ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 5, pp. 355–359. © Pleiades Publishing, Ltd., 2016.

Synthesis, Crystal Structure, and Luminescent Property of a Discrete Zn_3L_3 Metallomacrocycle Constructed from 5-Hydroxyisophthalic Acid[1]

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Received April 5, 2015

Abstract—An interesting discrete metallomacrocycle (MMC), $[Zn_3(L)_3(H_2O)_6] \cdot H_2O$ (**I**), has been prepared by means of self-assembly of Zn(II) salt, 5-hydroxyisophthalic acid (H_2L) as organic linker and 5,5'-(pyridine-2,6-diyl)diisophthalic acid (H_4L') as structure-directing agentunder hydrothermal condition. In complex **I**, the planar trinuclearmetal-organic macrocycles are arranged into 2D sheet layers connected by strong hydrogen bonded between OH groups of the ligands. Then they stack into 3D supramolecular architecture in –ABAB– array way to give a small 1D open channel along the *c* axis (CIF file CCDC no. 1053024). Additionally, thermal stability and luminescence properties of **I** were also investigated.

DOI: 10.1134/S1070328416050092

INTRODUCTION

Metallomacrocycles (MMCs) or metal-organic macrocycles (MOMs) [1, 2], as a class of coordination supramolecular host systems obtained via cyclic linkages of the metal ions and the bridging ligands, have attracted considerable attention in recent years due to their intriguing architectures and potential applications ranging from molecular recognition, storage and catalysis [3–6]. Rational design and construction of the desired MMC srequires complementarity between the coordination preferences of a metal ion and the spatial relationship between the metal-binding domains of the bridging ligand [7–9]. The prerequisite for cyclic structure formation is the use of at least one building component with bent geometry. There are two general methods typically adopted. The first uses the coordination geometry of the metal ion to define the internal angle of the MMCs in combination with rigid-rod ligands. For example, d^{10} transition metal zinc(II) ion is thegeometrical flexibility and this allows the coordination sphere to respond to environmental influences such as crystal packing interactions [10–14]. In coordination complexes, distortions within the local coordination environment of the metal ion are transmitted through bridging ligands. The second approach hinges upon the use of a ligand with a fixed internal angle. This strategy has been recently demonstrated by Housecroft through overview of competition between the formation of metallocyclic complexes versus polymers of 4,2':6',4"-terpyridine and its 4'-substituted derivatives [15]. Studies have shown that the careful design and modification of some selected residues of the ligands can be utilized to control the number of the components in the MMCs and the corresponding size and stereochemistry of the MMCs [16]. Other factors, such as pH values, solvents, templating agents, temperatures and so on, are all known to play important roles in the formation and nature of the final assemblies.

In the last few decades, many metallomacrocycles, such as $\{M_2\}$, $\{M_4\}$, $\{M_6\}$, $\{M_8\}$ and even high-nuclearitynanocages, have been successfully designed and synthesized [17–20]. However, it is still difficult to control the nuclearity and intercluster connection mode in MMCs. Herein, we report an unexpected discrete planar trinuclear MMC complex, $[Zn_3(L)_3(H_2O)_6] \cdot H_2O$ (**I**) which constructed from 5-hydroxyisophthalic acid (H_2L) as organic linker and Zn salt as precursors under hydrothermal condition with 5,5'-(pyridine-2,6-diyl)diisophthalic acid (H_4L') as structure-directing agent. We report its synthesis, crystal structure, and thermal and photoluminescence properties.

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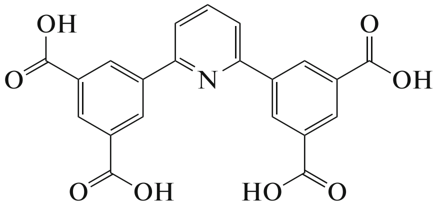
[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement summary for **I**

Parameter	Value
Formula	$C_{24}H_{28}O_{22}Zn_3$
F_w	864.56
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a, Å	17.191(2)
c, Å	7.1940(10)
V, Å^3	1841.2(4)
Z	2
ρ_{calcd}, g/cm^3	1.556
μ, mm^{-1}	2.019
F(000)	872
Crystal size, mm	0.30 × 0.30 × 0.30
Reflections collected/unique	9561/725
R_{int}	0.0305
GOOF on F^2	1.203
Number of refinement parameters	63
R_1 ($I > 2\sigma(I)$)*	0.0743
wR_2 (all data)**	0.2426
Largest diff. peak and hole, e Å^{-3}	2.223 and −1.245

$^*R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $^{**}wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.



