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ORIGINAL PAPER

Synthesis, Crystal Structure, and Properties of a 2D Cu(I) Coordination Polymer Based on Cu_3I_3 Chains Linked by 1,3-Di-(1,2,4-Triazole-4-yl)Benzene

Shao-Bin Miao[1] · **Chun-Ying Xu**[1] · **Dong-Sheng Deng**[1] · **Bao-Ming Ji**[1]

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Abstract

A new copper(I) iodide coordination polymer, $[(CuI)_3(dtb)]_n$ (**1**) (dtb = 1,3-di-(1,2,4-triazole-4-yl)benzene) has been synthesized solvothermally and structurally characterized by single crystal and powder X-ray diffractions, elemental analysis, IR, and thermogravimetric analysis. Overall, **1** exhibits a 2D hybrid structure containing dtb as structure-directing agents (SDAs) and 1D Cu_3I_3 chain as inorganic moiety. The copper-iodide chain can be regarded as two Cu_2I_2 rhomboids are connected by CuI fragments via Cu–I bonds. Dtb act as bridging ligands regularly link the Cu_3I_3 chains along both sides through Cu–N bonds to give the final 2D network. Moreover, solid state luminescent property of **1** has been investigated at room temperature.

Keywords Coordination polymer · Copper iodide · Crystal structure · Luminescence

Introduction

Coordination polymer (CPs) or organic–inorganic hybrid materials, constructed by inorganic secondary building units (SBUs) and organic bridging ligands has taken wide attention in recent years owing to their intriguing structures as well as distinctive properties such as catalytic, luminescence, gas adsorption, and magnetism [1–6]. It is well known that copper(I) halide culsters, particularly copper(I) iodide motifs have been employed widely as inorganic components in the constructions of CPs since their rich coordinate sites as well as their excellent photophysical properties [7–10]. Indeed, copper iodide clusters not only defined the frameworks of the CPs but also impart their distinctive properties to the frameworks. Various copper(I) iodide clusters with the formulae $(Cu_xI_y)^{x-y}$ have been reported in the past decades such as lower nuclearity or higher nuclearity clusters, discrete oligomers, polymeric chains or layers, cationic, anionic or neutral species [11–15]. These copper iodide hybrid clusters often constructed by so called structure-directing agents (SDAs) organic ligands (L) that contain N, P, S coordination atoms to give diverse copper iodide based CPs of the general formula $Cu_xI_yL_z$ [16–18]. Copper iodide clusters based luminescent CPs have gained considerable interest for their structural diversity and high emission quantum yields [19–22]. The luminescence properties of these CPs can arise from different mechanisms, for example metal-to-ligand charge transfer (MLCT) [23], halide-to-ligand charge transfer (XLCT) [24], halide to metal charge transfer (XMCT) [25], cluster centered (CC) charge transfer [26], and so on. Moreover, short Cu–Cu interactions may be capable of influencing the emission behavior [27–30]. Inspired by the above-mentioned opinions and as our continuous work on copper(I) CPs [31], herein we report the preparation and characterization of a new 2D coordination polymer based on Cu_3I_3 chains connected via 1,3-di-(1,2,4-triazole-4-yl)benzene (dtb), $[Cu_3I_3(dtb)]_n$ (**1**).

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✉ Bao-Ming Ji
lyhxxjbming@126.com

[1] College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, People's Republic of China

Experimental

Materials and Methods

All reagents and solvents for synthesis were purchased from commercial sources and used directly without further purifications. Infrared spectra (4000–600 cm^{-1}) were recorded on a Nicolet Avatar-360 spectrometer with KBr pellets. C, H, N analyses were carried out on a Flash 1112 elemental analyzer. The thermogravimetric measurement was carried out on a Perkin-Elmer TGA7 thermal analysis instrument at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Powder X-ray diffraction data were collected on a Bruker AXS D8-Advanced diffractometer with Cu–$K\alpha$ radiation ($\lambda = 1.5406$ Å). The solid-state luminescent spectra were performed on a FL-4500 fluorescent spectrometer using Xe lamp as the light source.

