Inorganic Chemistry Communications 36 (2013) 150–154

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A luminescent Cu(I)–CN-1,2,4-triazolate open-framework with unique 2-fold interpenetrated (4, 6)-connected fsc topology

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ARTICLE INFO

Article history:
Received 17 June 2013
Accepted 29 August 2013
Available online 5 September 2013

Keywords:
CuCN
3,5-Bis(4-pyridyl)-1,2,4-triazole
Open-framework
Photoluminescence
Topology

ABSTRACT

Self-assembly of CuCN, $K_3Fe(CN)_6$ and 3,5-bis(4-pyridyl)-1,2,4-triazole (BPy-4Trz) ligand under hydrothermal conditions generated a novel hybrid crystalline compound, namely, **{Cu_2(BPy-4Trz)(CN)}$_n$** (**1**). Two kinds of binuclear motifs, [$Cu_2(Trz)_2$] and [Cu_2CN], link each other through the 4-pyridyl and cyanide groups to give a three-dimensional (4,6)-connected open-framework of **1** with 2-fold interpenetrated fsc topology. The green fluorescence emissions are observed in the solid state at room temperature.

The continuous driving force for the development of new metal-organic open-framework materials derives from not only their fascinating architectures and topologies, but also the potential applications to fields as diverse as catalysis, gas sorption, and molecular electronics [1–5]. The exploitation of suitable organic components which introduce specific geometric requirements has been proposed as one effective strategy to control the structures of novel open-framework solids. Up to now, much effort has been focused on the rational design and controlled synthesis of metal-organic open-frameworks using multidentate ligands such as polycarboxylate and polypyridine ligands [2–4]. Recently, another type of organic ligands, five-numbered heterocycles especially 1,2,4-triazolate and its derivatives, have attracted much more attention, since they are able to combine both imidazoles and pyrazoles in their coordination and, in addition, the metal-triazolate frameworks exhibit special luminescent, magnetic, and favorable gas-adsorption abilities [6–8].

On the other hand, the structures and properties of metal-organic open-frameworks are also affected by their inorganic components. Copper cyanides have been widely used as inorganic components owing to their structural diversity and interesting photochemical and photophysical properties [9–12]. The inorganic cyanide anion usually exhibits versatile bridging abilities to act as a monodentate ligand as well as a μ_2-, μ_3-, or μ_4-bridging ligand to generate diverse inorganic motifs varying from discrete oligomers to polymeric chains and two-dimensional layers. Thus, the combination of triazolate ligands and cyanide ions as the co-ligands to link Cu(I) centers provides good chances to generate special and fascinating metal-organic structures. However, only a few examples of dense Cu(I)–cyanide–triazolate systems were reported [13–15], and such open-frameworks remain largely unexplored to date.

We have been interested in constructing open frameworks from diverse cuprous cyanide skeletons and polyazaheteroaromatic ligands, and recently a novel 3D copper(I)–CN–tetrazolate coordination polymer generated from the interpenetration of porous 2D double-layer motifs have been successfully obtained [16]. As an extension of our previous work, 3,5-bis(4-pyridyl)-1,2,4-triazole (BPy-4Trz), an angular dipyridyl derivative was further selected to construct new open frameworks with copper cyanide inorganic subunits. In this contribution, we report a novel 3D open-framework compound, namely, **{Cu_2(BPy-4Trz)(CN)}$_n$** (**1**), which exhibits a rare (4,6)-connected 2-fold interpenetrated fsc topology. To the best of our knowledge, compound **1** represents the first organic–inorganic hybrid open framework construct from pyridyl-substituted 1,2,4-triazole derivative ligand and copper(I) cyanide motif.

