ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2015. Том 56, № 8 *Декабрь* *С. 1642 – 1647*

UDC 541.49:546.641:548.73:541.6

A TWO-DIMENSIONAL YTTRIUM-ORGANIC COORDINATION POLYMER CONTAINING INFINITE $\{[Y_4(\mu_3\text{-OH})_4]^{8+}\}_n$ CHAIN

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Received July, 23, 2014

A two-dimensional (2D) coordination polymer, formulated as $[Y_4(\mu_3\text{-OH})_4(\text{hma})(\text{cba})_5]_n\cdot n(\text{Hcba})$ (**1**), is synthesized by the synergistic coordination of hemimellitate (H_3hma) and 4-chlorobenzoate (Hcba) ligands with Y_2O_3 under hydrothermal conditions. It has been characterized by single-crystal X-ray diffraction, powder XRD, thermogravimetric analysis, elemental analysis and infrared spectroscopy. Single-crystal X-ray diffraction reveals that it crystallizes in the triclinic crystal system, $P\overline{1}$ space group. Unit cell parameters: $a = 11.0280(6)$ Å, $b = 14.5791(10)$ Å, $c = 18.9515(12)$ Å, $\alpha = 72.233(6)°$, $\beta = 82.641(5)°$, $\gamma = 70.933(5)°$, $V = 2741.1(3)$ Å^3, $Z = 2$. The asymmetric unit contains a $[Y_4(\mu_3\text{-OH})_4]^{8+}$ core which is extended into an infinite $\{[Y_4(\mu_3\text{-OH})_4]^{8+}\}_n$ chain along the direction of *a* axis. Every $\{[Y_4(\mu_3\text{-OH})_4]^{8+}\}_n$ chain is further connected to two neighboring chains by hma^{3-} ligands along the direction of *b* axis, forming a 2D yttrium-organic layer in the *ab* plane. Adjacent layers are further packed with each other via hydrophobic interactions to form a three-dimensional (3D) structure.

DOI: 10.15372/JSC20150819

Keywords: yttrium, coordination polymer, crystal structure, hemimellitic acid.

Polynuclear hydroxocomplexes of rare earth (RE) metals are fascinating complexes that possesses not only aesthetically beautiful structures but also interesting physical properties [1—4]. The rational choice of supporting ligands is very important for the construction of RE hydroxy clusters. Until now, carboxylic acids, nitrophenols, amino acids and β-diketones have been employed as supporting ligands, and many RE clusters such as RE_4, RE_5, RE_6, RE_{12}, RE_{14}, RE_{15}, RE_{26}, RE_{36}, RE_{48}, RE_{60} have been synthesized [2—13]. Among these supporting ligands, carboxylic acids are most frequently and successfully used. In this work, a 2D coordination polymer with the formula $[Y_4(\mu_3\text{-OH})_4(\text{hma})(\text{cba})_5]_n\cdot n(\text{Hcba})$ (**1**) was obtained by hydrothermal reaction of hemimellitic acid, 4-chlorobenzoic acid and Y_2O_3. Herein, we report its crystal structure and photoluminescent properties.

EXPERIMENTAL

Materials and general methods. All chemicals were obtained from commercial sources and used without further purification. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum One instrument in a KBr pellet in the range of 4000—400 cm^{-1}. Elemental analyses for C and H were performed on a Vario MICRO E III elemental analyzer. Thermogravimetric analysis was performed on an SDT Q600 instrument at a heating rate of 10°/min under nitrogen atmosphere in the temperature range of 40—900 °C. Solid-state photoluminescence spectra were measured at room temperature with an Edinburgh FLS920 fluorescence spectrometer. The instrument is equipped with a Xe900 xenon arc lamp as excitation source.

