require multistep processes [23–32]. Chen's group has reported four supramolecular isomers based on a binary Cu(I)-2-pytz system *via in situ* solvothermal reaction of nitriles and ammonia, molecular chair, zipper, zigzag, and left-handed 4_1 helical chain (scheme 2a–d) [5]. Subsequently, the fifth supramolecular isomer of Cu(I) and 2-pytz was synthesized *via in situ* generation of nitriles and hydrazine, which is a right-handed 4_1 helical chain (scheme 2e) [27]. However, based on the possible conformations of 2-pytz, there are other supramolecular isomers which should exist but have not been found [5].

Herein, we report the synthesis, crystal structure, and fluorescence of an unexpected supramolecular isomer of Cu(I) and 2-pytz with the formula of $[Cu_2(2\text{-pytz})_2]_n$ (**1**), which has a rare meso-helical chain (scheme 2f) and is obtained in the course of our studies in the reaction mechanism of the triazolates generated from the *in situ* cycloaddition from nitriles and hydrazine hydrate in the presence of Cu(II) or Mn(II) ions [27, 28]. The 1 : 1 binary Cu(I)-2-pytz system has the maximum number of supramolecular isomers with structural characterization found for coordination polymers.



Scheme 2. Supramolecular isomers based on a binary Cu(I)-2-pytz system, in which the balls represent Cu(I) while sticks represent bridging 2-pytz.

2. Experimental

2.1. *Materials and instruments*

All solvents and reagents were of analytical grade and used without purification. C, H, and N microanalyses were performed on a Perkin-Elmer 1400C analyzer. Infrared (IR) spectra ($4000 \sim 400\,\text{cm}^{-1}$) were measured with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks. Emission spectra were taken using a Perkin-Elmer LS55 fluorescence spectrometer. Thermogravimetric analysis (TGA) was recorded on a 209 F3 Tarsus thermogravimetric analyzer.

2.2. *Synthesis of 1*

A mixture of 2-cyanopyridine (0.416 g, 4 mmol), $CuCl_2 \cdot 2H_2O$ (0.169 g, 1 mmol), $NH_2NH_2 \cdot H_2O$ (80%, 2 mL), and H_2O (5 mL) were heated in a 15 mL Teflon-lined vessel at 120°C for 3 days, followed by slow cooling ($5^{\circ}\text{C}\,\text{h}^{-1}$) to room temperature. After filtration and washing with H_2O, red block crystals were collected and dried in air (0.078 g, yield *ca* 27.3% based on Cu). Anal. Calcd for $C_{24}H_{16}Cu_2N_{10}$ (%): C, 50.43; H, 2.82; N, 24.51. Found: C, 50.93; H, 2.39; N, 25.02. Main IR (KBr, cm^{-1}): 3856(w), 2596(w), 3435(vs), 3062(s), 2439(s), 2345(w), 1920(w), 1852(w), 1608(s), 1569(m), 1505(vs), 1436(s), 1262(m), 1153(m), 1098(m), 997(m), 886(w), 794(vs), 745(s), 628(w).

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{24}H_{16}Cu_2N_{10}$
Formula weight	571.57
Temperature (K)	291(2)
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å, °)	
a	7.9515(6)
b	22.7394(17)
c	25.0040(18)
Volume (Å^3), *Z*	4521.0(6), 8
Calculated density (Mg m^{-3})	1.679
Absorption coefficient (mm^{-1})	1.919
F(000)	2304
Limiting indices	$-9 \leq h \leq 9$; $-28 \leq k \leq 27$; $-20 \leq l \leq 30$
Reflections collected	20,183
Independent reflection	4435 [$R(\text{int}) = 0.052$]
Parameters	325
Goodness-of-fit on F^2	1.057
R_1 [$I > 2\sigma(I)$]	0.0480
wR_2 (all data)	0.1105
Largest difference peak and hole (e Å^{-3})	0.45 and −0.29

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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

Cu1–N4	2.015(2)	Cu2–N1	2.093(3)
Cu1–N5	2.187(3)	Cu2–N2	1.995(3)
Cu1–N6	2.247(3)	Cu2–N8a	1.976(3)
Cu1–N9	1.976(2)	Cu2–N10a	2.142(3)
N4–Cu1–N5	80.68(12)	N1–Cu2–N2	80.52(12)
N4–Cu1–N6	101.40(10)	N1–Cu2–N8a	119.11(12)
N4–Cu1–N9	148.97(12)	N1–Cu2–N10a	118.88(12)
N5–Cu1–N6	126.65(12)	N2–Cu2–N8a	142.40(13)
N5–Cu1–N9	123.23(10)	N2–Cu2–N10a	120.28(12)
N6–Cu1–N9	80.61(10)	N8a–Cu2–N10a	80.18(11)

Symmetry code: a, $3/2 - x$, $-1/2 + y$, z.

