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Four coordination polymers based on 4'-(4-carboxyphenyl)-2,2':6', 2''-terpyridine: Syntheses, structures and properties

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A B S T R A C T

Four coordination polymers, $[CuCl(cptpy)\cdot 2H_2O]_n$ **(1)**, $[Mn_2Cl_2(cptpy)_2(phdat)H_2O]_n$ **(2)** and $[Ln(cptpy)_3]_n$ (Ln = La (**3**), Pr (**4**)) (Hcptpy = 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine, phdat = 2,4-diamino-6-phenyl-triazine) have been hydrothermally synthesized and characterized by IR spectra, X-ray single-crystal diffraction, powder X-ray diffraction (PXRD), elemental analyses and thermogravimetric analyses (TGA). Compounds **1**, **3** and **4** exhibit 2D or 3D structures comprising 1D linear chain connected by π…π stacking interactions. While, compound **2** contains two kinds of 1D chains, of which one is a linear chain and the other is a ladder chain, and further extends to 3D structure by π…π stacking and hydrogen bonding interactions. The electrochemical analysis shows that compound **1** has good catalytic activities for the reductions of both $NaNO_2$ and H_2O_2, and is a potential catalytic material. Magnetic analysis indicates that compound **2** exhibits antiferromagnetic behavior.

1. Introduction

Coordination polymers as a kind of multifunctional materials have been focused too much attention by chemists in recent years due to their specified structures and potentially interesting applications in magnetism [1–3], catalysis [4–6], luminescence [7–9], electrochemistry [10–12] and gas storage [13], etc..

However, as we know, the structural diversity and physicochemical property are largely determined by metal centers and organic ligands [14–16] and many target compounds have been successfully synthesized through the rational selection of metal atoms and specific ligands, of which the commonly used ligands are carboxylic acid ligands, N-heterocyclic ligands and N-heterocyclic carboxylic acid ligands [17–19]. Carboxylic acid ligand is one of the most widely studied ligands, which is flexible in coordination modes and has strong coordination ability. And the pore structure and space size of compounds can be adjusted through rational adjustment of the structure of ligands [20–22]. Compared with the carboxylic acid ligands, the coordination mode and coordination number of the nitrogen heterocyclic ligands are more clearly, which is more conducive to the regulation of the structure of the target compounds [23–25]. The heterocyclic carboxylic acids have both of the advantages, such as the representative ligand 4'-(4-carboxylphenyl)-2,2':6',2''-tripyridine (Hcptpy) [26–31]: (i) as a polydentate N and O donor bridging ligand, not only Hcptpy can connect to metal ions by various coordination modes (Scheme 1), but also the terpyridyl group can act as the chelating group or bridging group, which can extend the structure into high dimensional network; (ii) Hcptpy also has a large π-conjugated nonlinear structure that helps to form an excellent connection between the donor and acceptor to fulfill electron transport and consolidate the whole framework structures. By the same token, Hcptpy can be widely used as a rigid building block to obtain macroporous MOFs. 2,4-diamino-6-phenyl-triazine (phdat) as a N-heterocyclic auxiliary ligand, which contains three coordinating N-atoms and may act as a three-connected node. Morever, the existence of $-NH_2$ also can form hydrogen bonding interactions with either nitrogen or carboxyl-O atoms. Besides, the aromatic rings from phdat are capable to form π…π stacking interactions with other aromatic carboxylic acids.

Herein, based on the self-assembly of the Hcptpy ligand with 3d/4 f metal salts, four new coordination polymers $[CuCl(cptpy)\cdot 2H_2O]_n$ **(1)**, $[Mn_2Cl_2(cptpy)_2(phdat)H_2O]_n$ **(2)**, $[La(cptpy)_3]_n$ **(3)** and $[Pr(cptpy)_3]_n$ **(4)** have been obtained under the control of phdat ligand in hydrothermal conditions, of which compounds **3** and **4** are isomorphous. All compounds contain 1D chain and further extend to 2D or 3D framework by the hydrogen bonding and π…π stacking weak interactions. Furthermore, the electrochemical property of compound **1** and the magnetism of compound **2** are also discussed, respectively.

