**Novel 1D Mn(II) Complexes Containing Aromatic Dicarboxylic Acids**

D. Zhao*, T. Shi*, C. Chen*, Z. Si*, Q. Duan*,**, and L. Shi*

*School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, 130022 P.R. China

**College of Sciences, Zhejiang A & F University, Lin'an, 311300 P.R. China
e-mail: * szj@cust.edu.cn; ** danqian88@hotmail.com

Received April 26, 2013

Abstract—Three Mn(II) complexes of \([\text{MnL(Bipy)(H}_2\text{O)}]_n\) (I), \([\text{Mn}_3\text{(Phen)}_2\text{(HL)}_2\text{(L)}_2]_n\) (II), and \([\text{Mn}_2\text{(Phen)}_2\text{(HL)}(\text{OH})]\) (III), where \(L = 4,4'-(2\text{-acetylpropane-1,3-diyl})\text{dibenzoic acid, Bipy} = 2,2'\text{-bipyridine, and Phen} = 1,10\text{-phenanthroline, were hydrothermally synthesized and characterized by single crystal X-ray diffractions, infrared spectroscopy, thermogravimetric analyses, and magnetic analyses. Complexes I and II are one dimensional (1D) coordination polymers which can form the supramolecules with the help of the intermolecular hydrogen bond interactions. Finally, the landé factors are simulated by magentochemical analysis to be 2.15 and 1.80 for I and II with \(S = 5/2\), respectively.**

DOI: 10.1134/S1070328414030117

**INTRODUCTION**

Recently, the crystal materials of metal complexes were extensively studied [1–10] due to their potential applications in many fields, such as the magnetic fields catalysis and the molecular recognition. In order to obtain the metal complexes with interesting molecular structures and/or high performances, lots of novel organic compounds [11–17], including polypyridines [11, 12], cyclic ethers [13, 14], and organic acids [15–17], were applied as the coordination ligands. In the last several decades, the metal complexes based on the organic acids appealed most researchers’ attentions because the carboxyl groups with several coordination modes of organic acids can act as not only the coordination groups but also the donor and/or acceptors of the hydrogen bonds [18, 19]. There should mainly be two kinds of polycarboxylic acids of the non-aromatic polycarboxylic acids and the aromatic polycarboxylic acids, and they possess different advantages to construct metal complexes: (1) alkyl linkers of the non-aromatic polycarboxylic acids can change their spatial structures to meet the coordination requirements of the metal complexes [20–24]; (2) the aromatic rings can give the aromatic polycarboxylic acids some additional molecular forces, such as \(\pi--\pi\) stacking and \(\pi--\text{H}\) interactions [25, 26]. For example, the non-conjugated aromatic polycarboxylic acids with an atom between the aromatic rings are useful to prepare metal complexes with unexpected structures and/or excellent properties [21, 22]. According to the above mentioned researches, we designed and synthesized an non-conjugated aromatic dicarboxylic acids of 4,4’-(2-acetylpropane-1,3-diyl)dibenzoic acid (H$_2$L) which have 1,3-propylidene group between the aromatic rings and used it to hydrothermally synthesize three Mn(II) complexes of \([\text{MnL(Bipy)}(\text{H}_2\text{O})]_n\) (I), \([\text{Mn}_3\text{(Phen)}_2\text{(HL)}_2\text{(L)}_2]_n\) (II), and \([\text{Mn}_2\text{(Phen)}_2\text{(HL)}(\text{OH})]\) (III) (Bipy = 2,2’-bipyridine and Phen = 1,10-phenanthroline). At last, the X-ray single crystal diffraction, the infrared spectroscopy, thermogravimetric and magnetic analyses were applied to characterize the prepared Mn(II) complexes.

**EXPERIMENTAL**

Materials and methods. All chemicals and reagents from the commercial sources were used without further purification. IR spectra were recorded on a FTIR-8400S SHIMADZU spectrophotometer in the 4000–400 cm$^{-1}$ region with KBr pellets. The magnetic susceptibility data were collected in the magnetic field of 1000 Oe on a MPMS RSO with the temperature range 2–300 K.

