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STRUCTURE AND PHOTOLUMINESCENT PROPERTY OF A THREE-DIMENSIONAL PILLARED-LAYER La(III)—Cu(I) HETEROMETALLIC COORDINATION POLYMER

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A three-dimensional (3D) pillared-layer La(III)—Cu(I) heterometallic coordination polymer (HCP) formulated as $[La_2Cu_4I_3(Hina)_7(H_2O)]_n$ (**1**) (Hina = isonicotinic acid), is synthesized by a hydrothermal reaction of La_2O_3, CuI, and ina. The crystal structure is determined by single crystal X-ray diffraction. HCP **1** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters: $a = 17.0147(3)$ Å, $b = 18.4431(3)$ Å, $c = 16.7487(3)$ Å, $\beta = 102.469(2)°$, $V = 5131.84(15)$ Å^3, $Z = 4$. It features a 3D pillared-layer heterometallic organic framework, where Ln-ina layers are pillared by discrete $[Cu_8I_6(ina)_{12}]$ units along the direction of the *a* axis. In addition, the solid-state photoluminescent property is investigated.

K e y w o r d s: heterometallic coordination polymer, crystal structure, pillared-layer, photoluminescent property.

Recently, lanthanide transition metal (d—f) HCPs have been attractive due to their aesthetically beautiful structures and potential applications in magnetism, luminescence, adsorption, and chemical sensing [1—9]. Various N-heterocyclic aromatic carboxylate ligands have been employed to construct d—f hybrid HCPs [7—13]. Hina is one of the most popular ligands for the setting of both nitrogen and oxygen atoms on the opposite sites of its pyridyl ring. It can behave as a rigid linear linker, suitable for the construction of high dimensional structures and prone to form pillared-layer frameworks [7, 14—16]. Monovalent copper iodides are interesting coordination motifs with remarkable structural variation. The ball-shaped iodine anion has high affinity to monovalent copper ion and exhibits variable coordination modes ranging from μ_2-I to μ_4-I. Up to now, various structural motifs of Cu(I) iodides have been reported, for example, Cu_2I [15], Cu_2I_2 [17], Cu_3I_3 [17], Cu_4I_4 [18], Cu_5I_4 [14], Cu_6I_5 [19], Cu_6I_6 [20], Cu_7I_6 [14], Cu_8I_6 [16], and Cu_8I_7 [15]. According to the hard-soft acid base theory [21], the ina carboxylate group readily coordinates to hard lanthanide ions, while the nitrogen atoms can easily bond to a soft Cu(I) ion, making it feasible to incorporate Cu(I) iodide motifs into lanthanide coordination units. Recently, we have also reported three structural types of halide-containing or halide-free 3D Cu—Ln HCPs based on mixed isonicotinate and hemimellitate ligands [15]. In this contribution, we use ina, La_2O_3, and CuI to synthesize d—f hybrid HCP. A 3D pillared-layer HCP formulated as $[La_2Cu_4I_3(ina)_7(H_2O)]_n$ (**1**) was obtained. Herein, we report its crystal structure and photoluminescent property.

EXPERIMENTAL

Materials and general methods. All chemicals were obtained from commercial sources and used as received. An infrared (IR) spectrum was recorded on a PerkinElmer Spectrum One instrument as a KBr pellet in the range 4000—400 cm^{-1}. Elemental analyses of C, H, and N were measured on a Vario MICRO E III elemental analyzer. Thermogravimetric analysis (TGA) was performed on an SDT

Q600 instrument at a heating rate of 10 °C/min under the nitrogen atmosphere from 40 °C to 900 °C. A solid-state photoluminescent spectrum was measured at room temperature with an Edinburgh FLS920 fluorescence spectrometer. The instrument is equipped with a Xe900 xenon arc lamp as an exciting light source.

Syntheses of $[La_2Cu_4I_3(Hina)_7(H_2O)]_n$ (1). A mixture of La_2O_3 (0.40 mmol), CuI (0.84 mmol), ina (2.3 mmol) in deionized water (10 ml) was placed in a 23 ml Teflon-lined stainless autoclave. After 1 h of stirring, it was sealed and heated at 180 °C for 125 h, and then slowly cooled down to room temperature at a rate of 3 °C·h^{-1}. Orange crystals were collected by filtration, washed with distilled water and air dried. Yield: 90 % (based on CuI). Calcd for $C_{42}H_{30}N_7Cu_4I_3La_2O_{15}$ (%): C, 28.25; H, 1.69; N, 5.49. Found (%): C, 28.13; H, 1.71; N, 5.50. IR (KBr pellet, cm^{-1}): 3360 (br), 1630 (w), 1588 (s), 1543 (s), 1416 (s), 1224 (w).