The golden block crystals of complex **1** were produced by heating the mixture of CuCN, $K_3Fe(CN)_6$ and BPy-4Trz in 5 ml H_2O at 180 °C for 5 days [17]. In our experiments, the utilization of $K_3Fe(CN)_6$ as the CN^- source instead of KCN can effectively avoid the high toxicity. Moreover, the slow release of CN^- from $K_3Fe(CN)_6$ under hydrothermal conditions also plays an important role in the formation of such hybrid materials. The X-ray powder diffraction (XPRD) pattern (Fig. S1) measured at room temperature for the as-synthesized samples was in good agreement with that simulated from the single-crystal X-ray data, which indicates the high purity of bulk sample of **1**. A single band at 2108 cm^{-1} in the IR spectrum of **1** (Fig. S2) was assigned to the cyanide group, which is higher than that of terminal cyanide ions and is typical for bridging cyanide groups [13–15]. The other two series of bands in the ranges of 420–1003 and 1400–1700 cm^{-1} are ascribed

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http://dx.doi.org/10.1016/j.inoche.2013.08.036

to the vibrations of BPy-4Trz organic ligand, which are also found in the Raman spectrum of **1**. Compound **1** was also studied by thermal analysis in nitrogen gas from 40 to 1000 °C (Fig. S3). The TG curve well supports its chemical compositions, which shows that this open framework compound was stable up to ca. 400 °C. Over the range 400–550 °C, a sharp weight loss was due to the decomposition of BPy-4Trz ligands (exptl: 58.7%, calcd: 59.2%). Furthermore, the in-situ generated CuCN solid slowly decomposed when the temperature was increased, and the final residue should be copper powder (exptl: 32.4%, calcd: 33.9%).

The single-crystal structure analysis [18] shows that compound **1** crystallizes in the monoclinic space group *P*2/*m* and presents a 2-fold interpenetrated hybrid open framework. As depicted in Fig. 1, the structure of **1** possesses two Cu^{+} ions, one BPy-4Trz ligand, and two half of cyanide anions. Two independent copper centers both are in distorted trigonal geometries. However, the detailed coordination environments are different. Cu1 is coordinated by two triazole nitrogen atoms from BPy-4Trz and one μ_2-bridging cyanide group. Cu2 is coordinated by two pyridyl nitrogen donors of BPy-4Trz and one μ_2-bridging cyanide anion. The Cu–N and Cu–CN bond lengths are of 1.989(2)–2.0195(19) Å and 1.907(3)–1.918(4) Å, respectively. The corresponding bond angles are in the range of 104.90(11)–129.88(13)°. Two cyanide groups both act as μ_2-bridging to link two Cu1 and Cu2 atoms. The central triazole ring and two 4-pyridyl groups in BPy-4Trz ligand are completely co-planar. As usually observed in the metal-triazolate compounds, two adjacent Cu1 atoms are co-bridged by a pair of triazole groups using the neighboring N atoms to generate a $[Cu_2(Trz)_2]$ binuclear subunit with Cu···Cu separation of 3.5651(7) Å. However, unlike the typical Cu-triazolate binuclear cluster with four nitrogen and two Cu atoms in one plane [13,19,20], the $[Cu_2(Trz)_2]$ in **1** is severely distorted because the third coordination site of Cu1 is occupied by a short μ_2-CN group to link the adjacent binuclear motif. Moreover, as shown in Fig. 2a, four $[Cu_2CN]$ inorganic clusters generated by Cu2 centers are also connected by the $[Cu_2(Trz)_2]$ unit through four 4-pyridyl groups. Vice versa, each $[Cu_2CN]$ binuclear cluster links four $[Cu_2(Trz)_2]$ subunits (Fig. 2b). Two kinds of binuclear motifs interlinked each other to generate a 3D hybrid open framework of **1** (Fig. 2c). From a topological view, we can define the $[Cu_2CN]$ and $[Cu_2(Trz)_2]$ subunits as 4- and 6-connected nodes, respectively. Thus, the whole hybrid framework of **1** can be simplified as a (4,6)-connected fsc topological net (Fig. 2d) with the short Schläfli symbol of $(4^4\cdot6^2)(4^4\cdot6^{10}\cdot8)$. To the best of our knowledge, only two isomers constructed from $Cu_6I_6(DABCO)_4$ and $Cu_8I_8(DABCO)_6$ building blocks with fsc topology were reported to date [21].