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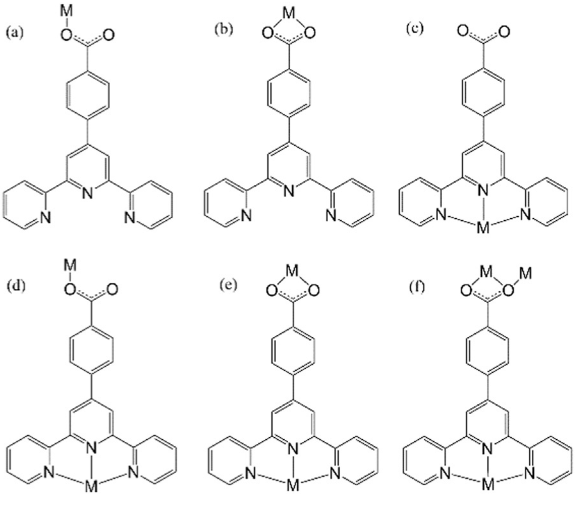

Scheme 1. Coordination modes of the ligand cptpy⁻.

2. Experiment section

2.1. Materials and methods

All chemicals were commercially available and when we used without further purification. Infrared spectra were tested on a Bruker VERTEX-70 FT-IR spectrophotometer by using KBr pellets in the range of 400–4000 cm^{-1}. Elemental analyses were recorded by Vario EL III Etro Elemental Analyzer. The Powder X-ray diffraction (PXRD) data were detected on X-PertPro diffractometer with CuKα radiation in the range $2\theta = 5–50$ °. Thermogravimetric analyses (TGA) measurements were collected by heating the samples from 35 to 1000 °C under a nitrogen flow with a heating rate of 20 °C/min on NETZSCH STA449F5 instrument. Electrochemical data were collected on a RST5200F electro-chemical workstation. Magnetic measurement was performed using a Quantum Design MPMS-XL SQUID magnetometer.

2.2. Syntheses of the compounds

2.2.1. Synthesis of [CuCl(cptpy)·2H$_2$O]$_n$ (1)

A mixture of CuCl$_2$·2H$_2$O (0.5 mmol, 0.085 g), Hcptpy (0.25 mmol, 0.088 g), phdat (0.25 mmol, 0.047 g) and H$_2$O (5 ml) were placed in a 25 ml Teflon-lined stainless steel vessel, stirred for 40 min and heated at 150 °C for 3 days. When it was cooled to room temperature, green block crystals were obtained (Yield: 0.103 g, 84.5% based on Hcptpy). Elemental analysis (%): Anal. Calcd: CuClC$_{22}$H$_{18}$N$_3$O$_4$ (%): C 54.25, H 3.73, N 8.59; Found: C 54.21, H 3.72, N 8.62. FT-IR (KBr pellet, cm^{-1}): 3534(m), 3237(w), 3031(w), 1606(s), 1555(s), 1479(m), 1362(s), 1250(w), 1015(m), 874(w), 790(m), 706(w), 659(w), 493(w).

2.2.2. Synthesis of [Mn$_2$Cl$_2$(cptpy)$_2$(phdat)H$_2$O]$_n$ (2)

The synthetic procedure was similar to that of compound **1** except that MnCl$_2$·4H$_2$O was used instead of CuCl$_2$·2H$_2$O, yellow block crystals of compound **2** were obtained (Yield: 0.072 g, 52.8%, based on Hcptpy). Elemental analysis (%): Anal. Calcd: Mn$_2$Cl$_2$C$_{53}$H$_{39}$N$_{11}$O$_5$ (%): C 58.31, H 3.63, N 14.09; Found: C 58.36, H 3.60, N 14.12. FT-IR (KBr pellet, cm^{-1}): 3321(m), 1616(s), 1531(s), 1396(s), 1161(w), 1006(w), 868(w), 828(w), 774(m), 716(w), 631(w).

2.2.3. Synthesis of [La(cptpy)$_3$]$_n$ (3)

CuCl$_2$·2H$_2$O of compound **1** was replaced by La(NO$_3$)$_3$·6H$_2$O (0.217 g, 0.5 mmol), yellow sheet crystals of compound **3** were obtained (Yield: 0.064 g, 64.2%, based on Hcptpy). Elemental analysis (%): Anal. Calcd: LaC$_{66}$H$_{42}$N$_9$O$_6$ (%): C 66.32, H 3.57, N 10.51; Found: C 66.28, H 3.54, N 10.54. FT-IR (KBr pellet, cm^{-1}): 3434(w), 1587(s), 1540(s), 1405(s), 1156(w), 1015(w), 783(s), 706(m), 621(w), 481(w).