Syntheses of $[Y_4(\mu_3\text{-OH})_4(hma)(cba)_5]_n \cdot n(Hcba)$ (1). A mixture of Y_2O_3 (0.50 mmol), H_3hma (0.45 mmol), Hcba (1.0 mmol) and deionized water (10 mL) was placed in a 23 mL Teflon-lined stainless autoclave. After 30 min of stirring, it was sealed and heated at 180 °C for 135 h, and then slowly cooled down to room temperature at a rate of 3 °C/h. The product was washed repeatedly with water and air-dried. Colorless small crystals were obtained in a 43 % yield (based on Y_2O_3). Calcd. for $C_{51}H_{32}Cl_6O_{22}Y_4$ (%): C 39.14, H 2.06. Found (%): C 39.09, H 2.10. IR (KBr pellet, cm^{-1}): 3439 (br), 1687 (w), 1591 (s), 1539 (vs), 1462 (w), 1424 (s), 1324 (w).

The TGA curve of **1** exhibits a plateau in the temperature range of 40—200 °C, indicating the structure to be thermally stable up to 200 °C. Further heating results in a continuous weight loss covering the temperature range of 200—900 °C, suggesting the decomposition of organic ligands. However, complete decomposition is not achieved even at 900 °C if assuming the final residue to be Y_2O_3 (theoretical/found: 28.9/44.6 %).

X-ray crystallographic study. Single crystal X-ray diffraction data of **1** was collected on 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 direct method and successive Fourier difference syntheses, and refined by full-matrix least-squares treatment on F^2 (SHELXTL Version 5.1) [14]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to C atoms and μ_3-OH$^-$ were generated into calculated positions and refined in a riding-mode approximation. 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 on the studied structure has been deposited with CCDC, deposition number 1001307, 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 **1** crystallizes in the triclinic $P\bar{1}$ space group. It forms a 2D coordination network in which infinite $\{[Y_4(\mu_3\text{-OH})_4]^{8+}\}_n$ chains are connected to each other by organic ligands. As shown in Fig. 1, the asymmetric unit consists of four crystallographically unique Y^{3+} ions, four μ_3-OH$^-$, one hma^{3-} ligand, five cba$^-$ ligands, and one lattice Hcba molecule. All atoms reside in general positions which are fully occupied in the

Table 1

Crystallographic data for **1**

Empirical formula	$C_{51}H_{32}Cl_6O_{22}Y_4$	μ, mm^{-1}	4.567
Formula weight	1565.11	Crystal size, mm	0.22×0.06×0.02
Crystal system	Triclinic	Reflections collected / unique	20943 / 11446
Space group	$P\bar{1}$	Data / parameters	11446 / 748
Temperature, K	293	R(int)	0.0647
a, b, c, Å	11.0280(6), 14.5791(10), 18.9515(12)	GOOF on F^2	1.001
α, β, γ, deg.	72.233(6), 82.641(5), 70.933(5)	R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0605, 0.1060
V, Å^3	2741.1(3)	R_1, wR_2 (all data)[a]	0.1244, 0.1404
Z	2	$\Delta\rho_{min\,/\,max}$, e/Å^3	0.880 / –0.973
D_c, g/cm^3	1.896		

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

Table 2

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

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
Y(1)—O(7)	2.272(5)	Y(4)—O(14)	2.233(5)	Y(3)—O(3)	2.319(4)	Y(2)—O(17)	2.285(5)
Y(1)—O(2)#1	2.301(4)	Y(4)—O(5)#4	2.374(5)	Y(3)—O(15)	2.338(5)	Y(2)—O(8)	2.303(5)
Y(1)—O(6)#2	2.602(4)	Y(4)—O(3)#4	2.416(4)	Y(3)—O(18)	2.395(5)	Y(2)—O(5)#2	2.413(4)
Y(2)—O(11)	2.296(5)	Y(1)—O(9)	2.297(5)	Y(4)—O(16)#4	2.260(5)	Y(3)—O(13)	2.328(5)
Y(2)—O(19)#3	2.330(4)	Y(1)—O(10)#1	2.304(5)	Y(4)—O(18)	2.385(5)	Y(3)—O(20)	2.369(5)
Y(2)—O(6)#2	2.635(5)	Y(1)—O(2)	2.605(5)	Y(4)—O(19)	2.427(4)	Y(3)—O(1)	2.679(5)
Y(3)—O(20)#4	2.331(4)	Y(2)—O(19)	2.303(5)	Y(1)—O(17)	2.298(4)	Y(4)—O(12)#3	2.370(5)
Y(3)—O(17)	2.385(4)	Y(2)—O(18)	2.388(4)	Y(1)—O(1)	2.436(4)	Y(4)—O(20)	2.413(4)