On the other hand, the structure of this (4,6)-connected framework can also be described in a step by step solution. As shown in Fig. S4, two independent copper centers are linked to each other by the BPy-4Trz ligand via two triazole N atoms and two pyridine N atoms to form a 1D ribbon. It is interesting that the $[Cu_4C_{16}N_8]$ 28-membered metal-organic rings are observed, which is uncommon in the coordination chemistry of such angular 4,4′-dipyridyl derivatives. Further, adjacent 1D ribbons are connected by the CN groups to give a 2D layer in the *a*, *c*-plane. The 2D layers are ultimately extended by the other independent CN anions to from the 3D open framework of **1**. It should be pointed out the two types of 1D channels along the *c*-axis direction with cross dimensions of about 4.4 × 8.0 $Å^2$ (A) and 5.0 × 10.7 $Å^2$ (B) are observed in this novel Cu(I)–cyanide–triazolate hybrid open framework (Fig. 2c). Two sets of such (4,6)-connected frameworks are packed alternately through π···π interactions between the 4-pyridyl groups (the center to center distances are of 3.694(3) Å) to give a 3D + 3D 2-fold interpenetrated structure of compound **1** (Figs. 3 and S5).

The luminescent properties of several metal-1,2,4-triazolate compounds explored by us and others have indicated that emission colors of organic spacers were remarkably affected by their incorporation into metal-containing coordination compounds [22–25]. Herein, the photoluminescence of compound **1** in the solid state under room temperature was investigated. As shown in Fig. 4, upon excitation of the solid sample at λ = 260 nm, two emission bands are observed at 366 nm and 541 nm, respectively. Our further experiments show that

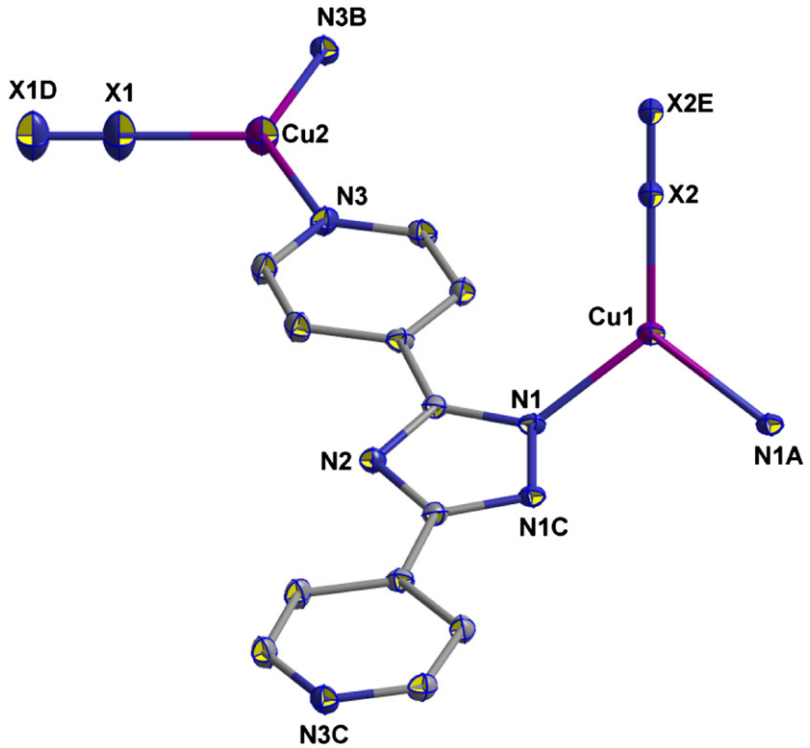

Fig. 1. ORTEP diagram of compound **1** showing the local coordination environments of copper(I) centers in the asymmetric unit and 30% thermal ellipsoids (symmetry codes: A x, 1 − y, z; B − x, y, 2 − z; C 2 − x, y, 1 − z; D − x, − y, 2 − z; E 2 − x, y, 2 − z.) Atoms from the disordered CN bridging groups are treated by adopting 50% C and N occupancies and labeled as X.