



## Short communication

# 1D Zn(II) coordination polymer of arylhydrazone of 5,5-dimethylcyclohexane-1,3-dione as a pre-catalyst for the Henry reaction



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## ABSTRACT

Reaction of a new hydrazone of  $\beta$ -diketone, 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)isophthalic acid ( $H_3L$ ), with zinc(II) nitrate hexahydrate in a mixture of DMF and water (1:1) under hydrothermal conditions affords the 1D coordination polymer  $[Zn(\mu_3-HL)(H_2O)_2]_n \cdot nH_2O$  (**1**), where one of the carboxylic groups links two Zn(II) centers in a bridging bidentate (*syn-syn*-type) mode and the remaining one ligates a third metal cation in a monodentate fashion. It was characterized by IR and NMR spectroscopies, ESI-MS, elemental and single-crystal X-ray crystal structural analyses. **1** acts as an efficient pre-catalyst for the Henry reaction at 40 °C in aqueous medium, providing  $\beta$ -nitroalcohols with good yields (67–86%) and diastereoselectivities (*syn:anti* 77:23–69:31).

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## 1. Introduction

The Henry (or nitroaldol) reaction provides a useful route for the synthesis of  $\beta$ -nitroalcohols and derived polyfunctionalized species, which are often used as key starting materials in the preparation of numerous biologically active compounds, including natural products, fungicides, insecticides and antibiotics *via* C—C bond formation [1–3]. A variety of metal catalysts derived from 1,3,5-triazapentadienes [4], hydrazones [5–7], Schiff bases [8,9] as well as chiral ligands [10], and organocatalysts [11] or biocatalysts [12] have been applied in this reaction. However, data on the use of coordination polymers in the Henry reaction are rather scarce [13]. Coordination polymers bearing organic ligands with different functionalities have received great attention due

to their intriguing structural motifs coupled with potential applications [14]. For instance, coordination polymers bearing arylhydrazones of  $\beta$ -diketone (AHBD) show high catalytic activity in the oxidation of alkanes and alcohols to the corresponding organic products [15].

Moreover, the presence of two carboxylic groups in the AHBD species increases the number of donor centers in these ligands and should enable the synthesis of coordination polymers and enhance the solubility of the isolated compounds in polar solvents, namely water. Based on these considerations, we have now synthesized a new AHBD ligand, 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)isophthalic acid ( $H_3L$ ) (Scheme 1), which contains two carboxylic acid groups and is water soluble.

In addition, zinc(II) complexes derived from different classes of ligands are known to catalyze the Henry reaction [6b,16–22]. However, yields and diastereoselectivities for most of the reported systems are moderate, and/or the common use of organic solvents is disadvantageous.

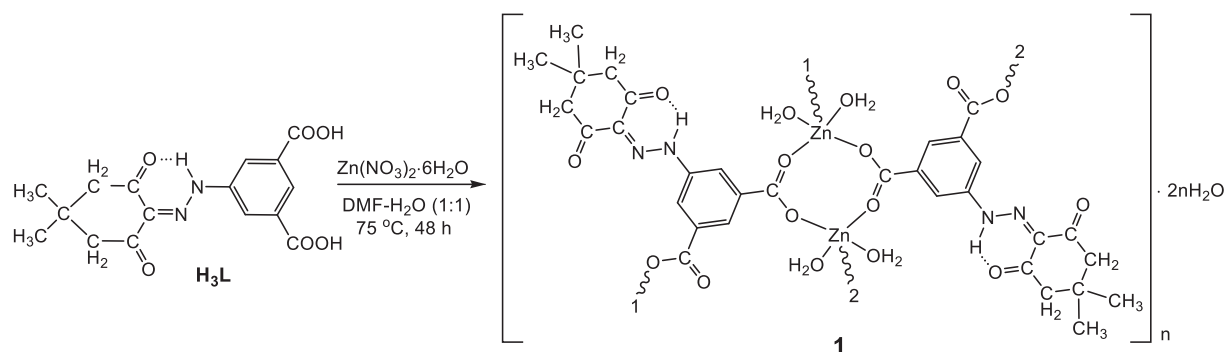
Therefore, the two main objectives of the current work are as follows: i) to synthesize an AHBD bearing two carboxylic groups ( $H_3L$ ) and apply it as a pro-ligand towards the formation of a water soluble Zn(II) coordination polymer; ii) to apply the derived coordination

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Scheme 1. Synthesis of **1**.

polymer as a homogeneous catalyst for the Henry reaction in aqueous medium.

## 2. Results and discussion

### 2.1. Synthesis and characterization of $H_3L$ and **1**

5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)isophthalic acid ( $H_3L$ ) (Scheme 1) was synthesized by the Japp-Klingemann reaction [15] of 3,5-dicarboxybenzenediazonium chloride and 5,5-dimethylcyclohexane-1,3-dione in basic medium. The  $^1H$  NMR spectrum of  $H_3L$  in DMSO- $d_6$  shows the resonance for the NH group adjacent to the aryl unit at  $\delta$  14.59 (Fig. S1 in Electronic Supplementary information). Moreover, the presence, in the  $^{13}C$  NMR spectrum, of two distinct resonances (at 192.86 and 196.86 ppm, Fig. S2 in ESI) for the carbonyl groups, indicate that one of these groups works as acceptor of the proton of the hydrazone NH moiety. This is in agreement with the IR data which clearly reveals the stretching bands for  $\nu(C=O)$  and  $\nu(C=O\cdots H)$  at 1678 and 1619  $cm^{-1}$ , respectively, the latter being shifted on account of the H-bond. Elemental analysis and the ESI-MS peak at 333.2  $[Mr + H]^+$  support the formulation of  $H_3L$ .

