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# PAPER



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# Zinc amidoisophthalate complexes and their catalytic application in the diastereoselective Henry reaction<sup>†</sup>

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Reactions of 5-propionamidoisophthalic acid (H<sub>2</sub>L1) and 5-benzamidoisophthalic acid (H<sub>2</sub>L2) with  $Zn(NO_3)_2 \cdot 6H_2O$  under different hydrothermal conditions lead to two pairs of Zn(II) compounds, *viz.* the mononuclear  $[Zn(L1)(H_2O)_3] \cdot H_2O$  (**1**) and  $[Zn(L1)(H_2O)_3] \cdot 3H_2O$  (**2**), and the 1D polymers  $[Zn(L2)(H_2O)_2]_n$  (**3**) and  $[Zn(L2)(H_2O)_2] \cdot 2H_2O]_n$  (**4**). They crystallize in orthorhombic [*Pbca* (**1**) and *P2*<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (**3**)] or triclinic (*P***1**, **2** and **4**) systems, and their formation depends on the particular reaction conditions. Compounds **1** and **2**, as well as **3** and **4**, are solvatomorphs, the latter presenting different 1D metal–organic polymeric chains. All of them act as heterogeneous catalysts for the diastereoselective nitroaldol (Henry) reaction of different aldehydes with nitroalkanes and can be recycled without losing activity.

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# Introduction

Crystal engineering of coordination polymers is a matter of current interest, namely in view of their unique and outstanding properties, such as gas storage and separation, magnetism and catalysis.<sup>1</sup> In particular, the solvent effects on coordination polymers are of inherent interest due to their complexity and difficulty in predicting the network connectivity.<sup>2</sup> The solvent concurs to influence namely the crystal growth, crystalline morphology and the lattice of the polymers. For such compounds, the occurrence of different crystal forms obtained from the same building blocks concerns "polymorphism",<sup>3a-g</sup> but if the solvent acts as a component incorporated in the crystal lattice that determines the final network of the coordination polymer, the polymorphism can be more appropriately termed as "solvatomorphism" (also known as pseudopolymorphism).<sup>3h-m</sup> Such different crystal forms often result from the variation of factors such as temperature, pH, the method of crystallisation or the crystallization solvent.<sup>4</sup> Polymorphism and solvatomorphism are important in terms of the modulation of the physicochemical properties of materials, of significance, e.g., in the pharmaceutical industry.5 Such systems have been well studied for organic compounds<sup>6a,b</sup> but only a few reports are available for coordination compounds or polymers.6c-e

The application of the formed coordination polymers in catalysis is the main general objective. For such a purpose, we have selected the Henry reaction, a base-catalyzed C-C coupling of a methylene-active nitroalkane and a carbonyl compound to afford nitroalkanols.<sup>7</sup> It is widely used for the synthesis of organic compounds of, e.g., pharmaceutical significance.8 Often this reaction is carried out in the presence of strong bases, leading to dehydration with concomitant formation of a nitroolefin.<sup>9</sup> The development of new catalysts and procedures for the Henry reaction is a matter of current interest, namely towards the reduction of toxic by-products and the increase of yield and diastereoselectivity. In the last two decades asymmetric catalysts have been developed to convert aldehydes or  $\alpha$ -keto esters into the corresponding nitroalkanols with good enantio- and diastereoselectivities.<sup>10</sup> Even though high yields were obtained for reactions performed using homogeneous catalysts, <sup>11b-g,12a-f</sup> the achievement of a high stereoselectivity is still challenging and moreover only scant examples are known<sup>11</sup> using heterogeneous catalysts.

Some iron, copper and zinc containing complexes have been reported by our group,<sup>12</sup> which catalyze the nitroaldol reaction, but most of them are homogenous catalysts, and now we wish to extend our study to heterogeneous systems. Recently, we have found that a few zinc amidoterephthalate coordination polymers are active towards the nitroaldol reaction,<sup>13</sup> and this promising line of research is worthwhile to be continued.

The development of cheap, new, efficient and selective heterogeneous catalysts, with the expected advantages over the homogenous ones, namely in terms of easier separation and catalyst recycling, would be a significant addition to this field.



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Thus, two main objectives of the current work are as follows: (i) to synthesize Zn(n)-complexes by using amidoisophthalate linkers; (ii) to apply the synthesized complexes as heterogeneous catalysts in the nitroaldol combination of nitroethane with various aldehydes.

Hence, in this work we focus on the synthesis and characterization of new ligands bearing different amide side functional groups, 5-propionamidoisophthalic acid (H<sub>2</sub>L1) and 5-benzamidoisophthalic acid (H<sub>2</sub>L2) (Scheme 1), which are then applied to the synthesis of Zn(II) coordination compounds,  $[Zn(L1)(H_2O)_3] \cdot H_2O$  (1),  $[Zn(L1)(H_2O)_3] \cdot 3H_2O$  (2),  $[Zn(L2)(H_2O)_2]_n$ (3) and  $[{Zn(L2)(H_2O)_2} \cdot 2H_2O]_n$  (4), whose structures are established by single crystal X-ray diffraction analysis. These complexes act as heterogeneous catalysts in the nitroaldol reaction of nitroethane with various aldehydes.

