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Research paper

Template synthesis of boron-capped cage metal complexes and assembly of supramolecular networks

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ABSTRACT

Template condensation on Mn(II) of 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde-1,3-dioxime (H_3hmbd) with 3-(acrylamidophenyl)boronic acid [3-aba$(OH)_2$] and 3-(methacrylamidophenyl)boronic acid [3-mba$(OH)_2$], afforded two boron-capped cage metal complexes containing reactive apical unsaturated groups, writing as $\{Mn^{II}_2(hmbd)_3[3\text{-aba}(OH)_2]_2\}\cdot Et_3NH\cdot H_2O$ (**1**), $\{Mn^{II}_2(hmbd)_3[3\text{-mba}(OH)_2]_2\}\cdot Et_3NH\cdot 2CH_3OH$ (**2**). Two Co(II) cage metal complexes, namely $\{Co^{II}_2(hmbd)_3[3\text{-aba}(OH)_2]_2\}\cdot Et_3NH\cdot H_2O$ (**3**), $\{Co^{II}_2(hmbd)_3[3\text{-mba}(OH)_2]_2\}\cdot Et_3NH\cdot 2CH_3OH$ (**4**), have been synthesized. The molecular structures of complex **1**–**4** were structurally characterized by single-crystal X-ray diffraction, elemental analysis, IR spectra, and UV–vis spectroscopy. The electrochemical property was analyzed by cyclic voltammetry. Every complex is composed of the $B^{III}Mn^{II}Mn^{II}B^{III}$ unit which has one negative charge counterbalanced by a protonated triethylamine ion. The four complexes are three dimensional cage structures with the terminal acylamino groups. The supramolecular networks are obtained by the non-covalent bonds between complexes, which are affected by the terminal substituents.

1. Introduction

Cage metal complex [1] is facing a vigorous development because of its importance in electrochemistry, physicochemical, catalytic chemistry and so on [2]. The advantage of the complex is easily obtained and widely used. The cage metal complex with *d*-metal, tri-dioximate and boronic acid can be synthesized by the direct template reaction [3–6]. In the process, the complex can be gotten by the dehydration reaction between boronic acids and the tri-dioximate. The tetrahedral geometry boron-containing structure can be synthesized by padding the vacant *p* orbital boron center to oxygen-containing σ-electron donors [7]. The three-dimensional macrobicyclic molecular architecture is held by the bonds between B, O, N, and C atoms [8,9]. The metal ions embedded into the center of the organic structure framework is isolated by macrobicyclic fragments. The structure of the complex is stable due to the coordination bond between metal ion and N, O atoms [10].

In the types of boron-capped tris-dioximate cage metal complex, the terminal reactive groups can provide different reaction nodes. Thus, the kind of complex is regarded as an important precursor to form macromolecular structures [11,12]. The 4-pyridylboronic acid has been synthesized by Mirela Pascu and co-workers [13]. Metal-organic frameworks (MOFs) are obtained by the coordination with pyridyl groups. Carboxylic acid ligand is also one of the most important groups for the synthesis of supermolecules. The boron containing cage complex with carboxyl groups has been obtained and used to synthesize supermolecular structures [14]. The cage metal complex which contains formyl groups is regarded as the precursor to synthesize infinite structure by hydrogen bonds [4]. Amide groups is easy to form molecular-molecular interaction by hydrogen bonds. So, the cage metal complex with amide groups is expected as important precursor to obtain supramolecular polymers.

In this paper, four cage metal complexes with acrylamide groups were obtained by the template condensation reaction (Scheme 1). The complexes exhibited some characteristics in structure and property. These complexes should be served as the units to obtain supramolecular networks with non-covalent bonds between the complex molecules. However, the vinyl groups in the ligands can be regarded as the important parts to synthesize polymers by crosslinker, which provides another way to form infinite structure [15,16].

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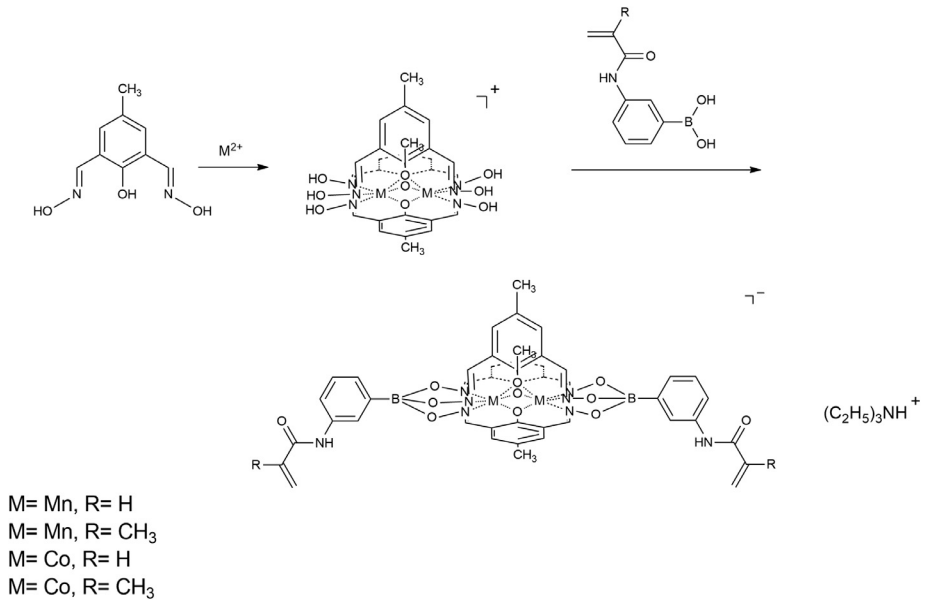

Scheme 1. The representation of the two-steps synthesis of complex **1**–**4**.