Synthesis of Compound $[Cu_3I_3(dtb)]_n$ (1)

A mixture of CuI (0.1 mmol, 19 mg), dtb (0.05 mmol, 11 mg), H_2O (6 mL) and acetonitrile (4 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 °C for 3 days. The reaction mixture was slowly cooled to room temperature at a rate of 3 °C/h, and the pink block crystals were obtained. Yield (based on Cu): 6.8 mg, 26%. Elemental analysis (%) for $C_{10}H_8Cu_3I_3N_6$, Found (calcd): C, 15.21(15.33); H, 1.09(1.03); N, 10.67(10.73). IR (KBr, cm^{-1}): 3066(w), 1601(m), 1537(s), 1361(w), 1290(m), 1100(m), 869(m), 791(m), 684(s).

X-ray Crystallography

Crystal structure determination of **1** by X-ray diffractions was carried on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods and refined by the full-matrix least-squares techniques on F^2 using SHELXTL-97 [32]. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. Hydrogen atoms were treated using a riding model. The crystallographic data for **1** are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

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

Empirical formula	$C_{10}H_8Cu_3I_3N_6$
Formula weight	783.54
Crystal system	Monoclinic
Space group	C2/m
a (Å)	14.9266(18)
b (Å)	12.4260(15)
c (Å)	10.1019(12)
α (°)	90
β (°)	105.4000(10)
γ (°)	90
Volume (Å^3)	1806.4(4)
Z	4
D_{calcd} (g cm^{-3})	2.881
Absorption coefficient (mm^{-1})	8.629
F(000)	1424
Crystal size (mm^3)	0.33 × 0.25 × 0.19
θ range for data collection (°)	2.74–25.50
Limiting indices	$-18 \le h \le 18$ $-15 \le k \le 15$ $-11 \le l \le 12$
Reflections collected/unique	6730/1761 ($R_{int} = 0.0274$)
Data/restraints/parameters	1761/0/110
Goodness of fit on F^2	1.004
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0685$
R indices (all data)	$R_1 = 0.0264$, $wR_2 = 0.0704$
Large diff. peak and hole (e Å^{-3})	0.425 and − 1.602

Results and Discussion

Crystal Structure

Single crystal X-ray diffraction study demonstrates that **1** crystallizes in the monoclinic space group $C2/m$, and shows a 2-D network with 1D Cu_3I_3 cluster chain. The asymmetric unit of **1** contains a Cu_3I_3 cluster and a dtb ligand (Fig. 1). Cu1 and Cu2 are both four-coordinated with distorted tetrahedral coordination environments. And the coordination spheres are completed by two iodine atoms and two nitrogen atoms from different dtb ligands. The τ_4 parameter for Cu1 and Cu2 is 0.85 and 0.80, respectively, showing the distortion of the geometry [33]. Cu3 are surrounded by three iodine atoms in a planar triangle arrangement. The Cu–I distances are in the range of 2.5056(8)–2.7264(8) Å and the Cu–N lengths are 2.028(3) and 2.007(3) Å (Table 2), respectively.

In **1**, iodine atoms show two different coordination modes, μ_2- and μ_3-bridging modes. Two Cu1 atoms are linked by two μ_3-I (I1) to form a rhombus Cu_2I_2 dimer, another Cu_2I_2 rhombic cluster is composed by two Cu3 atoms and two μ_3-I (I3). These two rhomboid cores are connected together by μ_2-I (I2) and Cu2 to give a 1D wavelike chain (Fig. 2). The distance of Cu1···Cu1 and Cu3···Cu3 are 2.6507(3) and 2.5517(10) Å, respectively, which are shorter than the sum of Cu···Cu Van der Waals radii (2.8 Å) and is within the range of other CuI clusters