(H_4L')

EXPERIMENTAL

Materials and methods. All reagents and solvents employed were commercially available and used as received without further purification. Thermal analyses were performed on a NETZSCH STA 449C microanalyzer with a heating rate of 10°C min^{-1} under N_2 atmosphere. Luminescence spectra for the solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer. The powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 advance powder diffractometer at 40 kV and 40 mA for CuK_α radiation (λ = 1.5418 Å) with a scan speed of 0.2 s/step and a step size of 0.02°.

Syntheses of I. A mixture of $Zn(NO_3)_2 \cdot 8H_2O$ (0.2 mmol), H_2L (0.2 mmol), H_4L' (0.1 mmol), 6 mL DMF, 0.5 mL water and four drops of HNO_3 (63%, aq.) was sealed in a 10 mL Teflon-lined reactor. The reactor was heated at 120°C for 72 h and then cooled to room temperature at a rate of 10°C h^{-1}. Colorless crystals of complex **I** were obtained in 58% yield based on H_2L.

For $C_{24}H_{28}O_{22}Zn_3$ (M = 864.69)

anal. calcd., %:	C, 33.34;	H, 3.26.
Found, %:	C, 33.42;	H, 3.13

IR (KBr; ν, cm^{-1}): 3323 s, 3243 m, 3182 m, 1612 s, 1565 v.s, 1429 s, 1401 s, 1363 s, 1274 m, 1090 w, 776 w, 724 m, 653 w, 540 w, 456 w.

X-ray structure determination. Crystallographic data for **I** were collected at room temperature with a Bruker Apex II Image Plate single-crystal diffractometer with graphite-monochromated MoK_α radiation source (λ = 0.71073 Å) operating at 50 kV and 30 mA in ω scan mode for **I**. A multi-scan absorption correction was applied with the use of SADABS. The structures were solved by direct methods and refined by full-matrixleast-squares refinements based on F^2 with the SHELXTL program [21]. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometricallyideal positionsand refined isotropically. The detailed crystallographic data and structure refinement parameters for **I** are summarized in Table 1 and selected bond lengths and angles are given in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 1053024; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I***

Bond	d, Å	Bond	d, Å
Zn(1)–O(1)	2.004(5)	Zn(1)–O(4)	2.009(6)
Angle	ω, deg	Angle	Angle
O(1)Zn(1)O(1)$^{\#1}$	98.4(3)	O(4)Zn(1)O(4)$^{\#2}$	119.2(4)
O(1)Zn(1)O(4)	109.29(14)		

* Symmetry codes: $^{\#1}$ $x, x - y, z$, $^{\#2}$ $x, y, -z + 1/2$.

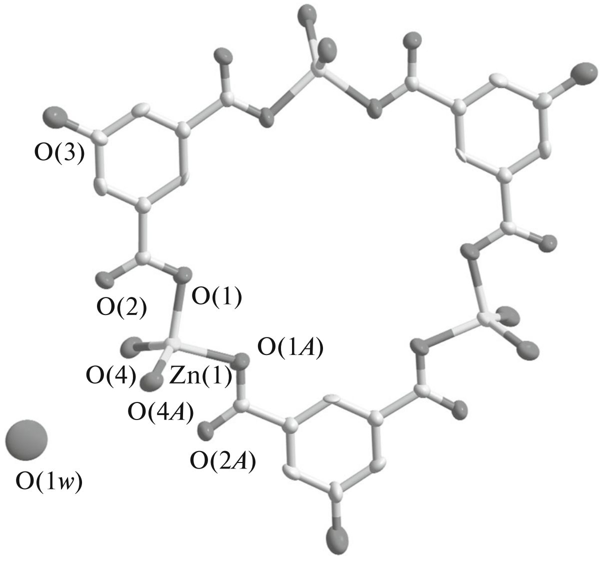


Fig. 1. The discrete trinuclearmetallomacrocycle of **I**. Symmetry code: (*A*) *x*, *x* – *y*, 0.5 – *z*.

