ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 2, pp. 93–99. © Pleiades Publishing, Ltd., 2014.

Two New Carboxylate-Bridged One-Dimensional Coordination Polymers Based on Macrocyclic Metallic Tectons[1]

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Received October 17, 2012

Abstract—Two new one-dimensional coordination polymers: $\{[Cu(L^1)(H_4TTHA)] \cdot H_2O\}_n$ (**I**), $\{[Cu_2(L^2)_2(H_4TTHA)_2] \cdot 10H_2O\}_n$ (**II**) (L^1 = 1,3,10,12,15,18-hexaazatetracyclodocosane; L^2 = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane), based on a flexible hexapodal ligand H_6TTHA (1,3,5-triazine-2,4,6-triamine hexaacetic acid), have been synthesized and structure characterized. Single-crystal X-ray diffraction analyses indicated that the central metal atom displays distorted six-coordinate octahedral coordination geometry by coordination with four nitrogen atoms of L^1 or L^2, and two oxygen atoms of H_6TTHA liagand. Both of the compounds show one-dimensional chain structures, which are constructed of $[Cu(L)]^{2+}$ and $[H_4TTHA]^{2-}$ anion with 1 : 1 ratio. Interestingly, the nature of the macrocycle influences the structure of the coordination polymer produced with H_6TTHA for each of the two compounds. TG, IR, PXRD, and photoluminescent of the compounds are investigated.

DOI: 10.1134/S1070328414020110

INTRODUCTION

Supramolecular architectures based on various macrocyclic metallic tectons were attracted continued attentions because of their appealing topological structures and fascinating applications in chemistry, biology, and materials science [1–5]. Square planar macrocyclic metallic compounds with bridged aromatic polycarboxylate ligands have been proved to be an effective strategy in constructing of coordination polymers and multi-dimensional supramolecular networks [6–10]. Suh [11] utilized the *tetrakis*[4-(carboxyphenyl)oxamethyl]-methane (TCM^{4-}) anion as a tetrahedral organic building block and $[Ni(Cyclam)]^{2+}$ (Cyclam = 1,4,8,11-tetraazacyclotetradecane) complex as a linear linker to construct an eightfold interpenetrating diamondoid network for gas storage. Moon [12] also used TCM^{4-} as a bridging ligand to construct a doubly catenated rhombic grids network, in which they introduced a nickel macrocyclic complex that contains two pyridyl pendant arms as the linker. Very recently, Jiang [13] employed a new ligand tri(4-carboxy-benzyl)amine (H_3TCBA) to construct three novel supermolecular frameworks with high adsorption capacity of N_2, H_2, and CO_2 molecules. To obtain more coordination polymers and understand how the structures and properties of coordination polymers can be tuned by the different azamacrocyclic ligands, a new hexapod carboxylic ligand H_6TTHA (H_6TTHA = 1,3,5-triazine-2,4,6-triamine hexaacetic acid) was utilized. Compared with the common aromatic polycarboxylate ligands: 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid, H_6TTHA ligand acts as a multiple ligand. H_6TTHA ligand can construct more novel unpredictable and interesting supramolecular networks due to its following characteristics: (1) H_6TTHA has six carboxyl groups for coordination, which exhibit diverse coordination fashions to construct various structures; (2) these carboxylate donor groups may be completely or partially deprotonated to compensate for the charges [14]; (3) the flexible iminodiacetic acid ligands can adopt versatile conformations according to the geometric requirements of different metal ions. Therefore, a series of coordination polymers and supramolecular compounds with different structures interesting topologies and properties are to be expected when this ligand assembled with metal building block.

Inspired by above ideas and our previous works [11–14], in this contribution, we report the syntheses, structures, and properties of two H_6TTHA-bridged one-dimensional compounds: $\{[Cu(L^1)(H_4TTHA)] \cdot H_2O\}_n$ (**I**), $\{[Cu_2(L^2)_2(H_4TTHA)_2] \cdot 10H_2O\}_n$ (**II**) (L^1 = 1,3,10,12,15,18-hexaazatetracyclodocosane; L^2 = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) by the self-assembly H_6TTHA ligand with different copper macrocyclic metallic tectons. X-ray crystallographic analyses of compounds dem-

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onstrate that the coordination modes of H_6TTHA ligand were dramatically dependent upon the introduction of substituent group on azamacrocyclic ligands. To the best of our knowledge, it is the first time that H_6TTHA has been systematic investigated as a bridged ligand linked with macrocyclic metallic tectons.