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

Cu(1)–N(1)	2.028(3)	Cu(2)–I(2)	2.6831(8)
Cu(1)–N(1)#1	2.028(3)	Cu(2)–I(1)	2.7264(8)
Cu(1)–Cu(1)#2	2.6507(12)	Cu(3)–I(2)	2.5056(8)
Cu(1)–I(1)	2.6803(4)	Cu(3)–Cu(3)#4	2.5516(14)
Cu(1)–I(1)#2	2.6803(4)	Cu(3)–I(3)	2.5798(5)
Cu(2)–N(2)	2.007(3)	Cu(3)–I(3)#4	2.5798(5)
Cu(2)–N(2)#3	2.007(3)		
N(1)–Cu(1)–N(1)#1	119.48(16)	N(2)#3–Cu(2)–I(2)	104.48(8)
N(1)–Cu(1)–I(1)	101.98(8)	N(2)–Cu(2)–I(1)	100.70(9)
N(1)#1–Cu(1)–I(1)	106.90(9)	N(2)#3–Cu(2)–I(1)	100.70(9)
N(1)–Cu(1)–I(1)#2	106.90(9)	I(2)–Cu(2)–I(1)	118.03(3)
N(1)#1–Cu(1)–I(1)#2	101.98(8)	I(2)–Cu(3)–I(3)	119.615(14)
I(1)–Cu(1)–I(1)#2	120.73(2)	I(2)–Cu(3)–I(3)#4	119.615(14)
N(2)–Cu(2)–N(2)#3	129.72(18)	I(3)–Cu(3)–I(3)#4	120.72(3)
N(2)–Cu(2)–I(2)	104.48(8)		

Symmetry transformations used to generate equivalent atoms: #1 − x, y, − z + 1; #2 − x, − y, − z + 1; #3 x, − y, z; #4 − x + 1, − y, − z + 2

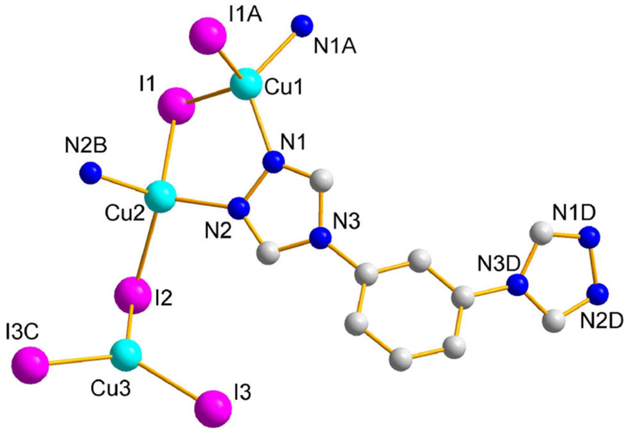

Fig. 1 Coordination environment of Cu$^+$ ions in **1**. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A −x, y, 1 − z; B x, − y, z; C 1 − x, –y, 2 − z; D x, 1 − y, z

[28]. The dtb adopt a μ_4-η^2N,N, η^2N',N' fashion and connect the 1D chains into a 2D sheet along *ab* plane (Fig. 3).

Powder X-ray Diffraction (PXRD) and Thermogravimetric Analysis (TGA)

The PXRD analysis was performed for **1** at room temperature (Fig. S1). All major peaks of the experimental pattern are in agreement with the simulated patterns, showing the purity of the crystals. The thermal behavior of **1** was evaluated by thermogravimetric analysis (TGA) from 30 to 900 °C (Fig. S2). The TGA curve of **1** displays a weight loss of 26.31% from 235 to 368 °C, which corresponds to the loss of dtb ligand (calc. 26.80%). Then the framework begins to collapse. The thermal decomposition temperature of **1** is similar to that of the coordination polymer we reported before [31].