2.2.4. Synthesis of [Pr(cptpy)$_3$]$_n$ (4)

CuCl$_2$·2H$_2$O of compound **1** was replaced by Pr(NO$_3$)$_3$·6H$_2$O (0.218 g, 0.5 mmol), light green sheet crystals of compound **4** were obtained (Yield: 0.071 g, 71.1%, based on Hcptpy). Elemental analysis (%): Anal. Calcd: PrC$_{66}$H$_{42}$N$_9$O$_6$ (%): C 66.19, H 3.61, N 10.50; Found: C 66.17, H 3.53, N 10.52. FT-IR (KBr pellet, cm^{-1}): 3425(w), 1592(s), 1540(s), 1405(s), 1166(w), 1015(w), 856(w), 783(s), 706(w), 617(w), 481(w).

2.3. Crystallographic data collection and refinement

Crystallographic data for compounds **1**–**4** were collected on a Bruker Apex-II CCD detector diffractometer with CuKα radiation (λ = 0.71073 Å) at 296(2) K. Data absorption correction and reduction were made with empirical methods. The structure was solved by directed methods using SHELXS-2014 [32] and refined by full-matrix least-squares techniques using SHELXL-2014 [33]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms on ligands are added in the riding model, while the hydrogen atoms of water molecules are located from the difference Fourier maps. Selected crystal data and structural refinements are summarized in Table 1. Selected bond lengths (Å) and angles (°) of compounds **1**–**4** are listed in Table S1 (Supporting information). Crystallographic data for the compounds **1**–**4** have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 1856236–1856239, which can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Crystal structure of compound 1

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in triclinic system *P*-1 space group. The asymmetrical unit contains one crystallographically independent Cu(II) atom, one Cl atom, one cptpy⁻ ligand and one lattice water molecule. As shown in Fig. 1, each Cu(II) atom is five-coordinated by a chlorine atom, three nitrogen atoms from one cptpy⁻ ligand and one carboxyl oxygen atom from another cptpy⁻ ligand, exhibiting a square pyramid configuration with three nitrogen and one oxygen atoms located at the bottom and the chlorine atom at the vertex, of which three nitrogen (N1, N2, N3), Cu1 and O1A atoms (A: $x, y, -1+z$) present an almost planar geometry with the mean deviation from the planarity of approximately 0.124 Å. Three pyridine rings are also almost in the same planar geometry with the average deviation from the horizontal plane of approximately 0.028 Å, and the dihedral angle between the pyridine ring and the phenyl ring is about 36.56°. The Cu–O bond lengths are 1.933 (2) Å and Cu–N bond lengths in the range of 1.940 (3)–2.030 (3) Å, shorter than the Cu–Cl bond length 2.5174 (11) Å. The O–Cu–Cl angle is 98.98 (8)° and the N–Cu–Cl angles are in the range of 95.07 (9)–98.17 (9)°, meaning that the Cu–Cl bond is almost perpendicular to the bottom. As shown in Fig. 2(a), Cu(II) atoms and cptpy⁻ ligands with Scheme 1(d) coordination mode connect alternately along *c*-axis direction, forming a 1D linear chain. The neighboring 1D linear chains are arranged into 2D layer structure through two kinds of π…π stacking interactions (Fig. 2(b)): (1) π (C7–C3–C4–C9–C16–N1)…π (C8–C5–C1–C13–C17–N2) with the dihedral angle of 10.93°, and the cg…cg (center of gravity) and the average vertical plane-plane distances of 3.739 Å and 3.459 Å, respectively, (2) π (C8–C5–C1–C13–C17–N2)···π (C15–C11–C14–C10–C18–N3) with the dihedral angle of 5.11°, and the cg…cg (center of gravity) and the average vertical plane-plane distances of 3.572 Å and 3.460 Å, respectively (Fig. 2(c)).