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

asymmetric unit. The hma^{3-} ligand exhibits a deca-topic coordination mode with five carboxylate oxygen atoms chelating-bridging six Y^{3+} ions, which can be denoted as μ_{10}-η^2: η^2: η^2: η^0: η^2: η^2. All the five cba$^-$ ligands adopt a bis-monodentate coordination mode by bridging two Y^{3+} ions in a *syn-syn* manner. The four Y^{3+} ions are all eight-coordinated by oxygen donors coming from μ_3-OH$^-$, hma^{3-} and cba$^-$ ligands, resulting in [YO$_8$] polyhedra, which can be best depicted as distorted square antiprisms. It is unusual that no aqua ligand is involved in coordination even though the reaction is conducted under hydrothermal conditions. The Y—O bond distances range from 2.233(5) Å to 2.679(5) Å, with the average value of 2.378 Å, which is reasonable for eight-coordinated Y^{3+} ions [15]. The inter-linking between Y^{3+} ions and μ_3-OH$^-$ leads to the formation of a $[Y_4(\mu_3\text{-}OH)_4]^{8+}$ core which is extended into an infinite $\{[Y_4(\mu_3\text{-}OH)_4]^{8+}\}_n$ chain along the direction of *a* axis (Fig. 2). It should be noted that this $[Y_4(\mu_3\text{-}OH)_4]^{8+}$ "cluster" is different from the commonly observed cuboidal $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ "clusters" [16, 17]. Every $\{[Y_4(\mu_3\text{-}OH)_4]^{8+}\}_n$ chain is further connected to two adjacent chains by hma^{3-} ligands along the direction of *b* axis, generating a 2D yttrium-organic layer in the *ab* plane (Fig. 3). The remaining coordination sites are completed by cba$^-$ ligands. The 4-chlorophenyl groups of cba$^-$ ligands

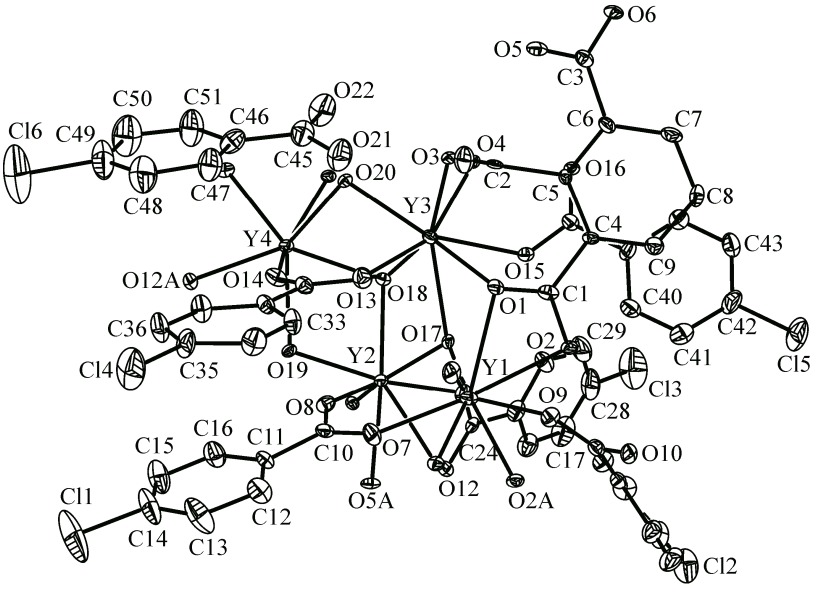

Fig. 1. Asymmetric unit of **1** with 30 % probability of thermal ellipsoids. Hydrogen atoms and the lattice Hcba molecule are omitted for clarity

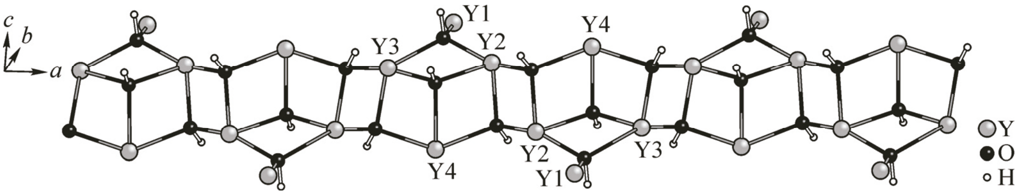

Fig. 2. Structure of the infinite $\{[Y_4(\mu_3\text{-}OH)_4]^{8+}\}_n$ chain in **1**