EXPERIMENTAL

All reagents were purchased commercially and used without further purification. The ligand H_6TTHA was prepared as described in literature [15]. Elemental analyses (C, H, and N) were performed using a Vario ELIII CHNS/O elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet Avatar 370 Fourier Transform Infrared spectrometer. The powder X-ray diffraction measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer. Thermogravimetric analysises were performed on a Diamond TG-DTA 6300 equipment in flowing N_2 atmosphere with a heating rate of 10°C min^{-1}.

Synthesis of I. The macrocyclic complex $[Cu(L_1)](ClO_4)_2$ was prepared as described in literature [16]. An aqueous solution (5 mL) of $[Cu(L_1)](ClO_4)_2$ (0.050 g, 0.10 mmol) was layered with a H_2O-CH_3OH (v/v = 1 : 1) solution (5 mL) of H_6TTHA (0.050 g, 0.10 mmol) at room temperature. After about 2 days, purple crystals suitable for X-ray analysis formed. The yield was 20 mg.

For $C_{31}H_{48}N_{12}O_{13}Cu$

anal. calcd., %:	C, 43.28;	H, 5.62;	N, 19.54.
Found, %:	C, 42.18;	H, 5.88;	N, 19.50.

IR (ν, cm^{-1}): 1718 (–COOH), 1488 ($-COO^-$), 1311 ($-COO^-$).

Synthesis of II. The macrocyclic complex $[Cu(L_2)](ClO_4)_2$ was prepared as described in literature [17]. A 10 mL aqueous solution solution of $[Cu(L_2)](ClO_4)_2$ (150 mg, 0.3 mmol) added to 10 mL water of H_6TTHA (150 mg, 0.3 mmol), the solution were mixed together with sitring, and then filtration and slow evaporation of the resulting solution gave red crystals in two weeks with a yield of 60 mg.

For $C_{51}H_{83}N_{24}O_{36}Cu_2$

anal. calcd., %:	C, 35.30;	H, 4.82;	N, 19.37.
Found, %:	C, 34.28;	H, 5.82;	N, 18.93.

IR (ν, cm^{-1}): 1724 (–COOH), 1491 ($-COO^-$), 1312 ($-COO^-$).

X-ray structure determination. Single crystal X-ray diffraction data for the compounds were collected on a Bruker Apex CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 296 K. The structure was solved by direct methods and SHELXL-97 [18] and refined by full-matrix least-squares on F^2 [19]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the carbon and nitrogen atoms were located in a Fourier map and refined as riding on their C or N atoms. The detailed crystallographic data and structure refinement parameters for the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for structures **I**, **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 882005 (**I**) and 882006 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As shown in Fig. 1a, the X-ray single crystal structure analysis shows that compound **I** has an infinite one-dimensional structure. The asymmetric unit of compound **I** consists of one $[Cu(L_1)]^{2+}$ fragment, a TTHA ligand, and one uncoordinated water moleculars (as shown in Fig. 1b). The Cu(1) is six-coordinated by two carboxylate oxygen atoms (O(9), O(11)) from two TTHA ligands and four nitrogen atoms (N(1)–N(4)) from $[Cu(L_1)]^{2+}$. The center Cu(1) atom adopts a distorted octahedral coordinated environment. The distances between Cu(1) and coordinated nitrogen atoms are in the range from 2.006 to 2.035 Å. Due to the Jahn–Teller effect, the axial Cu–O bond length (Cu(1)–O(9) 2.500, Cu(1)–O(11) 2.561 Å) is longer than the Cu–N bond lengths, which are almost the same as that in the related complex $[Cu(L)]_3[BTC]_2 \cdot 9PhOH \cdot 6H_2O$ (L = 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane, BTC = 1,3,5-benzenetricarboxylate) [20]. The axial Cu–O bonds are not perfectly perpendicular to CuN_4 plane. In compound **I**, the hexapod H_6TTHA ligand is not completely deprotonated, only two carboxylic acid groups deprotonated for balance the charges.