Synthesis of H$_2$L. The mixture of K$_2$CO$_3$ (6.9000 g, 0.050 mol), pentane-2,4-dione (5.1 mL, 0.015 mol), and 50 mL DMF was stirred 1 h, and then the methyl 4-(chloromethyl)benzoate (9.2300 g, 0.050 mol) was dropped into the mixture which was stirred another 24 h. The raw product of dimethyl 4,4’-(2,2-diacylpropene-1,3-diyl) dibenzoate was collected by the filtration after the mixture was poured into 300 mL H$_2$O. The precipitate (65.0 mg) and H$_2$O (3 mL) were sealed in a Teflon-lined stainless autoclave and heated at 170°C for 1 day under autogenous pressure and then
cooled to room temperature during 10 h. Colorless prism like crystals of H$_2$L suitable for X-ray analysis were obtained with yield of ~60.0%.

IR (KBr; $\nu$, cm$^{-1}$): 3010, 2966, 2667, 2547, 1697, 767.

$^1$H NMR (400 MHz; $\delta$, ppm): 1.908 (3H, s.), 2.735 (2H, tetra), 2.943 (2H, tetra), 7.303 (4H, d., $J$ = 8), 7.848 (4H, d., $J$ = 8), 12.847 (2H, s.).

**Synthesis of I.** A mixture of Mn(CH$_3$COO)$_2$·4H$_2$O (24.5 mg, 0.1 mmol), H$_2$L (34.0 mg, 0.1 mmol), and Bipy (19.2 mg, 0.1 mmol) was stirred in water (3.0 mL) and the pH of the mixture was adjusted to 6.5 with an aqueous ammonia solution, and then sealed in a 5-mL Teflon-lined stainless-steel container, which was heated to 170°C for 72 h and then cooled to room temperature at a rate of 5°C h$^{-1}$. Yellow block crystals were obtained with yield of ~49.1%.

IR (KBr; $\nu$, cm$^{-1}$): 3429, 1607, 1402, 1047, 1018, 928, 764, 619.

**Synthesis of II.** A mixture of Mn(CH$_3$COO)$_2$·4H$_2$O (24.5 mg, 0.1 mmol), H$_2$L (34.0 mg, 0.1 mmol), and Phen (19.80 mg, 0.1 mmol) was stirred in water (3 mL) and the pH of the mixture was adjusted to ~6.5 with an aqueous ammonia solution, and then sealed in a 5-mL Teflon-lined stainless-steel container, which was heated to 170°C for 72 h and then cooled to room temperature at a rate of 5°C h$^{-1}$. The yellow block crystals of II were obtained with the yield of ~49.0%.

IR (KBr; $\nu$, cm$^{-1}$): 3492, 1607, 1402, 1047, 1018, 928, 764, 619.

**Synthesis of III.** A mixture of Mn(CH$_3$COO)$_2$·4H$_2$O (24.5 mg, 0.1 mmol), H$_2$L (34.0 mg, 0.1 mmol), and Phen (37.6 mg, 0.2 mmol) was stirred in water (3.0 mL) and the pH of the mixture was adjusted to 5.5 with an aqueous ammonia solution. It was then sealed in a 5-mL Teflon-lined stainless-steel container, which was heated to 170°C for 72 h and then cooled to room temperature at a rate of 5°C h$^{-1}$, and yellow block crystals of III were obtained with yield of ~48.0%.

IR (KBr; $\nu$, cm$^{-1}$): 3412, 2395, 1709, 1607, 1468, 1400, 1103, 937, 847, 729, 675.

The crystal structures of H$_2$L and complexes I–III of were measured on a Bruker Smart Apex CCD single-crystal diffractometer using MoK$_\alpha$ radiation, $\lambda$ = 0.7107 Å at 293 K. An empirical absorption correction based on the symmetry-equivalent reflections was applied to the data using the SADABS program. The structures were solved using the SHELXL-97 program [27–29]. The crystal data of H$_2$L and complexes I–III are listed in Table 1, and the corresponding selective bond distances and the bond angles are given in Table 2. Supplementary material for structures H$_2$L and I–III has been deposited with the Cambridge Crystallographic Data Centre (nos. 889123 (H$_2$L); 826826 (I); 826825 (II); 826824 (III); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**RESULTS AND DISCUSSION**

The ORTEP view of H$_2$L single crystal with orthorhombic lattice is presented in Fig. 1a. The dihedral angle between the two benzene groups is 45.606°, which suggests that H$_2$L belong to the V-shaped aromatic di-boxylate ligand. The hydrogen bond length of O(5)–H(5)…O(2) and O(1)–(1)…O(4) (O…O) should be 2.6969(18) and 2.5635(19) Å, respectively, and these intermolecular hydrogen interactions (make the H$_2$L molecules) form one dimensional (1D) supermolecular chains (Fig. 1b).