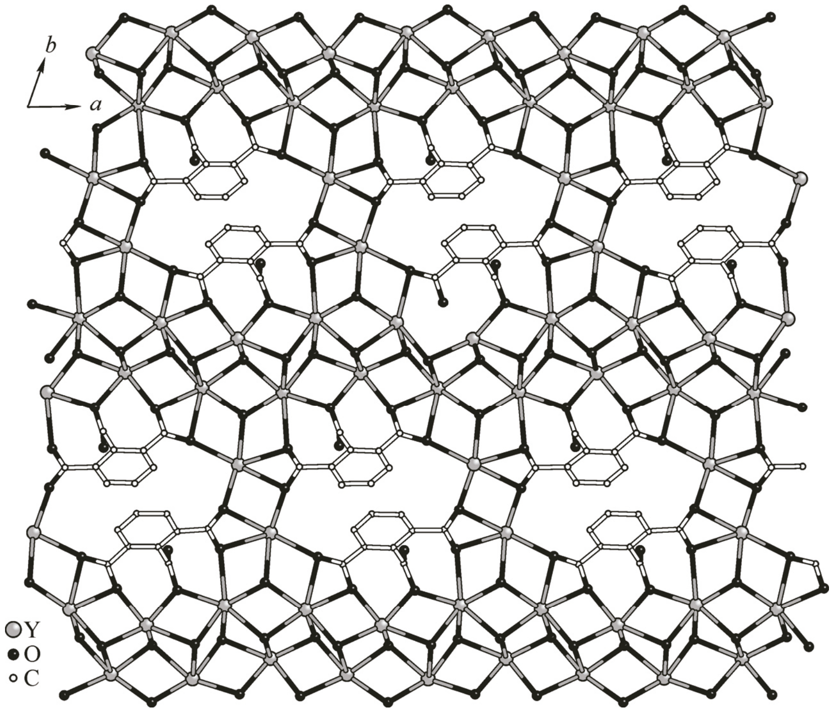

Fig. 3. Structure of the 2D yttrium-organic layer in **1**.
Coordinated cba^- ligands are omitted for clarity

arrange along the direction of *c* axis to form hydrophobic interactions with adjacent yttrium-organic layers, giving rise to a 3D packing structure (Fig. 4). The inter-layer space is completely filled up by hydrophobic 4-chlorophenyl groups, and no hydrogen bonding is observed between two adjacent layers. It is interesting that not water molecules, but a free Hcba molecule is captured in the lattice. Further evidence of the presence of lattice Hcba can be found in the IR spectrum. As shown in Fig. 5, the peaks at 1687 cm^{-1} and 1462 cm^{-1} are assigned to the asymmetric and symmetric stretching vibration of the protonated —CO_2H group of lattice Hcba. The Hcba molecule is fixed in the lattice by both hydrophobic interactions and hydrogen bonds. Detailed hydrogen bonding parameters are listed in Table 3.

Photoluminescent properties. As shown in Fig. 6, upon ultraviolet excitation, the solid-state Hcba and H_3hma ligands exhibit emission peaks at 357 nm (λ_{ex} = 305 nm) and 364 nm (λ_{ex} = 315 nm), respectively. Coordination polymer **1** displays an emission peak at 414 nm (λ_{ex} = 359 nm), which can be attributed to ligand-centered fluorescence with the emission red-shifted about 50 nm as compared to the free ligands.

This work was financially supported by NSFC Program (21301201) and The Education Department of Guizhou Province (KY [2013]147).