2. Experimental section

2.1. Reagents and measurements

The H_3hmbd was synthesized by a reported route [17]. Other reagents and solvents were purchased from commercial sources and used without further purification.

IR spectra (KBr pellets) were recorded on a Perkin Elmer Specture One spectrometer in range of 4000–400 cm^{-1}. UV–Vis reflection spectra were obtained in dichloromethane solution by using a Purkinje General TU-1901 recording spectrophotometer in the range of 200–500 nm. Elemental analyze data (C, H, and N) was performed on an EA3000 elemental analyzer. Electrochemical data of cyclic voltammogram for the complexes was collected in dichloromethane solutions with 0.1 M *n*-Bu_4NPF_6 as electrolyte utilizing a BAS100W electrochemical workstation (CHI 600E, Shang Hai Chen Hua, China) in a conventional and one-compartment three-electrode cell (solution: 40 mL). A platinum electrode was served as a working electrode. An $Hg/HgCl_2$ reference electrode was chosen. The measurement was controlled at scan rate of 100 $mV{\cdot}s^{-1}$ at room temperature. Electrochemical investigations of complex **1**–**4** were carried out by cyclic voltammetry. The electrochemical data of the complexes **1**, **2**, **3** and **4** was evidenced by cyclic voltammetry in CH_2Cl_2 (0.1 M *n*-Bu_4NPF_6) in the potential range.

2.2. Synthesis and characterization

2.2.1. Synthesis of $\{Mn^{II}_2(hmbd)_3[3\text{-}aba(OH)_2]_2\}{\cdot}Et_3NH{\cdot}H_2O$ (**1**)

A mixture of H_3hmbd (0.75 mmol), 3-aba$(OH)_2$ (0.5 mmol) and $MnCl_2{\cdot}4H_2O$ (0.5 mmol) were added to methanol and stirred for 30 min at room temperature. Then, triethylamine was spread into the solution, slowly. After two weeks, yellow block crystals of complex **1** were obtained and dried at room temperature. Yield 46.5%. IR (KBr, cm^{-1}): 1324, 1385, 1546, 1605, 1626, 1443. Anal. calcd. For $C_{51}H_{55}B_2Mn_2N_9O_{12}$: C 54.81, H 4.96, N 11.28. Found: C 54.45, H 4.88, N 11.06.

2.2.2. Synthesis of $\{Mn^{II}_2(hmbd)_3[3\text{-}mba(OH)_2]_2\}{\cdot}Et_3NH{\cdot}2CH_3OH$ (**2**)

Complex **2** was obtained in the similar way as complex **1** except that 3-mba$(OH)_2$ was used instead of 3-aba$(OH)_2$. The single crystals of complex **2** were also yellow, being obtained at room temperature after about three weeks. Yield 48.7%. IR (KBr, cm^{-1}): 1328, 1383, 1545, 1607, 1657, 1444. Anal. calcd. For $C_{55}H_{65}B_2Mn_2N_9O_{13}$: C 55.43, H 5.50, N 10.58. Found: C 55.52, H 5.11, N 10.84.

2.2.3. Synthesis of $\{Co^{II}_2(hmbd)_3[3\text{-}aba(OH)_2]_2\}{\cdot}Et_3NH{\cdot}H_2O$ (**3**)

The synthesis method of complex **3** was similar to that of complex **1** except that $CoCl_2{\cdot}6H_2O$ was used instead of $MnCl_2{\cdot}4H_2O$. After 3 weeks, we got orange block crystals of complex **3**. Yield 43.6%. IR (KBr, cm^{-1}): 1326, 1385, 1554, 1611, 1657, 1448 Anal. calcd. For $C_{51}H_{55}B_2Co_2N_9O_{12}$: C 54.42, H 4.93, N 11.20. Found: C 53.91, H 4.84, N 11.08.

2.2.4. Synthesis of $\{Co^{II}_2(hmbd)_3[3\text{-}mba(OH)_2]_2\}{\cdot}Et_3NH{\cdot}2CH_3OH$ (**4**)

Complex **4** was obtained in the similar way as complex **1** except that $CoCl_2{\cdot}6H_2O$ was used instead of $MnCl_2{\cdot}4H_2O$, and 3-mba$(OH)_2$ was used instead of 3-aba$(OH)_2$. The way of synthesis of complex **1** can also get complex **4** with $CoCl_2{\cdot}6H_2O$. The orange crystals can be found after 3 weeks. Yield 47.1%. IR (KBr, cm^{-1}): 1326, 1382, 1553, 1613, 1650, 1448. Anal. calcd. For $C_{55}H_{65}B_2Co_2N_9O_{13}$: C 55.07, H 5.46, N 10.51. Found: C 55.41, H 5.16, N 11.02.

3. Results and discussion

3.1. Crystal structures determinations

X-ray diffraction analysis of the complex **1**–**4** can be obtained by Mo-Kα X-radiation (λ = 0.71073 Å) on a Bruker APEX-II CCD at 293(2) K.

The collected data was simplified with the SAINT program and empirical absorption correction was finished by using the SADABS program [18,19]. Structures were solved by the direct method and refinements were done by full-matrix least-squares method on F^2 for all data with anisotropic thermal parameters for all non-hydrogen atoms [20]. The experimental details, crystallographic data, and refinement results are listed in Table S1.

Crystallographic data for the structural analysis has been deposited with CCDC Nos. 1582148, 1582149, 1582150 and 1582151 for complexes **1**, **2**, **3** and **4**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road,