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Novel bipyridinyl oxadiazole-based metal coordination complexes: High efficient and green synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones through the Biginelli reactions

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ABSTRACT

Three new metal coordination complexes, namely, $[Co(\mathbf{BPO})_2(H_2O)_4](\mathbf{BS})_2(H_2O)_2$ (1), $[Co(\mathbf{BPO})_2(H_2O)_4](\mathbf{ABS})_2(H_2O)_2$ (2), $[Co(\mathbf{BPO})_2(H_2O)_4](\mathbf{MBS})_2(H_2O)_2$ (3) [**BPO**=2,5-di(pyridin-4-yl)-1,3,4-oxadiazole, **BS**=benzenesulphonate, **ABS**=4-aminobenzenesulphonate, **MBS**=4-methylbenzenesulphonate] were obtained under hydrothermal conditions. Complexes **1–3** were structurally characterized by single-crystal X-ray diffraction, powder X-ray diffraction, IR and thermogravimetric analyses (TGA). All of them display a zero-dimensional motif, in which strong intermolecular hydrogen bonding interactions (O–H···O/N) and packing interactions (C–H···π and π···π) make them achieve a three-dimensional supramolecular architecture. The primary catalytic results of these three complexes show that high efficiency for the green synthesis of a variety of 3,4-dihydropyrimidin-2(1*H*)-ones was observed under solvent free conditions through Biginelli reactions. The present catalytic protocols exhibit advantages such as excellent yield, easy isolation, eco-friendly conditions, and short reaction time.

1. Introduction

Metal coordination complexes (**MCCs**) with catalytic functions have attracted extensively attention owing to their unique features for catalysis [1–3] and promising application in many organic reactions including Knoevenagel, Suzuki, Sonogashira, Friedel-Crafts alkylation and acylation, aldol, and alkene expoxidation reactions [4]. Additionally, **MCCs** possess potential for optics [5], gas separation and storage [3b,6], magnetism [7], drug delivery [8], and sensoring [9]. Typically, a known metal coordination complex, Tetrakis(triphenylphosphine)palladium(0), has been successfully applied to the field of organic chemistry and material chemistry. Su studied a kind of new catalyst Cu_2I_2(BTTP4) (BTTP4=benzene-1,3,5-triyltriisonicotinate) for the synthesis of *N*-oxysulfonyl amidines through the three-component reactions of azides, alkynes, and amines [10]. Co-based MCCs can catalysis triple condensations of alkynes to afford the 1,3,5-triarylbenzenes [11]. Though many farming and novel catalysts based on **MCCs** have been designed and developed [12,13], there exist a limited scope of catalysis. Therefore, to further develop and extend the catalytic fields, the rational design of **MCCs** with new catalytic functions remains still a formidable challenge.

3,4-dihydropyrimidine-2-(1*H*)-ones (DHPMs) and derivatives obtained through the Biginelli reaction [14] involving aldehyde, ester and urea are of important interest in both industrial and academic communities because of their potentially biological activities such as calcium-channel blocker [15], alpha-la-antagonism [16], antitumor [16,17], antibacterial [16–18] antihypertensive agents [19] and neuropeptide Y antagonism [19c,20]. Notably, the potent HIV gp-120-CD4 can be effectively inhibited by the Batzelladine A and B possessing the DHPM core [21]. However, the original synthesis of DHPMs was employed under harsh reaction conditions and its yield was poor. To improve the yield and mild reaction conditions, many elegant and novel works about the Biginelli reaction have been documented [22,23]. A variety of detailed catalytic systems [24] have been performed for the synthesis of DHPMs, including classical conditions, solvent-free [25], ionic liquid [26,27], solid phase synthesis [28], ultrasound [29] and microwave [30] irradiation in the presence of catalysts with BrØnsted and Lewis acid [31,32] and organic base [33]. Though a considerable progress of the catalyzed Biginelli reaction has been made, there still exist some issues such as low yield, long reaction time, purification issues, tedious work-up, and amenable reaction

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conditions. Especially, in the case of some aromatic aldehydes with the sensitive substituents, the desired product in low yield was obtained through the Biginelli reaction, which can be ascribed to the strongly acidic conditions and the prolonged reaction time [24q,24r,24aa]. Thus, searching the significantly catalytic protocols for the synthesis of DHPMs under green conditions still remains a great challenge.