The X-ray single crystal structure reveals that compound **II** also crystallizes in an infinite one-dimensional structure. The asymmetric unit of compound **II** consists of two independent $[Cu(L_2)]^{2+}$ segment, two TTHA ligands, and ten uncoordinated water molecules (as shown in Fig. 1b). The Cu(1) atom in $[Cu(L_2)]^{2+}$ segment adopts a slightly distorted octahedral coordinate geometry with four nitrogen atoms of the macrocycle occupying the equatorial positions, and two oxygen atoms of TTHA located at the axial sites. Similarly, for the other $[Cu(L_2)]^{2+}$ structure, the Cu(2) is six-coordinated by two carboxylate oxygen atoms from two TTHA ligands and four nitrogen atoms of the L^2 ligand. The Cu–O bond lengths in compound **II** are longer than the Cu–N bond lengths due to the Jahn–Teller effect (Cu(1)–O(3) 2.429,

Table 1. Crystallography data and refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	860.35	1735.49
Crystal size, mm	0.22 × 0.21 × 0.20	0.25 × 0.24 × 0.21
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	19.267(3)	10.1279(19)
b, Å	10.1429(16)	17.206(3)
c, Å	19.918(3)	22.342(4)
α, deg	90	81.967(2)
β, deg	99.715(2)	81.701(2)
γ, deg	90	77.494(2)
V, Å^3	3836.6(10)	3737.4(12)
Z; ρ_c, mg/m^3	4; 1.489	2; 1.542
μ, mm^{-1}	0.649	0.676
F(000)	1804	1806
θ Range for data collection, deg	2.07–26.00	2.10–26.00
Reflections collected	20870	21008
Independent reflections, R_{int}	7548 (0.0473)	14423 (0.0307)
Reflections with, $I > 2\sigma(I)$	4834	9555
Data/restraints/parameters	7548/0/526	14423/13/1039
GOOF*	1.007	1.030
Final R indices, $I > 2\sigma(I)$	$R_1 = 0.0513$, $wR_2 = 0.1097$	$R_1 = 0.0591$, $wR_2 = 0.1481$
R indices, all data	$R_1 = 0.0917$, $wR_2 = 0.1279$	$R_1 = 0.0964$, $wR_2 = 0.1737$
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e Å^{-3}	0.417/–0.406	1.445/–0.672

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

Cu(1)–O(21) 2.510, Cu(2)–O(10) 2.540, Cu(2)–O(29) 2.744 Å).

As noted above, though similar synthetic strategies were employed for the crystallization of those crystals, polymorphs with different structural features were formed. In compound **I**, $[H_4TTHA]^{2-}$ connected two copper atoms by one iminodiacetic acid, $[H_4TTHA]^{2-}$ rank on both side of the chain to form a zigzag structure (Fig. 2a). For compound **II**, $[H_4TTHA]^{2-}$ connected two copper atoms by two different iminodiacetic acid groups to form 1D chain (Fig. 2b). Although all the H_6TTHA partially deprotonated in compounds **I**, **II** forming $[H_4TTHA]^{2-}$ anion to compensate for the charges, the conformation of TTHA completely different when it is interaction with different azamacrocyclic ligands, showing three types of configuration, as shown in Fig. 3. In conclusion, it is evident that the introduction of different groups on the macrocyclic