The reaction of  $Zn(NO_3)_2 \cdot 6H_2O$  with  $H_3L$  in a mixture of DMF and water (1:1) at 75 °C for 48 h leads to the new Zn(II) coordination polymer  $[Zn(\mu_3-HL)(H_2O)_2]_n \cdot nH_2O$  (**1**) (Scheme 1). In the  $^1H$  NMR spectrum of **1** the original carboxylic protons of  $H_3L$  (detected at  $\delta$  13.37 for  $H_3L$ , Fig. S3 in ESI) have disappeared (due to coordination) and the hydrazone proton is shifted downfield (14.89 ppm) relative to the value shown for  $H_3L$  (see above). Due to coordination carboxylic carbon atom is also shifted from 166.01 (in  $H_3L$ ) to 170.16 ppm in **1** (Fig. S4 in ESI). Several bands in the IR spectrum of **1**, viz. 3421 and 3080 (br)  $\nu(H_2O)$ , 2953  $\nu(NH)$ , 1625, 1581 and 1550  $\nu(C=O)$ , 1508  $\nu(C=N)$   $cm^{-1}$ , are significantly shifted in comparison with the corresponding ones (see ESI file) of the pro-ligand. The ESI-MS peak observed at 396.6  $[Mr-3H_2O + H]^+$  (Fig. S5) accounts for the existence of a monomeric unit in solution. The elemental analyses are consistent with the proposed formulation, which is proved by single crystal X-ray crystallography (Fig. 1, Fig. S6, Tables S1–S3, for the discussion of structure of **1** see the Electronic Supplementary information).

### 2.2. Catalytic activity of **1** in the Henry reaction

The catalytic activity of **1** towards the Henry reaction between benzaldehyde and nitroethane (Scheme 2) was studied, and the influence of varying the solvent, catalyst amount, time and temperature was evaluated (Table 1). No reaction was observed between benzaldehyde and nitroethane in water at room temperature (entry 1), while in the presence of zinc salts the low yields of 14% [with  $Zn(NO_3)_2$ , entry 2] and 35% [with  $Zn(OAc)_2$ , entry 3] were obtained. The catalytic activity of  $H_3L$  and **1** were evaluated in the presence and absence of various solvents

(entries 2–11). The best results were obtained when **1** was used as a catalyst in water (entry 11), and thus water was chosen as the sole solvent for further studies. The variation of the catalyst amount (entries 11–14) allowed to conclude that 6 mol% loading is optimal for the given reaction conditions and thus this amount was applied for the next steps.

The effect of temperature on the performance of this protocol was evaluated over a temperature range of 20–80 °C (entries 13, 15–17), where 40 °C was found to be optimum to produce  $\beta$ -nitroaldol in 80.1% yield after 24 h (entry 15). More interestingly, an increase in the temperature from 40 °C to 80 °C in the Henry reaction leads to a decrease of the product yield (entries 15–17). This may be due to the dissociation of **1** to  $Zn^{2+}$  and  $HL^{2-}$ . The increase of reaction time up to 3 h (within the 0.25–15 h range) led to higher conversions (entries 15 and 18–22). Under such optimized conditions, a product yield of 80% with *syn:anti* molar ratio of 76:24 was obtained (entry 20), whereas  $H_3L$  shows low activity (entry 23). The increase reaction time from 3 h to 24 h is practically not affect the yield of  $\beta$ -nitroaldol and its *syn:anti* ratio (entries 15, 20–22).

The electronic properties of the aldehydes influence the yields and diastereoselectivities of the reaction catalysed by **1** (Table 2). Thus, aryl aldehydes bearing an electron-withdrawing group (nitro or bromo) lead to higher yields of product as compared to those having an electron-donating moiety (entries 1 and 2 vs. 4, Table 2). Moreover, the steric effect is also perceived when *para*-, *meta*- and *ortho*-methyl-

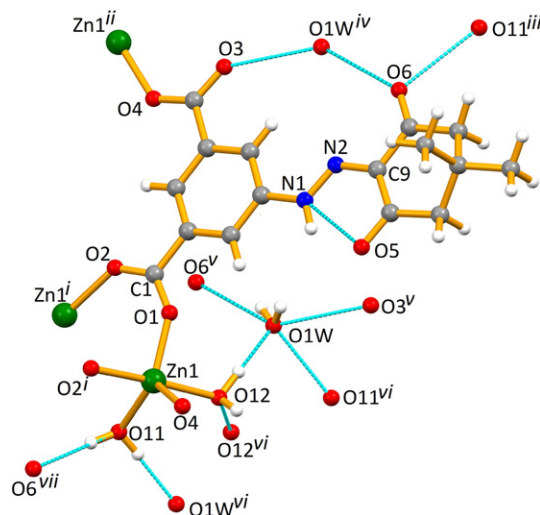


Fig. 1. The molecular structure of **1** with partial atom numbering scheme. H-bond interactions are drawn in dashed light-blue colour. Symmetry codes to generate equivalent atoms: i)  $1 - x, y, 1/2 - z$ ; ii)  $-1/2 + x, 1/2 - y, -1/2 + z$ ; iii)  $-1/2 + x, 1/2 - y, 1/2 + z$ ; iv)  $1/2 - x, 1/2 - y, 1 - z$ ; v)  $1/2 - x, 1/2 - y, 1 - z$ ; vi)  $1 - x, 1 - y, 1 - z$ ; vii)  $1/2 + x, 1/2 - y, -1/2 + z$ .

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