The TG curve displays two main steps of weight losses. The weight loss from 40 °C to 145 °C is about 1.28 %, corresponding to the loss of the coordinated water molecule (theoretical value 1.01 %). It exhibits a plateau in the temperature range 145—370 °C. Above this temperature, the weight loss is attributed to the decomposition of organic ligands and the framework collapse of the coordination polymer.

X-ray crystallographic study. Single crystal X-ray diffraction data of HCP **1** was collected on an Oxford Xcalibur E CCD-based diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature. The intensity data set was collected with the ω-scan technique. The CrysAlisPro (Version 1.171.34.49) software was used for data reduction and empirical absorption correction. The structure was solved by a direct method and successive Fourier difference syntheses, and refined by full-matrix least-squares on F^2 (SHELXTL Version 5.1) [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to C atoms were generated theoretically and refined by a riding mode with isotropic thermal parameters fixed at 1.2 times that of the mother atoms. Hydrogen atoms bonding to the coordinated water molecule was placed in the calculated positions and refined with isotropic thermal parameters fixed at 1.5 times that of O atoms. Detailed crystallographic data and structure refinement parameters are summarized in Table 1. Selected bond lengths are listed in Table 2. CIF file containing complete information

T a b l e   1

Crystallographic data for HCP **1**

Empirical formula	$C_{42}H_{30}Cu_4I_3La_2N_7O_{15}$
Formula weight	1785.41
Crystal system, Space group	Monoclinic, $P2_1/c$
a, b, c, Å	17.0147(3), 18.4431(3), 16.7487(3)
β, deg.	102.469(2)
V, Å^3	5131.84(15)
Z; D_c, g·cm^{-3}	4; 2.311
μ, mm^{-1}	5.132
Crystal size, mm	0.17×0.08×0.06
Reflections collected / unique	25943 / 10752
Data / restraints / parameters	10752 / 0 / 658
R(int)	0.0313
GOOF on F^2	1.056
R_1, wR_2 (I > 2σ(I))^a	0.0319, 0.0771
R_1, wR_2 (all data)^a	0.0498, 0.0966
$\Delta\rho_{min}$ / $\Delta\rho_{max}$, e/Å^3	1.085 / −1.667

$^aR = \sum||F_0| - |F_c||)/\sum|F_0|$, $wR = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

Selected bond distances (Å) *for HCP* **1**

Bond	d	Bond	d	Bond	d
La(1)—O(7)	2.429(4)	La(1)—O(5)	2.439(3)	La(1)—O(9)#1	2.442(4)
La(1)—O(13)	2.548(4)	La(1)—O(3)	2.563(4)	La(1)—O(2)	2.607(4)
La(1)—O(1)	2.719(4)	La(1)—N(1)#2	2.769(4)	La(2)—O(8)#3	2.443(4)
La(2)—O(12)	2.456(4)	La(2)—O(14)#3	2.469(4)	La(2)—O(4)	2.475(4)
La(2)—O(6)	2.518(4)	La(2)—O(1)	2.551(3)	La(2)—O(15)	2.554(4)
La(2)—O(10)	2.594(4)	I(1)—Cu(2)	2.5452(11)	I(1)—Cu(1)	2.5879(11)
I(2)—Cu(3)	2.5685(11)	I(2)—Cu(2)	2.6236(12)	I(2)—Cu(1)	3.2992(16)
I(3)—Cu(1)	2.4924(10)	I(3)—Cu(4)	2.8704(11)	I(3)—Cu(4)#4	2.8798(12)
Cu(1)—N(4)	1.981(5)	Cu(1)—Cu(2)	2.5461(16)	Cu(2)—N(7)#5	1.986(5)
Cu(3)—N(6)#6	1.965(6)	Cu(3)—N(2)#1	1.991(5)	Cu(4)—N(3)#5	1.982(5)
Cu(4)—N(5)	1.994(5)				

Symmetry codes for: **1** (#1) x, $-y+1/2$, $z-1/2$. (#2) $-x+1$, $y+1/2$, $-z+3/2$. (#3) x, $-y+1/2$, $z+1/2$. (#4) $-x+2$, $-y$, $-z+2$. (#5) $x+1$, $-y+1/2$, $z+1/2$. (#6) $x+1$, $-y+1/2$, $z-1/2$.