2.3. *Determination of crystal structures*

Diffraction intensities for both compounds were collected on a Bruker SMART CCD diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). Absorption corrections were applied by using multiscan program SADABS [33]. The structures were solved by direct methods and refined with full-matrix least-squares with SHELXTL [34]. Anisotropic thermal parameters were applied to all the non-hydrogen atoms. Organic hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinement for 1 are summarized in table 1. Selected bond distances and angles are listed in table 2.

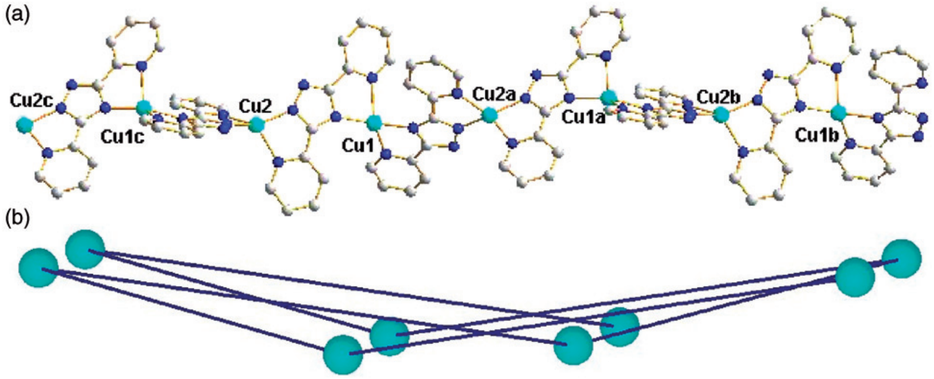


Figure 1. Structures of the 1-D chain (a) and the meso-helical chain (b) of **1** along the crystallographic *b*-axis. In (b), for clarity, the balls represent Cu(I) and strings represent *trans*-bridging 2-pytz ligands.

3. Results and discussion

3.1. *Crystal structure of 1*

Single-crystal X-ray diffraction reveals that **1** crystallizes in the orthorhombic system, *Pbca* space group, with the asymmetric unit of two crystallographically independent Cu(I) ions, which arise from excess hydrazine reduction of Cu(II) salts [8], and two 2-pytz ligands. Both Cu1 and Cu2, with four nitrogen atoms from two chelating 2-pytz, display a distorted tetrahedral geometry (figure 1a). However, the two nitrogen atoms of 1,2,4-triazolates ligating to Cu1 are on the 1-position, while the two nitrogen atoms of 1,2,4-triazolates coordinating to Cu2 are on the 2-position. Each 2-pytz is tetradentate in **1**, bridging the tetrahedral Cu(I) ions in *trans*-bridging fashion into a 1-D chain running along the crystallographic *b*-axis (figure 1a). Four adjacent 2-pytz ligands, together with four Cu(I) ions can be regarded as a repeating unit in the chain, with the angles between adjacent 2-pytz planes of 56.45°, 77.05°, 56.41°, and 77.05°, respectively (figure 1a). The 1-D chain has a pseudo 4_1-screw axis, in which quarters of the screw distance are of opposite handedness, resulting in a rare meso-helical chain (figure 1b). Even though meso-helices widely exist in nature, such as the tendrils of a variety of plants, meso-helical structures in coordination polymers and organic supramolecules are rare, despite their potential applications in information storage and processing nanotechnology [35–47]. Obviously, the meso-helical chain is different from the five other supramolecular isomers of Cu(I) and 2-pytz: molecular chair (scheme 2a), zipper (scheme 2b), zigzag (scheme 2c), left-handed (scheme 2d), and right-handed (scheme 2e) 4_1 helical chains.

The 1-D chain of **1** looks like a butterfly viewed along the crystallographic *b*-axis (figure 2a). Butterfly-like chains are parallel along the crystallographic *c*-axis, and alternately packed in hand to hand and tail to tail modes along the third axis, resulting in ABAB arrangement, as shown in figure 2(b).