### Results and discussion

#### Syntheses and characterization

The syntheses of complexes  $[Zn(L1)(H_2O)_3] \cdot H_2O$  (1),  $[Zn(L1)-(H_2O)_3] \cdot 3H_2O$  (2),  $[Zn(L2)(H_2O)_2]_n$  (3) and  $[\{Zn(L2)(H_2O)_2\} \cdot 2H_2O]_n$  (4) were carried out (see the "Experimental" section) under hydrothermal/solvothermal conditions, by reacting 5-propionamido-isophthalic acid (H<sub>2</sub>L1) or 5-benzamidoisophthalic acid (H<sub>2</sub>L2) with zinc( $\pi$ ) nitrate hexahydrate in the presence of a DMF and methanol (for 1 and 3) or DMF and 1,4-dioxane mixture (for 2 and 4) (Schemes 2 and 3, respectively).

In the IR spectra, the characteristic strong bands of the coordinated carboxylate groups appear at 1584–1550 cm<sup>-1</sup> for the asymmetric  $\nu$ (C=O) stretching and at 1367–1338 cm<sup>-1</sup> for

the symmetric one. The corresponding  $\nu$ (C–O) stretching is observed in the 1278–1242 cm<sup>-1</sup> range, whereas  $\nu$ (OH) of water molecules is in the 3355–3316 cm<sup>-1</sup> region. For complexes **1** and **2**, a strong band at 1637–1625 cm<sup>-1</sup> appears due to the non-coordinated carboxylate groups.<sup>14</sup> These complexes are also characterized by X-ray diffraction, elemental and thermo-gravimetric analyses.

#### Crystal structure analyses

The solvent variant (DMF–MeOH/DMF–dioxane) hydrothermal reactions of 5-propionamidoisophthalic acid (H<sub>2</sub>L1) or 5-benzamidoisophthalic acid (H<sub>2</sub>L2) with the zinc( $\pi$ ) salt lead to the formation of the zinc( $\pi$ ) complexes (1–4). According to the X-ray diffraction analysis, compounds 1 and 2 are solvatomorphs, their crystal structures presenting similar mononuclear metal complexes but different numbers of crystallization water molecules. Compounds 3 and 4 are also solvatomorphs, presenting different 1D metal–organic polymeric chains, but the latter has additional crystallization water molecules. They crystallize in different space groups (1 in *Pbca*, 3 in *P2*<sub>1</sub>2<sub>1</sub>2<sub>1</sub> and 2 and 4 in *P*1̄). The coordination polymers 3 and 4 have helical and zig-zag type one dimensional structures, respectively.

The asymmetric units of 1 and 2 contain a tri-aqua  $zinc(\pi)$ entity coordinated by an O-carboxylate from a L1<sup>2-</sup> ligand, as well as one (1) or three (2) crystallization water molecules (Scheme 2 and Fig. S4, ESI<sup> $\dagger$ </sup>). Both the Zn(II) centres in 1 and 2 present tetrahedral geometries ( $\tau_4 = 0.88$  and 0.97, respectively).<sup>15</sup> The M-O<sub>L1</sub> bond distances are 2.0008(19) Å in 1 and 1.9680(18) Å in 2, whereas the remaining M-O ones vary in the 2.008(3)-2.026(3) Å range. The C-O bond lengths in the noncoordinated carboxylate groups differ by 0.038 Å in 1 but only by 0.007 Å (a non-significant difference) in 2 (Table S3 in ESI†). The structures also differ in the twisting of the carboxylate groups from the phenyl rings; although no great disparity was found for the free COO group  $(17.17^{\circ} \text{ in } 1 \text{ and } 16.68^{\circ} \text{ in } 2)$ , the coordinated carboxylate deviates by 19.53° in 1 and only by  $3.39^{\circ}$  in 2. The minimum Zn···Zn distance reaches 6.1286(8) Å in 1 and 5.1906(4) Å in 2.

