Journal of Solid State Chemistry 228 (2015) 199–207

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Syntheses, crystal structures, and properties of four complexes based on polycarboxylate and imidazole ligands

Rui Qiao [a], Shui-Sheng Chen [a,b,*], Liang-Quan Sheng [a], Song Yang [a], Wei-Dong Li [a]

[a] School of Chemistry and Chemical Engineering, Fuyang University, Fuyang 236041, China
[b] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:
Received 12 February 2015
Received in revised form
24 April 2015
Accepted 27 April 2015
Available online 5 May 2015

Keywords:
Metal–organic frameworks
Crystal structures
Luminescent property
Gas sorption property

ABSTRACT

Four metal–organic coordination polymers $[Zn(HL)(H_2O)]\cdot 4H_2O$ (**1**), $[Zn(HL)(L_1)]\cdot 4H_2O$ (**2**), $[Cu(HL)(H_2O)]\cdot 3H_2O$ (**3**) and $[Cu(HL)(L_1)]\cdot 5H_2O$ (**4**) were synthesized by reactions of the corresponding metal (II) salts with semirigid polycarboxylate ligand (5-((4-carboxypiperidin-1-yl)methyl)isophthalic acid hydrochloride, $H_3L\cdot HCl$) or auxiliary ligand (1,4-di(1*H*-imidazol-4-yl)benzene, L_1). The structures of the compounds were characterized by elemental analysis, FT-IR spectroscopy and single-crystal X-ray diffraction. The use of auxiliary ligand L_1 has great influence on the structures of two pairs of complexes **1**, **2** and **3**, **4**. Complex **1** is a uninodal 3-connected rare 2-fold interpenetrating ZnSc net with a Point (Schlafli) symbol of (10^3) while **2** is a one-dimensional (1D) ladder structure. Compound **3** features a two-dimensional (2D) honeycomb network with typical 6^3-hcb topology, while **4** is 2D network with (4, 4) sql topology based on binuclear Cu^{II} subunits. The non-covalent bonding interactions such as hydrogen bonds, $\pi\cdots\pi$ stacking and C–H$\cdots\pi$ exist in complexes **1**–**4**, which contributes to stabilize crystal structure and extend the low-dimensional entities into high-dimensional frameworks. And the photoluminescent property of **1** and **2** and gas sorption property of **4** have been investigated.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Over the past two decades, the construction of metal – organic frameworks (MOFs) has attracted immense of interest owing to their intriguing structural architectures as well as their potential applications in luminescence, gas storage, ion-exchange, heterogeneous catalysis, and porous materials [1–6]. In terms of the fabrication of MOFs, the assembly with desired structural types is totally dependent on the judicious choice of appropriate organic spacers, and reaction conditions such as temperature, solvent, pH value, and metal center are significant parameters for directing the structures of the resulting coordination polymers [7–10]. In additional, the various weak non-covalent bonding interactions including hydrogen bonds [11,12], $\pi\cdots\pi$ stacking [13,14] and C–H$\cdots\pi$ [15,16] also have important influence on the construction of supramolecular frameworks. It is well known that polycarboxylate groups are excellent building blocks for the construction of MOFs because they may induce core aggregation and link these discrete clusters into extended frameworks by virtue of theirs bridging ability [17–19]. Besides the polycarboxylate linkers, the N-donor imidazolyl ligands such as 1,4-di(1*H*-imidazol-4-yl)benzene (L_1) are efficient and versatile organic building unit for construction of coordination architectures and have been widely used in our previous studies [20–23]. The L_1 ligand can not only utilize differently positioned nitrogen atoms of imidazolyl groups to ligate metal atoms with *cis*- or *trans*-configuration, but the NH or N atom of imidazolyl groups acting as a hydrogen bonding donor or acceptor can benefit the construction of supramolecular structures [24]. Moreover, the N-donor together with different carboxylate ligands may possess super compatibility in the construction of MOFs [25–29]. Taking the exceptional coordination ability of carboxylate ligands into account, we elaborately design a new semirigid polycarboxylate ligand—5-((4-carboxypiperidin-1-yl)methyl)isophthalic acid hydrochloride ($H_3L\cdot HCl$). Apparently, this ligand contains the flexible $–CH_2–$ group, and its bilateral carboxyl groups could freely twist along the $–CH_2–$ group to meet the requirements of the coordination geometries of metal centers in the assembly process. Moreover, it can be effective building blocks to construct MOFs together with multi-N ligands due to their superior compatibility. In this paper, we focus our attention on the study on reactions of ligand ($H_3L\cdot HCl$) containing polycarboxy groups together with N-donor (L_1) ligand and metal salts for the assembly of MOFs as an extension of our work. Herein, we report the synthesis, crystal structure of four coordination

---

* Corresponding author. Tel.: +86 558 2593836; fax: +86 558 2596249.
E-mail address: chenss@fync.edu.cn (S.-S. Chen).

http://dx.doi.org/10.1016/j.jssc.2015.04.041
0022-4596/© 2015 Elsevier Inc. All rights reserved.

polymers $[Zn(HL)(H_2O)]\cdot 4H_2O$ (**1**), $[Zn(HL)(L_1)]\cdot 4H_2O$ (**2**), $[Cu(HL)(H_2O)]\cdot 3H_2O$ (**3**) and $[Cu(HL)(L_1)]\cdot 5H_2O$ (**4**), and their photoluminescent and adsorption properties were also investigated.

2. Experimental

2.1. Materials and methods

All commercially available chemicals are of reagent grade and were used as received without further purification. The $H_3L\cdot HCl$ and L_1 ligands were prepared according to the literature [30,31]. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240 C elemental analyzer at the analysis center of Nanjing University. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm, and all the measurements were carried out under the same experimental conditions. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu $K\alpha$ (λ=1.5418 Å) radiation at room temperature. Nitrogen (N_2), carbon dioxide (CO_2) and water (H_2O) vapor sorption experiments were carried out on an Autosorb-iQ gas sorption instrument in Quantachrome Instruments U.S. The sample was activated by using the “outgas” function of the surface area analyzer for 24 h at 160 °C.