Luminescent Property

The luminescent property of complex **1** was investigated in the solid state at room temperature (Fig. 4). Complex **1** exhibits a broad green emission band at 557 nm with excitation at 360 nm. The emission is reminiscent of other CuI cluster-containing coordination polymers with different N-heterocyclic ligands [34, 35]. The luminescence is

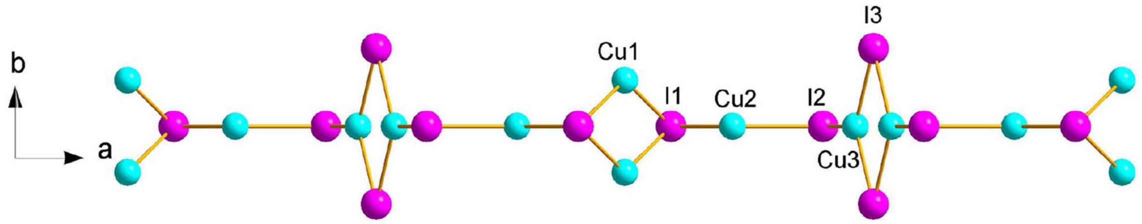

Fig. 2 View of 1D Cu$_3$I$_3$ chain

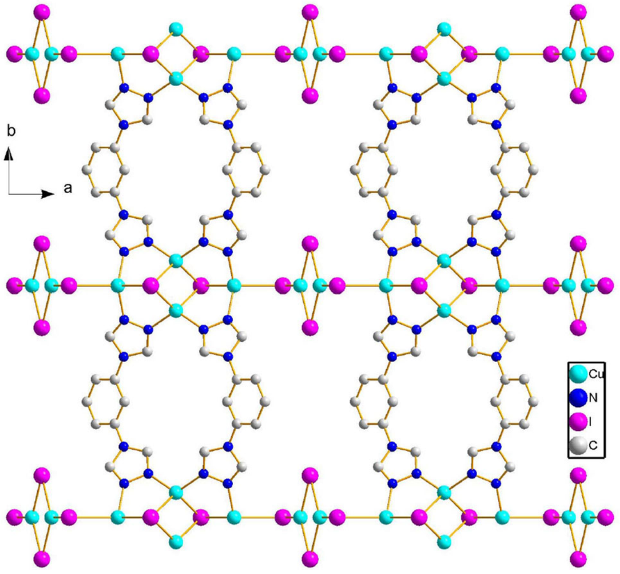

Fig. 3 View of 2D network of **1**. Hydrogen atoms are omitted for clarity

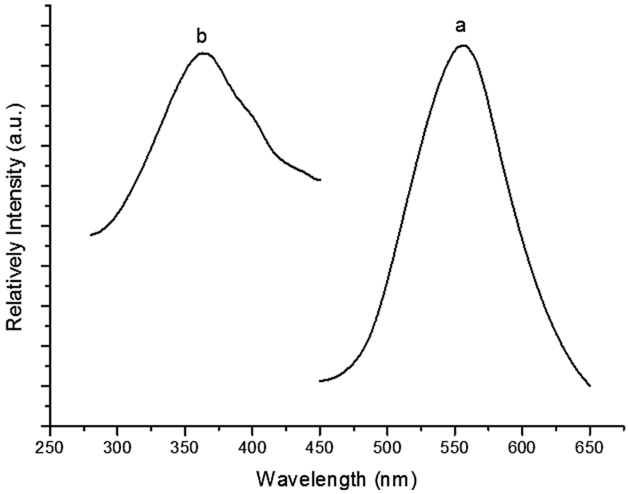

Fig. 4 Solid-state emission spectra (*a*) and excited spectra (*b*) of **1** at room temperature

might be derived from a cluster-centered excited state (CC) of Cu_3I_3, which is supported by the short Cu···Cu distances [16, 17]. The emission maximum observed for **1** is within the range of similar CC emission [26].

Conclusions

In summary, a unique 2D CP based on 1D Cu_3I_3 chain and 1,3-di-(1,2,4-triazole-4-yl)benzene has been synthesized under solvothermal condition. Moreover, **1** displays green solid luminescence at room temperature which can be assigned to CC transitions. Concerning the special structures and properties of copper(I) iodide clusters based CPs, further studies are currently in progress.

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