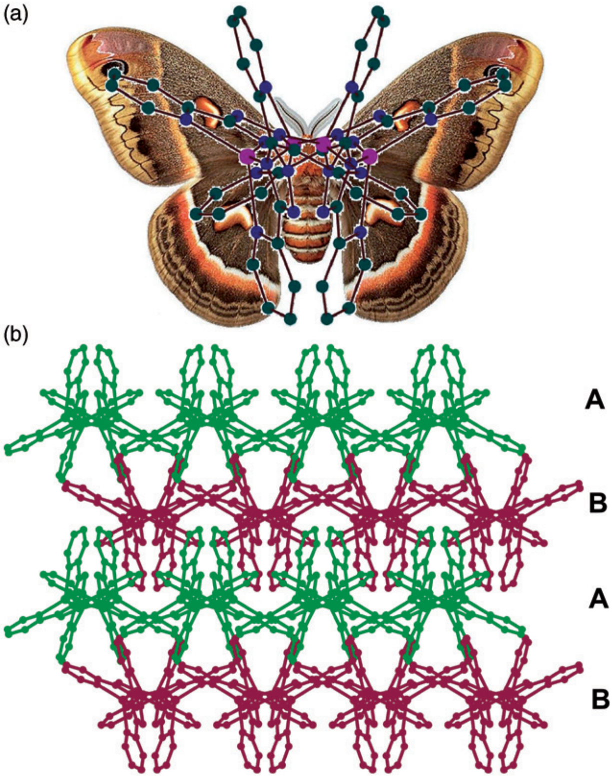


Figure 2. The butterfly-like chain (a) and the ABAB arrangement (b) in **1**.

3.2. *TGA*

To study the thermal stability of **1**, TGA was performed under nitrogen atmosphere from 16°C to 686°C with a heating rate of 10°C min^{-1}, as shown in "Supplementary material." The TGA curve for the compound shows that there is no weight loss between 16°C and 400°C, indicating that **1** exhibits high thermal stability. Then a weight loss of 69.3% of the total weight occurs, which can be assigned to decomposition of 2-pytz (Calcd 77.7%) and the collapse of the whole framework.

3.3. *Luminescence*

The luminescence spectra of **1** and free 3,5-di-2-pyridyl-1,2,4-triazole (2-Hpytz) in the solid state at room temperature are investigated, shown in figure 3. Complex **1** was excited at 320 nm and the main emission bands of **1** were at 374 nm. The emission can be assigned to the intra-ligand (π–π*) emission because similar emission is observed at 365.5 nm for the free ligand when excited at 320 nm. Compared with 2-Hpytz, the enhancement and red-shift of 8.5 nm in **1** is probably due to coordination of 2-pytz to Cu(I) increasing the ligand conformational rigidity, thereby reducing the non-radiative decay of the intraligand (π–π*) excited state [48–50].

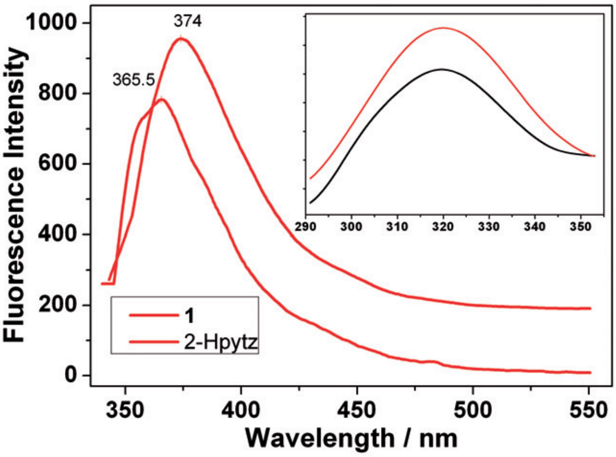


Figure 3. Luminescence spectra of **1** and 2-Hpytz in the solid state at room temperature. Inset: excitation spectra of **1** and 2-Hpytz.

4. Conclusions

We have synthesized and characterized the sixth supramolecular isomer of Cu(I) and 3,5-di-2-pyridyl-1,2,4-triazolate *via in situ* solvothermal reaction. The structure is a rare meso-helix making the number of genuine supramolecular isomers of coordination polymers six. Complex **1** displays luminescent properties, indicating that it may have applications as an optical material.

Supplementary material

CCDC reference number 827949 contains the supplementary crystallographic data for this article. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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