on the studied structure was deposited with CCDC, deposition number 886449, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Crystal structure description. Single crystal X-ray diffraction reveals that HCP **1** crystallizes in the monoclinic space group $P2_1/c$. It is a 3D pillared-layer heterometallic-organic framework in which Ln-ina layers are pillared by discrete $[Cu_8I_6(ina)_{12}]$ units along the direction of the crystallographic a axis. As shown in Fig. 1, the asymmetric unit of **1** consists of two crystallographically unique La(III) ions, four Cu(I) ions, three I⁻ ligands, seven ina⁻ ligands, and one aqua ligand. All atoms locate in ge-
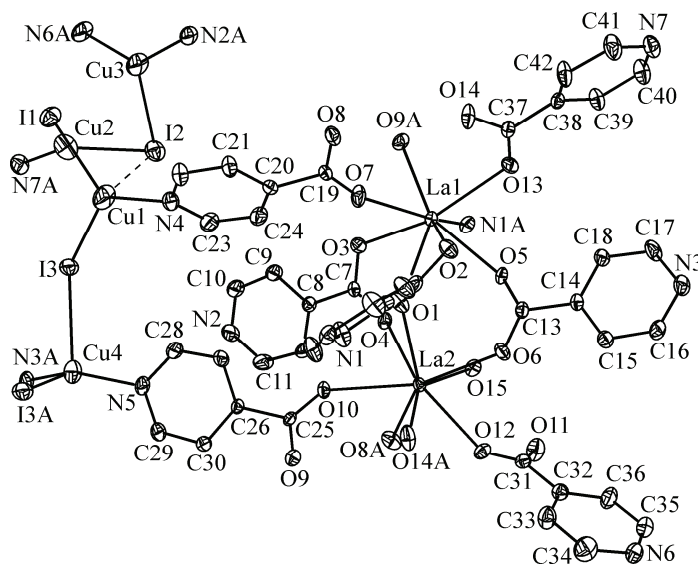

Fig. 1. ORTEP drawing of the asymmetric unit of **1** with 30 % probability thermal ellipsoids. Hydrogen atoms are omitted
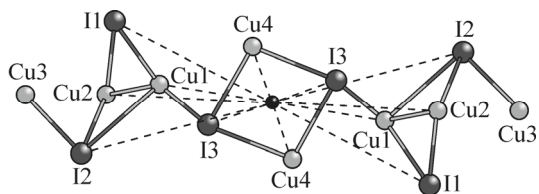
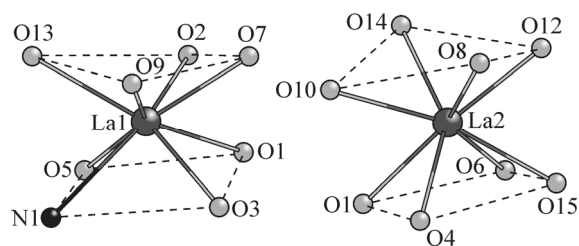Fig. 2. View of the centrosymmetric [Cu₈I₆] cluster in **1**. The inversion center is drawn as a black ball

Fig. 3. Perspective view of the coordination polyhedra of La(III) ions

neral positions. It has a similar formula to two previously published HCPs $[Ln_2Cu_4I_3(ina)_7(H_2O)]_n$ (Ln = Nd, Gd), but the coordination modes of Cu(I) ions and I^- ligands are notably different [16]. Cu(1) and Cu(4) are four-coordinated in a distorted tetrahedral geometry with the $[CuI_3N]$ and $[CuI_2N_2]$ coordination environment respectively. Cu(2) and Cu(3) adopt a planar trigonal coordination geometry with the $[CuI_2N]$ and $[CuIN_2]$ environment respectively. It is different from those in the literature (two tri-coordinated Cu(I) with the $[CuIN_2]$ environment and two four-coordinated Cu(I) with the $[CuI_3N]$ environment, although the authors described that four Cu(I) ions were tri-coordinated) [16]. I(1) is μ_2-I, while both I(2) and I(3) are μ_3-I. It is also different from those in the literature (two μ_2-I and one μ_3-I), presenting another example of the remarkable structural variation of Cu(I) iodide motifs. The different coordination modes of Cu(I) ions and I^- ligands result in a different aggregation of the Cu(I) iodide cluster. As shown in Fig. 2, the linkage of Cu(I) ions by μ_2-I and μ_3-I generates a centrosymmetric discrete $[Cu_8I_6]$ cluster. The Cu—I bond lengths range from 2.5452(11) Å to 3.2992(16) Å (Table 2). An unusual feature of this cluster is its short Cu···Cu distance. The Cu(1)···Cu(2) distance bridged by I(1) and I(2) is about 2.546 Å, obviously shorter than the van der Waals radius of two monovalent Cu ions (1.4×2 Å), suggesting a strong Cu—Cu interaction. The remaining ligand sphere of Cu(I) ions are completed by ina^- nitrogen atoms to form a $[Cu_8I_6(ina)_{12}]$ unit, which plays the role of a pillar.