Table 2. Selected bond distances (Å) and angles (deg) for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Cu(1)–N(3)	2.006(3)	Cu(1)–N(2)	2.035(3)
Cu(1)–N(1)	2.012(3)	Cu(1)–O(9)	2.500(3)
Cu(1)–N(4)	2.015(3)	Cu(1)–O(11)	2.561(3)
	II		
Cu(1)–N(1)	2.007(3)	Cu(2)–N(14)	1.993(3)
Cu(1)–N(2)	2.009(3)	Cu(2)–N(15)	2.003(3)
Cu(1)–N(4)	2.012(3)	Cu(2)–N(13)	2.005(3)
Cu(1)–N(3)	2.014(3)	Cu(2)–N(16)	2.017(3)
Cu(1)–O(3)	2.429(3)	Cu(2)–O(29)	2.744(4)
Cu(1)–O(21)	2.510(3)	Cu(2)–O(10)	2.540(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
	I		
N(3)Cu(1)N(1)	85.93(12)	N(3)Cu(1)N(2)	173.03(12)
N(3)Cu(1)N(4)	93.91(13)	N(1)Cu(1)N(2)	93.82(11)
N(1)Cu(1)N(4)	176.11(12)	N(4)Cu(1)N(2)	86.81(12)
	II		
N(1)Cu(1)N(2)	93.92(13)	N(4)Cu(1)O(3)	94.87(12)
N(1)Cu(1)N(4)	85.89(12)	N(3)Cu(1)O(3)	86.73(13)
N(2)Cu(1)N(4)	179.73(14)	N(14)Cu(2)N(15)	93.52(14)
N(1)Cu(1)N(3)	179.42(15)	N(14)Cu(2)N(13)	86.18(14)
N(2)Cu(1)N(3)	86.20(13)	N(15)Cu(2)N(13)	177.42(14)
N(4)Cu(1)N(3)	94.00(13)	N(14)Cu(2)N(16)	179.73(16)
N(1)Cu(1)O(3)	93.85(13)	N(15)Cu(2)N(16)	86.46(13)
N(2)Cu(1)O(3)	85.32(13)	N(13)Cu(2)N(16)	93.86(13)
N(14)Cu(2)O(29)	89.75(14)	N(14)Cu(2)O(10)	90.99(14)
N(15)Cu(2)O(29)	84.82(12)	N(15)Cu(2)O(10)	89.05(12)
N(13)Cu(2)O(29)	92.61(12)	N(13)Cu(2)O(10)	93.52(13)
N(16)Cu(2)O(29)	90.52(13)	N(16)Cu(2)O(10)	88.73(13)
O(10)Cu(2)O(29)	173.86(10)		

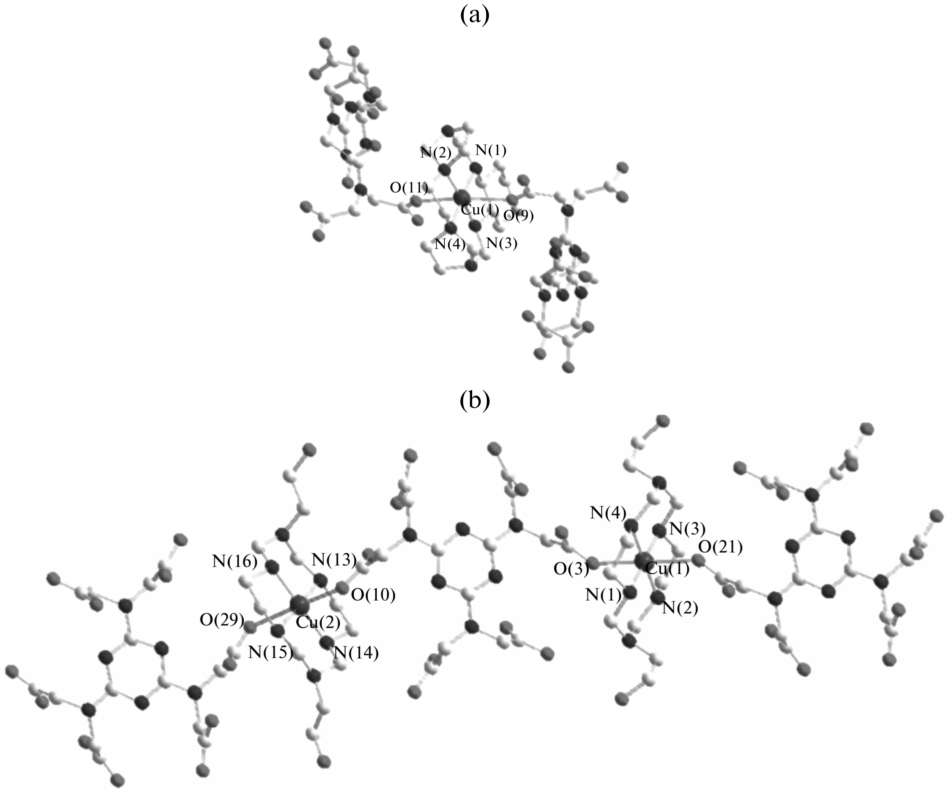

Fig. 1. Coordination environment of the Cu^{2+} ions in compound **I** (a) and **II** (b).

