



Syntheses, structures and luminescence of three copper(I) cyanide coordination polymers based on trigonal 1,3,5-tris(1H-imidazol-1-yl)benzene ligand



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ABSTRACT

Three Cu(I)-cyanide coordination polymers based on trigonal 1,3,5-tris(1H-imidazol-1-yl)benzene (tib) ligand, namely $[\text{Cu}_3(\text{CN})_3(\text{tib})]_n$ (**1**), $[\text{Cu}_4(\text{CN})_4(\text{tib})]_n$ (**2**), and $[\text{Cu}_2(\text{CN})_2(\text{tib})]_n$ (**3**), have been prepared and characterized by elemental analysis, IR, PXRD, thermogravimetry and single-crystal X-ray diffraction analysis. Complex **1** displays a 3D metal-organic framework with nanosized pores. Complex **2** is a 3D coordination polymer assembled by three μ_2 -cyanides and a μ_3 -cyanide with a very short Cu(I)···Cu(I) metal bond (2.5206 Å). Complex **3** is a 2D coordination polymer constructing from 1D Cu(I)-cyanide zigzag chain and bidentate tib spacer. Three Cu(I) complexes are thermally stable up to 250–350 °C. Complexes **1–3** show similar orange emission band at 602 nm originating from LMCT mechanism.

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1. Introduction

Coordination polymers have attracted wide attention owing to their intriguing structural motifs and interesting functional properties such as luminescence, magnetism, catalysis, and porous absorption [1–3]. The diversity in the coordination structures was attributed to the selection of metal ions and organic ligands as well as synthetic methods. Much effort has been focused on the rational design and controlled synthesis of coordination polymers using neutral N-heterocyclic ligands such as trigonal 1,3,5-tris(1H-imidazol-1-yl)benzene (tib) [4–6] and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) [7,8], and multidentate anionic ligands such as polycarboxylates [9], thiocyanate [10] and cyanide [11–13]. Over the past two decades, transition metal cyanides have been studied extensively due to their great importance in magnetism and electron transfer. Copper(I) cyanide system is attractive from the viewpoint of crystal engineering, because the cyanide group, as a small anion with little steric hindrance, is a perfect candidate as

linear connector [14]. The Cu(I)-cyanide chains and networks combined with N-heterocycles have afforded a number of coordination polymers with beautiful structural motifs and various luminescent properties [15–18].

The coordination modes of cyanide group in transition metal complexes show considerable diversity. Guo and Mak have pointed out that there are nine types of cyanide coordination modes in metal cyanide complexes [19]. However, the coordination in Cu(I)-cyanide complexes is quite simple. Except few terminal cyanide-coordinated Cu(I) complexes, Pike has depicted that there exist three types of cyanide-bridging coordination modes, μ_2 -C,N, μ_3 -C,C,N and $(\mu_3\text{-C,C,N})_2\text{Cu}_2$ dimer with Cu···Cu interaction [20]. In the course of our investigation to Cu(I)-cyanide coordination polymers [21–23], we combine CuCN with tib ligand and harvest three novel Cu(I)-cyanide coordination polymers (Scheme 1). Herein, we report their synthesis, crystal structures, thermal stability and luminescence.

2. Experimental

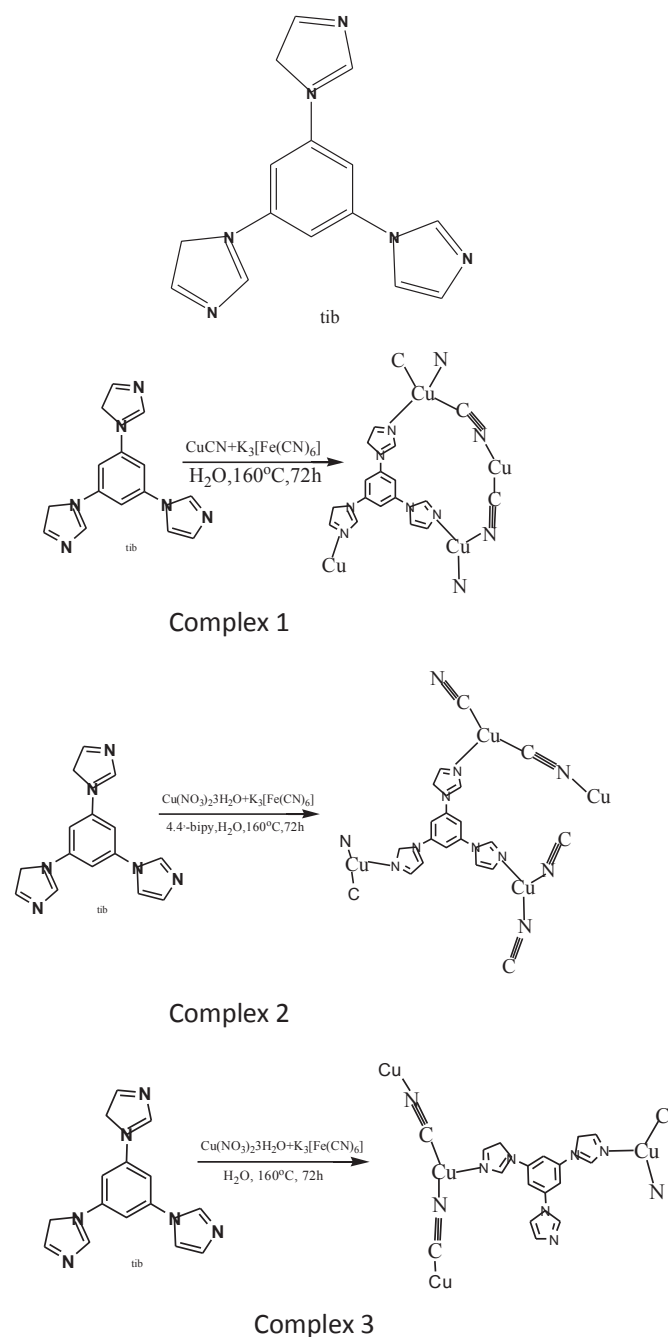
2.1. Materials and methods

Tib ligand was synthesized according to the literature procedure

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Scheme 1.