La(1) is eight-coordinated with a $[O_7N]$ donor set, forming a slightly distorted square antiprism coordination polyhedron (Fig. 3). Seven O atoms derive from six ina^- ligands and the N atom comes from an ina^- pyridyl group. La(2) is also eight-coordinated but with a $[O_8]$ donor set, the coordination polyhedron of which can be described as a distorted square antiprism (Fig. 3). The ligand sphere of La(2) is occupied by one aqua ligand and seven O atoms from seven distinct ina^- ligands. The La···O bond lengths range from 2.429(4) Å to 2.719(4) Å, with an average value of about 2.520(1) Å, shorter than the La···N bond (2.769(4) Å) (Table 2). As displayed in Fig. 4, the connection between La(III) ions and ina^- ligands leads to a La-ina layer extending on the crystallographic *bc* plane. The neighboring layers are further pillared by $[Cu_8I_6(ina)_{12}]$ units along the direction of the *a* axis, giving rise to a 3D framework (Fig. 5). The structure is the strictly alternate arrangement of La-ina layers and $[Cu_8I_6(ina)_{12}]$ pillars.
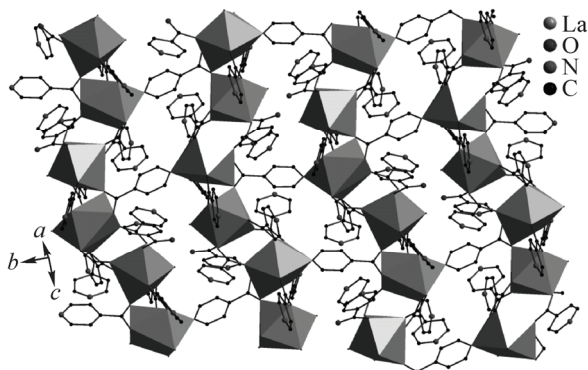

Fig. 4. View of the La-ina layer along the *a* axis. $[LaO_8]$ and $[LaO_7N]$ are drawn as pale polyhedra
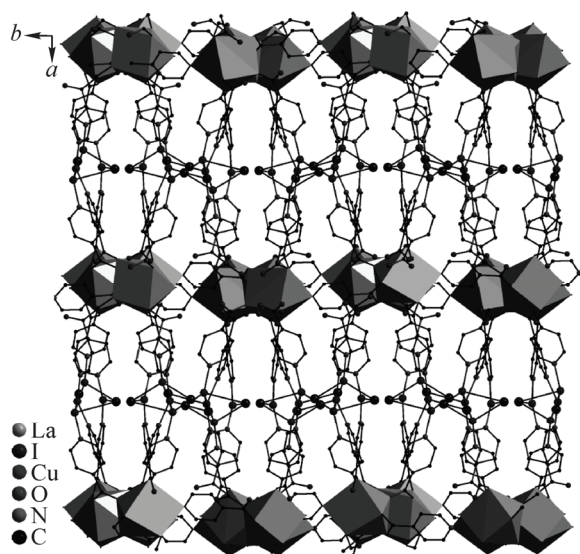
Fig. 6. Solid-state emission spectrum
of **1** (λ_{ex} = 370 nm)

Fig. 5. View of the 3D pillared-layer structure of **1** along the
c axis. [LaO$_8$] and [LaO$_7$N] are drawn as pale polyhedra

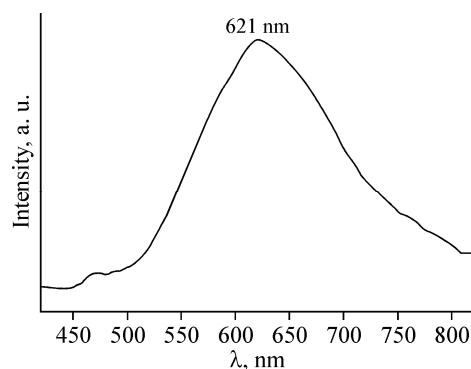**Photoluminescent Property.** HCP **1** exhibits a broad emission peak centered at 621 nm upon excitation at 370 nm (Fig. 6). The emission is assigned to Cu(I)-based ligand-to-metal or metal-to ligand charge transfer or d $\rightarrow$ s electronic transition of copper ions since there is a strong Cu—Cu interaction within the cluster.

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