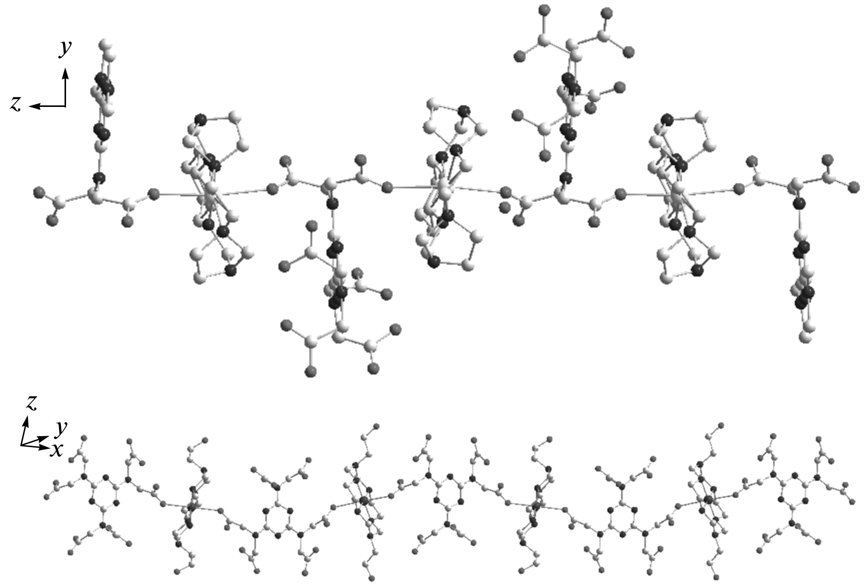

Fig. 2. The 1D chain structure of **I** (a) and **II** (b).

ligand into the crystal engineering plays a significant role in the architecture of solid materials.

The IR spectra of compounds **I**, **II** show characteristic bands of carboxylate group at 1550–1580 cm^{-1} for the antisymmetric stretching and at 1310–1320 cm^{-1} for symmetric stretching. The signals in the range of 1710–11720 cm^{-1} indicates the deprotonation of TTHA ligand not completely, which corresponds

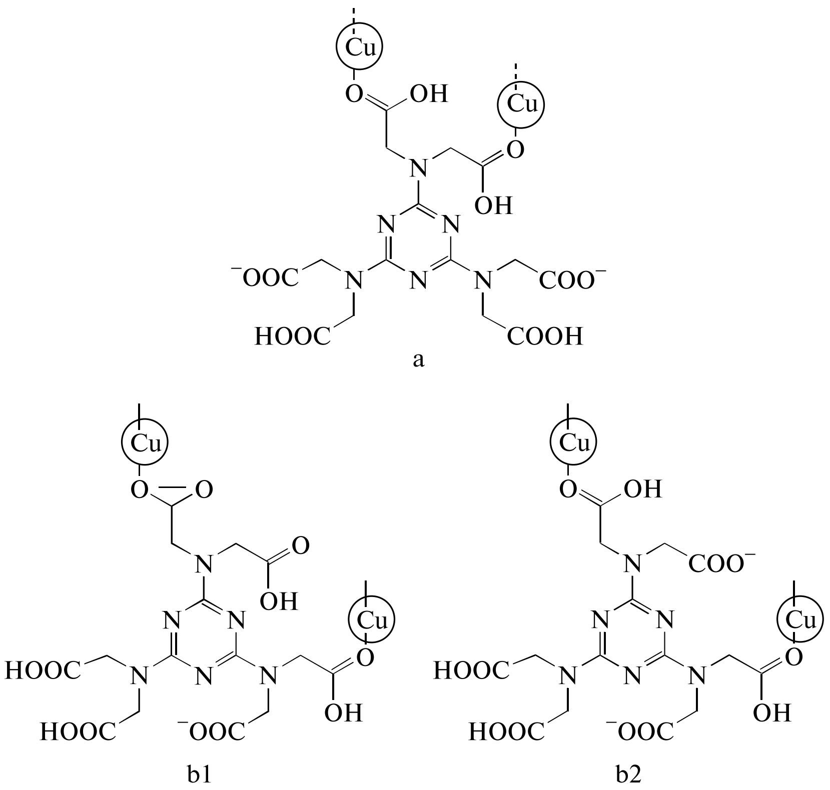

Fig. 3. Versatility H_6TTHA moieties in coordination for compound **I** (a) and **II** (b).