[24]. All other chemicals were of reagent grade and used as received without further purification. C, H and N microanalyses were measured on a Vario EL-III elemental analyzer. Infrared spectra were recorded on a Nicolet A370 FT-IR spectrometer using KBr pellets in the 400–4000 cm^{-1} region. Powder X-ray diffractions were recorded at a scanning rate of 5°min^{-1} on a Rigaku DLMAX-2550 diffractometer. Thermogravimetric analyses were measured on a Netzsch STA 449C thermal analyzer at a heating rate of $10^\circ \text{C min}^{-1}$ in air. Luminescence spectra were completed on a Shimadzu RF-5301 spectrophotometer.

2.2. Synthesis of $[\text{Cu}_3(\text{CN})_3(\text{tib})]_n$ (**1**)

A mixture of CuCN (0.20 mmol), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.10 mmol), tib

(0.05 mmol) and water (8 mL) was sealed in a 15-mL Teflon-lined reactor, which was heated at 160°C for 72 h and then cooled to room temperature at a rate of 10°C h^{-1} . Colorless crystals of **1** were obtained with 26% yield based on tib. Anal. Calc. for $\text{C}_{18}\text{H}_{12}\text{Cu}_3\text{N}_9$ (%): C, 39.67; H, 2.22; N, 23.12. Found: C, 39.69; H, 2.42; N, 22.75. IR (KBr, cm^{-1}): 3442br, 3118w, 2118s, 2093m, 1614s, 1501s, 1243m, 1066m, 815m, 647m.

2.3. Synthesis of $[\text{Cu}_4(\text{CN})_4(\text{tib})]_n$ (**2**)

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.30 mmol), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.20 mmol), tib (0.05 mmol), 4,4'-bipyridine (0.05 mmol) and water (8 mL) was sealed in a 15-mL Teflon-lined reactor, which was heated at 160°C for 72 h and then cooled to room temperature at a rate of 10°C h^{-1} . Light yellow crystals of **2** were obtained in 23% yield based on tib. Anal. Calc. for $\text{C}_{19}\text{H}_{12}\text{Cu}_4\text{N}_{10}$ (%): C, 35.96; H, 1.91; N, 22.06. Found: C, 35.87; H, 1.96; N, 22.11. IR (KBr, cm^{-1}): 3443br, 3118w, 2154w, 2119s, 1602s, 1503s, 1407m, 1249w, 1064m, 1015w, 803s, 744m, 630m.

2.4. Synthesis of $[\text{Cu}_2(\text{CN})_2(\text{tib})]_n$ (**3**)

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.3 mmol), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.20 mmol), tib (0.05 mmol) and water (8 mL) were combined in a 15-mL Teflon-lined reactor, which was heated at 160°C for 72 h and then cooled to room temperature at a rate of 10°C h^{-1} . Colorless crystals of **3** were obtained in 20% yield based on tib. Anal. Calc. for $\text{C}_{17}\text{H}_{12}\text{Cu}_2\text{N}_8$ (%): C, 44.83; H, 2.66; N, 24.59. Found: C, 44.15; H, 3.25; N, 25.08. IR (KBr, cm^{-1}): 3447br, 3119w, 2118s, 1616s, 1503s, 1409w, 1240m, 1066s, 1014m, 811m, 758w, 648m, 630m.

2.5. X-ray crystallography

The well-shaped single crystals of **1–3** were selected for X-ray diffraction study. Data collections were performed with graphite-monochromatic Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Smart Apex-II CCD diffractometer at room temperature. Determinations of the crystal system, orientation matrix and cell dimensions were performed according to the established procedures. Lorentz polarization and absorption correction were applied. The structures were solved by the direct methods and refined by full-matrix least-squares on F^2 with SHELXTL program [25]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position. Crystallographic data and refinement results are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. Structure of $[\text{Cu}_3(\text{CN})_3(\text{tib})]_n$ (**1**)

Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit is composed of three crystallographically independent Cu(I) atoms, three cyanides and a tib ligand. As shown in Fig. 1a, Cu1 and Cu2 are both three-coordinated by two cyanide groups (C/N) and an imidazole group to complete a trigonal geometry. The Cu1-C/N (cyanide) bond distances vary from 1.854(9) to 1.913(12) \AA . The Cu1-N4(im) and Cu2-N7(im) bond distances are 2.032(9) and 2.047(8) \AA , respectively. Cu3 is four-coordinated by three cyanide groups and an imidazole group to form a distorted tetrahedral geometry. Cu3-C3, Cu3-N2B, Cu3-N9 and Cu3-N2A bond distances are 1.940(10), 1.961(12), 2.099(9) and 2.531 \AA , respectively. Obviously, Cu3-N2A is a weak coordination bond. Cu3 and Cu3B are linked by

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