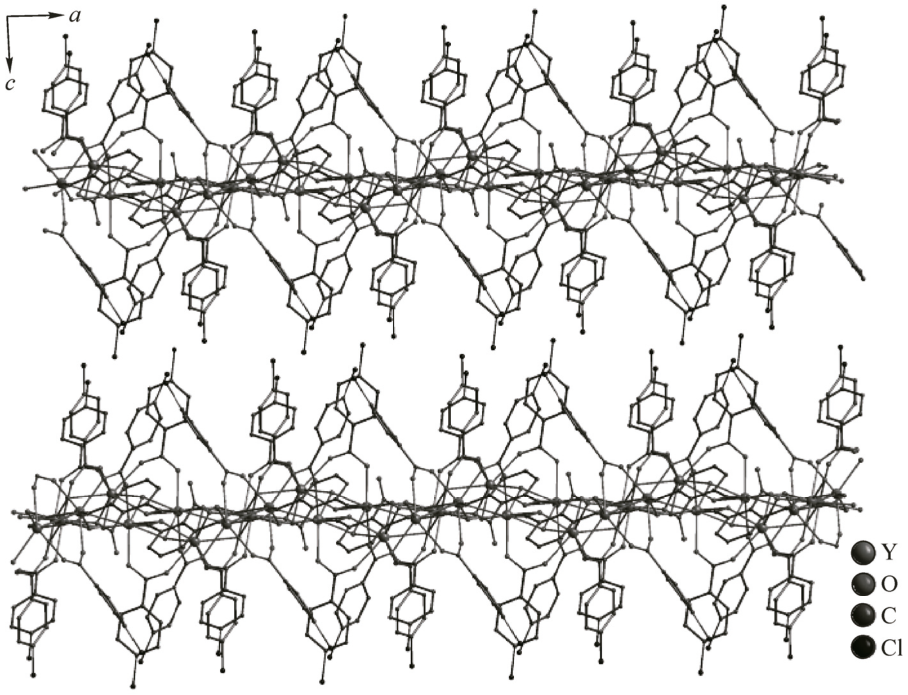

Fig. 4. The 3D packing in the structure of **1**

Table 3

Hydrogen-bonding parameters (Å *and* deg.) *in* **1**

D—H...A	D—H	H...A	D...A	∠DHA
O(18)—H(18A)…O(22)#4	0.98	2.20	3.087(8)	149.2
O(20)—H(20B)…O(22)	0.98	2.01	2.897(8)	148.7
O(21)—H(21A)…O(4)	0.82	1.81	2.607(9)	162.4

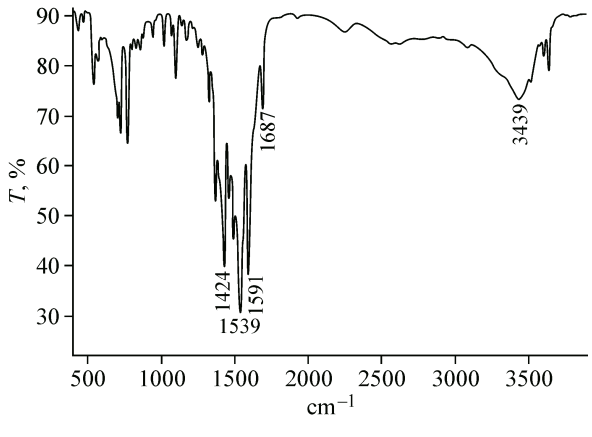

Fig. 5. IR spectrum of **1**

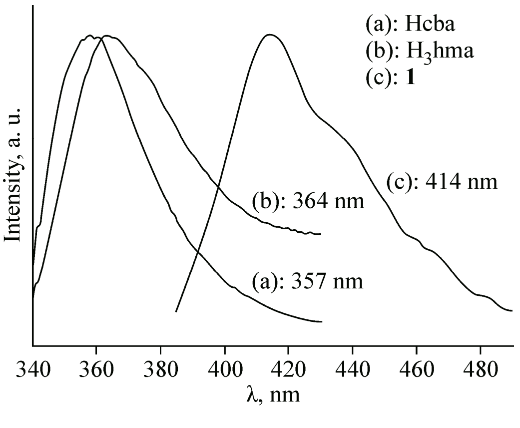

Fig. 6. Solid-state photoluminescent spectra of Hcba, H_3hma ligands and **1**. (λ_{ex} = 305 nm for Hcba, 315 nm for H_3hma and 359 nm for **1**)

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