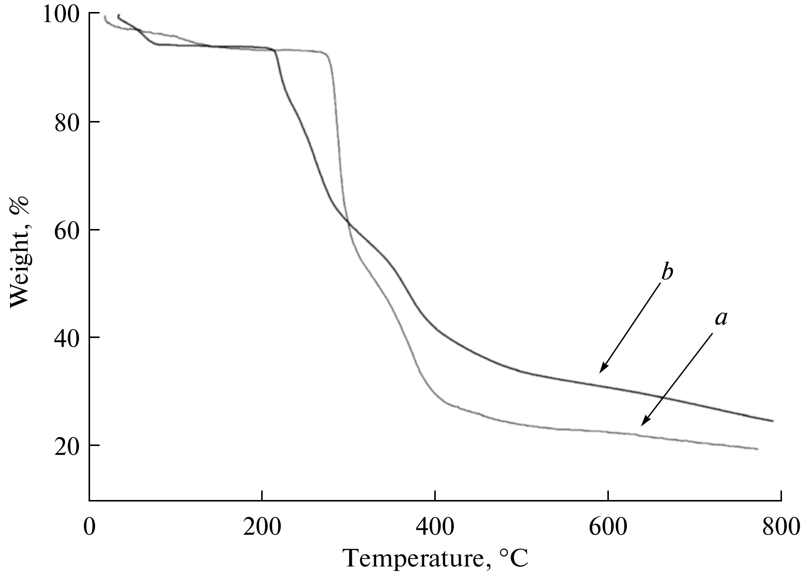

Fig. 4. Thermal behavior curves of compounds **I** (*a*) and **II** (*b*).

to the X-ray single crystal structure analysis. Powder X-ray diffraction pattern consist with the simulated one based on the X-ray diffraction analysis. Diffraction peaks on both patterns are corresponded well in positions, indicating the phase purity of the as-synthesized sample. To investigate the exact number of the free guest molecules and thermal stability of the compounds, the thermal weight measurements of compounds are carried out (Fig. 4). Compound **I** losses all the free water molecules and in the range of 30–

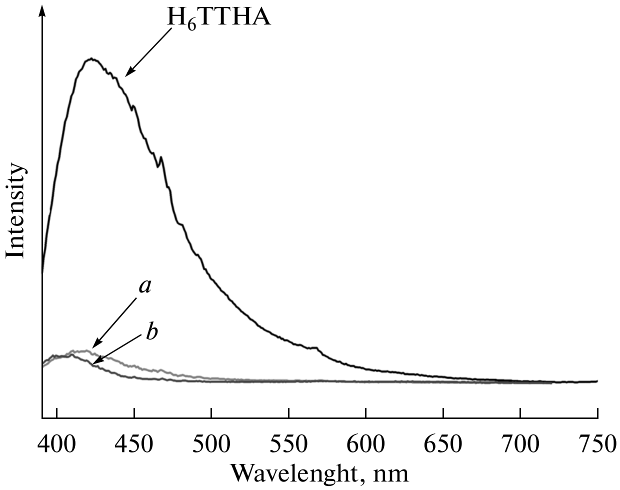

Fig. 5. The photoluminescence spectra of the H_6TTHA ligand and compounds **I** (*a*) and **II** (*b*).

100°C (calcd. 2.10%, found 2.70%). The framework is stable up to 260°C and then begins to decompose upon further heating. Similarly, for compound **II**, the first weight loss of 7.50% (calcd. 7.3%) is attributable to the release of guest molecules.

The photoluminescence spectra of the H_6TTHA ligand and compounds **I**, **II** in the solid state were measured at room temperature (Fig. 5). The free H_6TTHA ligand emits fluorescent light at 425 nm due to the intra-ligand $\pi-\pi^*$ transition. However, the fluorescence is effectively quenched in the compounds **I**, **II**, this phenomenon may be due to the Cu^{2+} ion possesses low-energy half-filled *d* levels suitable for electron transfer process with H_6TTHA ligand. Similar phenomenon has been observed before.

ACKNOWLEDGMENTS

This project was supported by the Fundamental Research Founds for National University, China University of Geosciences (Wuhan) (no. 1210491B03) and the College Students' Innovative Experiment Project of China (no. 091049148).

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