Keeping this mind, we could envision that the catalytic systems with Co-based **MCCs** are easily constructed through bipyridinyl-oxadiazole and phenyl sulfonate. On the other hand, metal ions such as Co^{2+} and Fe^{3+} play in a key role in the fields of orgranic synthesis and catalysis [11a,34], but also phenyl sulfonate can promote the yield of organic product [3g]. Thus, when Co-based **MCCs** are combined and assembled by Cobalt ions, phenyl sulfonate and bipyridinyl-oxadiazole, it may improve the reaction condition and the yield of the product, and possess high performance for the synthesis of the DHPMs with excellent yield under solvent-free conditions. To our knowledge, there is no report on a series of cobalt-based **MCCs** containing bipyridinyl-oxadiazole as catalysts. Herein, we would like to report the first application of cobalt-based **MCCs** having bipyridinyl-oxadiazole as catalysts for one-pot solvent-free Biginelli reaction to afford 3,4-dihydropyrimidin-2(1*H*)-ones. In this paper, the catalytic parameters such as the temperature, the reaction time, the amount of catalyst and the solvent have been investigated for the Biginelli reaction. Additionally, we would wish to report the synthesis, and crystal structures, namely, [Co(**BPO**)$_2$(H$_2$O)$_4$](**BS**)$_2$(H$_2$O)$_2$ (1), [Co(**BPO**)$_2$(H$_2$O)$_4$](**ABS**)$_2$(H$_2$O)$_2$ (2), [Co(**BPO**)$_2$(H$_2$O)$_4$](**MBS**)$_2$(H$_2$O)$_2$ (3) [**BPO**=2,5-di(pyridin-4-yl)-1,3,4-oxadiazole, **BS**=benzenesulphonic acid, **ABS**=4-aminobenzenesulphonic acid, **MBS**=4-methylbenzenesulphonic acid].

2. Results and discussion

2.1. Structure description of complex (1)

The results of X-ray crystallographic analysis reveal that complex **1** is a zero-dimensional (0D) structure, and crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit of **1** consists of half of Co(II) ion, one **BPO** ligand, two coordinated water molecules, one **BS** anion and one lattice water molecule. As illustrated in Fig. 1a, Co is six-coordinated with a distorted octahedral coordination environment, surrounded by two nitrogen atoms from two different **BPO** ligands and four oxygen atoms from four ligated water molecules. The Co–O bond distances in **1** range from 2.070 (2) to 2.083(3) Å; the Co–N bond length is 2.140(3) Å, which are in good agreement with those found in documents published previously [35].

As illustrated in Fig. 1b, we can find there exit three kinds of O–H···O intermolecular hydrogen bonding in **1**. (i) The intermolecular hydrogen bonding originates from the coordinate water molecules and the free water molecules (O2W–H2WA···O3W^c 2.673(3) Å, ^{c}1/2−x, −1/2+y, 1/2−z). (ii) O–H···O intermolecular hydrogen bonding comes from the lattice water molecules and the oxygen atoms from the **BS** anions (O1W–H1WA···O2^a, O1W–H1WB···O2^b and O2W–H2WB···O3^d 2.843(4), 2.760 (3) and 2.706(4) Å, respectively, ^{a}−1+x, −1+y, z. ^{b}1−x, −y, 1−z. ^{d}−1+x, y, z). (iii) O–H···O intermolecular hydrogen bonding occurs between the free water molecules and the oxygen atoms from the **BS** anions (O3W–H3WA···O4^e 2.764(4) Å, ^{e}3/2−x, −1/2+y, 1/2−z). As a result, one-dimensional chain along the crystallographic *b* axis is generated via these three kinds of hydrogen bonding interactions (Fig. 1b).