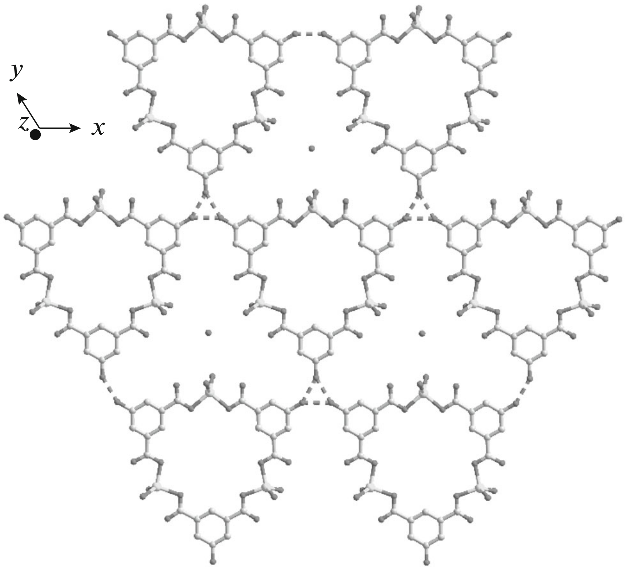


Fig. 2. The 2D sheet layer in *xy* plane.

RESULTS AND DISCUSSION

It is our original intention to synthesis of ternary compound of Zn-L'-L. The HNO_3 is used as mineralizer according to the synthetic methods of metal-organic frameworks when multi-carboxylates were chosen as the ligands [22–24]. Unexpectedly, hydro(solvo)thermal reaction of H_2L and H_4L' with $Zn(NO_3)_2 \cdot 6H_2O$ in a DMF–H_2O system at 120°C resulted in the formation of complex **I** in crystalline state. It was failed to prepare **I** without the addition of H_4L'. This result indicate that H_4L' maybe serve as structure-directing agent. Single crystal X-ray analysis revealed **I** crystallizes in the hexagonal space group $P6_3$/mmc and it is a planar 24-membered metallomacrocycle formed by three ligands and three Zn(II) centers as shown in Fig. 1. Each Zn center is tetrahedrally coordinated by two carboxylic O atoms (O(1) and O(1*A*)) from two distinct L^- ligands (Zn–O 2.004(5) Å), and two O atom of the coordinated water molecules (O(4) and O(4*A*)) (Zn–O 2.009(6) Å). Each ligand bridges two zinc(II) ion via its two monodentate coordinated carboxylate groups.

Interestingly, three such Zn(II) centers and three such L^- ligands are arranged alternately to form a coplanar metallomacrocycle with the Zn···Zn separation of 8.8202(12) Å and the angles of Zn···Zn···Zn all being 60.00(1)°. While two coordinated H_2O molecules are found above and below this plane, respectively. Then the coplanar trinuclear metallomacrocycles are linked with each other by strong hydrogen bonded between OH groups of the ligands to form a 2D sheet layer (Fig. 2).

Furthermore, the trinuclear metallomacrocycles of the adjacent sheets are parallel to each other and connected by weak intermolecular hydrogen bonds between coordinated water molecules and between coordinated water and carboxyl groups of the ligands as shown in Fig. 3. On the other hand, the adjacent sheets are stacked in –ABAB– array to give a 1D dodecagon open channel along the *z* axis, which are occupied by uncoordinated water molecules (Fig. 4). The distance of two O atoms of two coordinated water

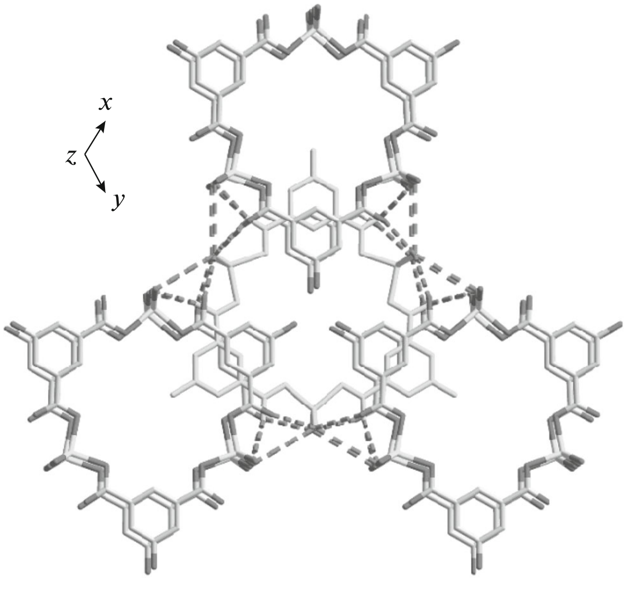


Fig. 3. The intermolecular hydrogen bonds between metallomacrocycles of the adjacent sheets.