Extensive H-bond interactions could be found in both complexes (Fig. 1). The amide group in 1 donates to the free O-atom of the coordinated carboxylate moiety in a vicinal molecule and thus generates a 1D chain that spreads along the crystallographic *b* direction. By means of the coordinated water molecules that donate







Fig. 1 H-bond networks of 1 (A) and 2 (B) [hydrogen bonding interaction drawn using black dotted lines].

to the uncoordinated water (which also acts as a donor) and to neighbouring *O*-carboxylates or *O*-amide groups, the structure of **1** expands into the third dimension. A 3D network could also be found in **2** resulting from the amide group which donates to one of the free water molecules, and the remaining ones which work as donors (and also as acceptors) to other free or coordinated water molecules. The asymmetric units of **3** and **4** include a deprotonated ligand

 $(L2^{2-})$  linked to a di-aqua Zn(II) cluster together with, for 4, two

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uncoordinated water molecules (Scheme 3 and Fig. S5, ESI<sup>†</sup>). Both carboxylate groups coordinate to a tetrahedral metal cation  $(\tau_4 = 0.92 \text{ for 3 and } 0.89 \text{ for 4})^{15}$  in *anti* (3) or *syn* (4) fashion, this fact being the driving force for the 1D (along the crystallographic *b* axis), helical- or comb-type polymeric chain, respectively (Fig. 2). This also disturbs the relative orientation of the phenyl groups of  $L2^{2-}$  and consequently the least-square planes of adjacent ligands in 3 make an angle of  $52.55^{\circ}$  while in 4 that angle is nil. Moreover, in 3 both the metal carboxylate bond distances [1.969(2) and 1.958(2) Å] are shorter than the metal water bond lengths [2.006(3) and 2.018(3) Å] but in 4 such a difference is lessened, with the  $\text{Zn-O}_{\text{carboxylate}}$  distances [1.9929(19) and 2.014(2) Å] closer to the  $\text{Zn-O}_{\text{water}}$  ones [2.008(3) and 2.016(3) Å] (Table S3, ESI†). Thus, the intra chain  $\text{Zn}\cdots\text{Zn}$  distance reaches 9.5556(7) Å in 3, but 10.153(2) Å in 4.



**Fig. 2** The 1D structures of **3** (A) and **4** (C) with partial atom labelling schemes and a representation of the helical structure of **3** (B). Symmetry operations to generate equivalent atoms: (i) -x, 1/2 + y, 1/2 - z; (ii) x, 1 + y, z; (iii) -x, -1/2 + y, 1/2 - z (**3**). (i) x, 1 + y, z; (ii) x, -1 + y, z (**4**).

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As in 1 and 2, the extensive H-bond contacts that are found in 3 and 4, all of them involving the coordinated and the free (in 4) water molecules, spread both structures into 3D (Fig. 3A and B). Such interactions impact upon the interchain  $Zn \cdots Zn$  distances which reach 6.785 Å in 3, but 4.289 Å in 4.

The topological analysis of 3 and  $4^{16}$  indicates that they can be represented as 2-connected uninodal nets with topology of type 2C1 (Fig. S2, ESI<sup>†</sup>).

#### Thermogravimetric analyses

Thermogravimetric analyses were carried out under dinitrogen in the range from room temperature to *ca.* 750 °C at a heating rate of 10 °C min<sup>-1</sup>. Features of the thermal stability of complexes **1–4** are illustrated in Fig. 4. Complex 1 shows a weight loss of 19.0% between 42 and 318 °C, corresponding to the loss of three coordinated and one non-coordinated water molecules (calcd: 19.3%). Similarly, complex 2 exhibits a weight loss of 25.8% in the 43–275 °C temperature range which accounts for the total removal of the six water molecules (calcd: 26.4%). Both derived species are stable up to 355 °C, but above this temperature further decomposition occurs towards the final product ZnO.

Complex 3 exhibits a weight loss of 9.5% in the 204–327 °C temperature range, which accounts for the removal of the two coordinated water molecules (calcd: 9.3%). The remaining material is stable up to 371 °C beyond which it starts to decompose. Complex 4 shows a three-step decomposition process. In the first step it loses 8.3% of its weight within 65–124 °C, most likely due to the loss of two non-coordinated



Fig. 3 (A) Hydrogen bonding network of 3 (H-interaction drawn using black dotted lines). (B) Hydrogen bonded networks of 4 (hydrogen bonding represented using black dotted lines and water molecules represented using a spacefill model).

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water molecules (calcd: 8.5%). In the second step, in the temperature range of 125-210 °C, it loses the two coordinated water molecules, corresponding to a weight loss of 8.8% (calcd: 9.4%). In the final step, the remaining material starts to decompose at 369 °C up to 541 °C.

#### Catalytic activity towards the Henry reaction

We have tested the catalytic activity of compounds 1–4 as solid heterogeneous catalysts in the nitroaldol (or Henry) reaction of nitroethane with various aldehydes. In a typical reaction, a mixture of aldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and the Zn-catalyst (3.0 mol%) in 2.0 mL of MeOH, contained in a capped glass vessel, was stirred at 70 °C for 48 h, whereupon the solution was filtered to remove the catalyst. The solvent was evaporated in a vacuum, giving the crude product as a mixture of the  $\beta$ -nitroalkanol diastereoisomers (*syn* and *anti* forms, with predominance of the former; Scheme 4) which was analyzed by <sup>1</sup>H NMR.