2.2. Preparation of $[Zn(HL)\cdot H_2O]\cdot 4H_2O$ (1)

A reaction mixture of $H_3L\cdot HCl$ (34.3 mg, 0.1 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL H_2O was sealed in a 16 mL Teflon lined stainless steel container and heated at 120 °C for 3 d. After cooling to the room temperature, colorless block crystals of **1** were collected by filtration and washed by water and ethanol for several times with a yield of 72%. Anal. calcd for $C_{15}H_{25}NO_{11}Zn$ (%): C, 39.10; H, 5.47; N, 3.04; found: C, 39.22; H, 5.53; N, 2.92. IR (KBr pellet, cm^{-1}): 3701–2885 (m, br), 1636 (s), 1584 (s), 1448 (s), 1415 (s), 1357 (s), 1247 (m), 1150 (w), 1111 (w), 936 (m), 917 (m), 774 (s), 729 (s), 632 (w), 606 (w), 560 (w), 489 (w), 464 (w), 438 (w).

2.3. Preparation of $[Zn(HL)(L_1)]\cdot 4H_2O$ (2)

A mixture containing $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol), $H_3L\cdot HCl$ (34.3 mg, 0.1 mmol), L_1 (21.0 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL H_2O was sealed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure to 120 °C for 72 h. Colorless block crystals of **2** were collected in 85% yield after washed by water and ethanol several times. Anal. Calcd for $C_{27}H_{33}N_5O_{10}Zn$: C, 49.66; H, 5.09; N, 10.73%. Found: C, 49.52; H, 5.12; N, 10.61%. IR (KBr pellet, cm^{-1}): 3620–3200 (m, br), 1620 (s), 1579 (s), 1370 (s), 1132 (w), 1073 (w), 970 (w), 842 (w), 778 (m), 719 (w), 627 (w), 550 (w), 429 (w).

2.4. Preparation of $[Cu(HL)(H_2O)]\cdot 3H_2O$ (3)

Complex **3** was prepared in a similar way to that described for **1**, except that $Zn(NO_3)_2\cdot 6H_2O$ was replaced by $Cu(NO_3)_2\cdot 3H_2O$ (0.1 mmol, 24.2 mg). Blue block crystals of **3** were isolated by filtration and washed by water and ethanol several times in 64% yield. Anal. Calcd for C_{15} $H_{23}NO_{10}Cu$: C, 40.86; H, 5.26; N, 3.18%. Found: C, 40.72; H, 5.37; N, 3.02%. IR (KBr pellet, cm^{-1}): 3690–2865 (m, br), 2538 (w), 1626 (s), 1556 (s), 1443 (s), 1412 (m), 1367 (s), 1242 (m), 1116 (w), 920 (m), 795 (m), 769 (m), 725 (s), 700 (w), 625 (w), 549 (w).

2.5. Preparation of $[Cu(HL)(L_1)]\cdot 5H_2O$

Complex **4** was synthesized by the same procedure as that used for preparation of **2**, except that $Cu(NO_3)_2\cdot 3H_2O$ (0.1 mmol, 24.2 mg) was used instead of $Zn(NO_3)_2\cdot 6H_2O$. Blue needle crystals of **4** were obtained in 78% yield. Anal. Calcd for $C_{27}H_{35}N_5O_{11}Cu$ (%): C, 48.46; H, 5.27; N, 10.47; found: C, 48.38; H, 5.37; N, 10.58. IR (KBr pellet, cm^{-1}): 3653–2815 (m), 1620 (s), 1569 (vs), 1424 (m), 1361 (s), 1241 (m), 1141 (m), 1078 (m), 971 (w), 952 (w), 858 (w), 813 (w), 776 (m), 725 (m), 694 (w), 656 (m), 536 (w).

Table 1
Crystal data and refinement results for complexes **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{15}H_{25}NO_{11}Zn$	$C_{27}H_{33}N_5O_{10}Zn$	$C_{15}H_{23}NO_{10}Cu$	$C_{27}H_{35}N_5O_{11}Cu$
Formula weight	460.65	652.89	440.82	669.07
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/n$	$P2/c$	$P-1$
a (Å)	16.7194(15)	13.6095(12)	13.2818(8)	10.3519(19)
b (Å)	9.2357(8)	8.4234(8)	9.8927(6)	11.0647(19)
c (Å)	25.383(2)	25.538(2)	14.9377(9)	13.486(2)
α (°)	90	90	90	100.958(3)
β (°)	106.735(2)	100.386(2)	113.6800(10)	94.385(3)
γ (°)	90	90	90	96.717(3)
V ($Å^3$)	3753.5(6)	2879.7(5)	1797.45(19)	1498.4(4)
Z	8	4	4	2
D_c (g cm^{-3})	1.595	1.487	1.599	1.461
F(0 0 0)	1840	1328	884	678
θ range /°	2.55–27.47	1.59–27.48	2.06–27.56	1.55–27.70
Reflections collected	11799	18275	11378	10464
Independent reflections	4265	6515	4105	6949
Goodness-of-fit on F^2	1.088	1.096	1.075	1.053
R_1 $[I>2\sigma(I)]^a$	0.0392	0.0438	0.0365	0.0486
wR_2 $[I>2\sigma(I)]^b$	0.1164	0.1374	0.1183	0.1290

Download English Version:

https://daneshyari.com/en/article/1331507

Download Persian Version:

https://daneshyari.com/article/1331507

Daneshyari.com