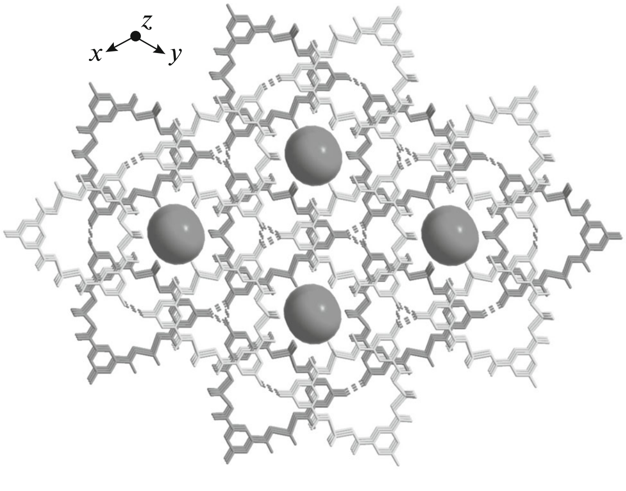


Fig. 4. The 2D sheet layers stack into 3D supramolecular architecture in –ABAB– array way to give a small 1D open channel along *z* axis.

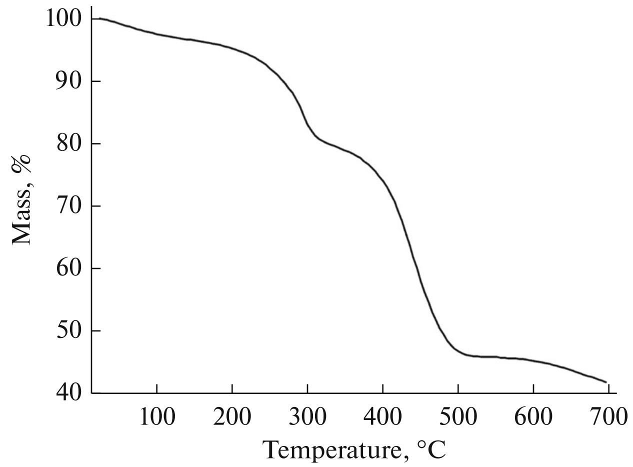


Fig. 5. TGA plot of the sample of **I**.

molecules and two carboxylates in a diagonal position is about 7.0 and 8.5 Å (excluding van der Waals radii), respectively.

The experimental and simulated PXRD patterns of **I** are in good agreement with each other and this indicates there are no compound of H_4L' in it. Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability of compound **I** (Fig. 5). It showed a weight loss of 2.4% in 24–97°C assigned to the release of lattice water molecules (calcd. 2.1%). The structure is almost thermally stable up to 230°C. Further weight loss observed in the range of 230–310°C which can be ascribed to the removal of coordinated water molecules (obsd. 13.0% and calcd. 12.5%). Subsequently, the rapid weight loss wasattributed to decomposition of the coordination framework.

The solid-state luminescence of **I** was investigated at room temperature. The emission peak is observed at 398 nm (λ_{ex} = 330 nm) which is similar to that of the free H_2L ligand (λ_{max} = 368 nm, λ_{ex} = 289 nm) [25]. So the emission can be assigned to ligand-centered emission ($\pi^* \rightarrow \pi$ and/or $\pi^* \rightarrow n$ transition). While the large red shift of **I** may be the result of the coordination interactions which effectively increase the rigidity of the ligand and decrease the intra-ligand HOMO–LUMO energy gap [12, 26–29].

In summary, we have synthesized and characterized an interesting discrete planar trinuclear metallomacrocycle by using geometrical flexible zinc(II) ion and rigid V-shaped 5-hydroxyisophthalic acid ligand, as well as a large V-shaped multicarboxylateas structure-directing agent. The result indicates that the rational selection of metal ions and rigid V-shaped-tetra-carboxylate ligands as well as rational control of the reaction condition can design unique metallomacrocycle complexes. Thermal stability and photoluminescence property of compound **I** have been also investigated.

ACKNOWLEDGMENTS

We are grateful for financial support from the Education Committee of Sichuan Province, China (14ZB0220, 12ZA090, 15ZB0222, 15ZB0214 and 14ZB0212), Sichuan University of Science and Engineering (2015RC26, 2015RC38, 2014RC34, 2014PY01 and 2015PY03), the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of High Education (LYJ1207 and LYJ1301).

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