Apart from these three kinds of O–H···O intermolecular hydrogen bonding interactions, there also exists other two kinds of hydrogen bonding interactions ((O3W–H3WB···N4^f, 2.825(4) Å, ^{f}1−x, −y, −z); (C15–H15A···N2^g 3.460(5) Å, ^{g}3/2−x, 1/2+y, 1/2−z)), through which a 2D supramolecular layer is constructed (Fig. 1c).

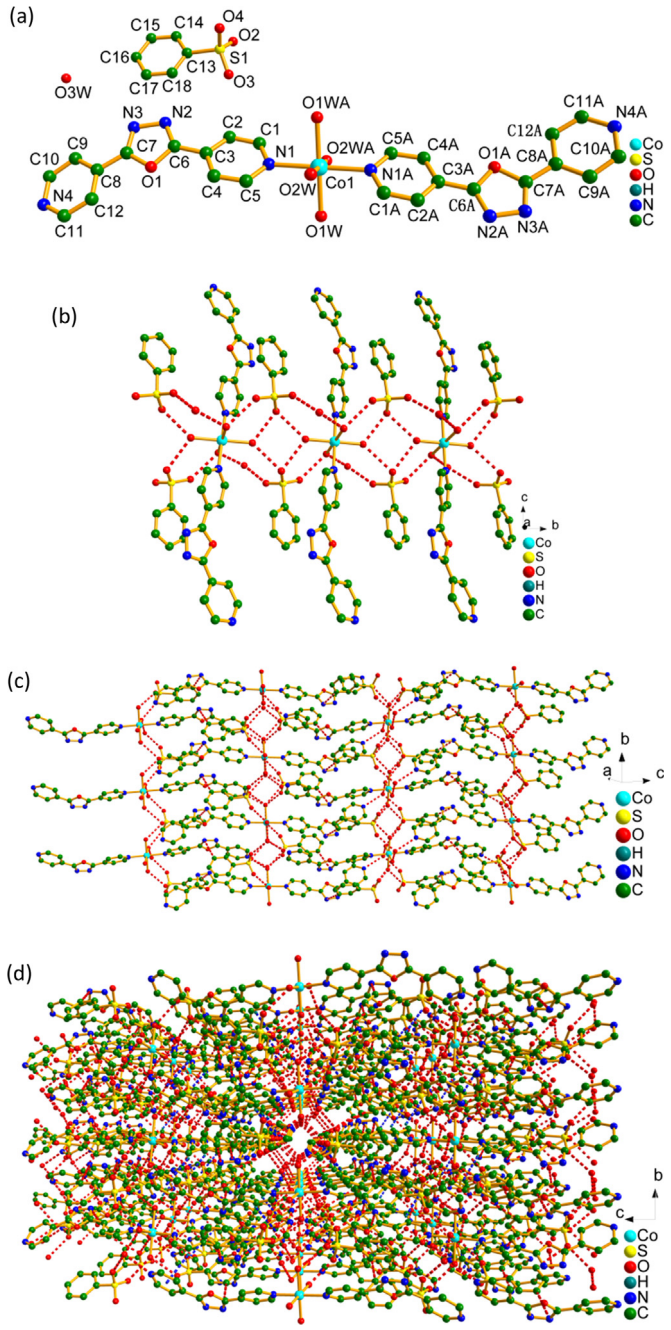

Fig. 1. (a) A perspective view of the coordination geometry of the Co center in **1**. (b) A 1D chain along the *b* axis in compound **1**. (c) A 2D supramolecular layer along the *bc* plane in **1**. (d) The packing diagram of **1**. For clarify, the hydrogen atoms have been deleted.

Meanwhile, we can also find one kind of C–H···O (C17–H17A···O4^e 3.310(5) Å). Interestingly, the weak C–H···π packing interactions (C2–H2A···$\pi_{(N4–C11)}$ 3.505(4) Å) can observed. Those hydrogen bonds and C–H···π packing interactions can extend the 2D supramolecular layers to a 3D supramolecular architecture (Fig. 1d).

2.2. Structure description of complex (2)

Single crystal X-ray crystallographic analysis reveals that complex **2** is a mononuclear structure and crystallizes in the