By using benzaldehyde as a test compound, we found that **3** showed a higher activity than the other complexes, for the same reaction time and the same temperature. Consequently, the optimization of the reaction conditions (temperature, reaction time, the amount of catalyst and solvent) was carried out in a model nitroethane–benzaldehyde system with catalyst **3** (Scheme 4 and Table 1).

A blank test was carried out with benzaldehyde in the absence of any metal catalyst, at 70  $^{\circ}$ C in methanol. No  $\beta$ -nitroalkanol was detected after a reaction time of 48 h. The nitroaldol reaction



Scheme 4 Nitroaldol (Henry) reaction.

also did not take place by using compound  $H_2L1$  or  $H_2L2$  instead of the metal catalyst (Table 1, entries 21 and 22, respectively). We have also checked the reactivity of  $Zn(NO_3)_2 \cdot 6H_2O$  in methanol medium and the obtained reaction yield was much lower, *i.e.*, 15% (entry 20, Table 1), than in the presence of any of the catalysts 1–4.

When 3 mol% of **3** is used as a catalyst, a conversion of 87% (*syn*: *anti* = 85:15) of benzaldehyde into  $\beta$ -nitroalkanol is reached (entry 7, Table 1). With **1**, **2** and **4** conversions of 78% (*syn*: *anti* = 84:16), 76% (*syn*: *anti* = 82:18) and 82% (*syn*: *anti* = 81:19) were obtained, respectively (entries 16–18, Table 1). Extending the reaction time to 72 h did not increase the yield of the reaction. The plot of yield *versus* time for the Henry reaction of benzaldehyde and nitroethane with complex **3** is presented in Fig. 5A.

We have also tested the effects of the catalyst amount, solvents and temperature for the Henry reaction. An increase of the catalyst amount from 1.0 to 3.0 mol% enhances the product yield from 76 to 87%, respectively (entries 8 and 7, Table 1), but a further increase decreases the reaction yield to 80% (entry 9, Table 1).

To select the most suitable solvent, experiments using various solvents (CH<sub>3</sub>CN, THF, MeOH and H<sub>2</sub>O) have been carried out with catalyst 3 (entries 7 and 10–12, Table 1) and the results indicate that MeOH (87% yield) is the best polar solvent for this catalytic reaction, whereas CH<sub>3</sub>CN is the worst (0% yield). In water and THF, the yields of 70% or 75%, respectively, were obtained (entries 11 and 10, Table 1).

Varying the temperature from 20 to 70 °C improved the yield of  $\beta$ -nitroalkanol from 12 to 87% (entries 7 and 13–14, Table 1) but a further increase in the reaction temperature had a negative effect (entry 15, Table 1). The systems exhibit diastereoselectivity towards the *syn* isomer, typically leading to *syn*: *anti* molar ratios in the range of 88:12 to 80:20 using nitroethane as a substrate. The size of the nitroalkane chain also affects the yield and with nitropropane the lower yield of 66% was achieved (entry 23, Table 1).

We have also compared the activities of catalyst 3 in the reactions of a variety of *ortho-*, *meta-* or *para-*substituted aromatic and aliphatic aldehydes with nitroethane, producing the corresponding  $\beta$ -nitroalkanols with yields ranging from 37 to 97% (Table 2). Aryl aldehydes bearing an electron-withdrawing group exhibit higher reactivities (Table 2, entries 1 and 3) as compared to those having electron-donating moieties, which may be related to an increase of the electrophilicity of the substrate in the former case.

In order to examine the stability of **3** in the Henry reaction, this catalyst was recycled for six consecutive experiments and it was observed that its activity remained almost the same (Fig. 5B). We have also performed the six recycling experiments for all the other catalysts (Fig. S6, ESI<sup>†</sup>) and observed only a slight decrease in reaction yields over the 4th–6th cycles. There were no significant changes in the FT-IR spectra of all the catalysts (**1–4**) recorded before and after the reaction (Fig. S3A and S7A–S9A, ESI<sup>†</sup>), suggesting the integrity of the polymeric structure of the solid. This was confirmed by PXRD also performed before and after the Henry reaction (Fig. S3B and S7B–S9B, ESI<sup>†</sup>).

Table 1 Optimization of the parameters of the Henry nitroaldol reaction between benzaldehyde and nitroethane with 3 as the catalyst<sup>a</sup>

Entry	Catalyst	Time (h)	Amount of catalyst (mol%)	T (°C)	Solvent	Yield <sup>b</sup> (%)	Selectivity <sup>c</sup> (syn/anti)	TON <sup>d</sup>
1	3	2	3.0	70	MeOH	34	84:16	11.3
2	3	4	3.0	70	MeOH	47	85:15	15.6
3	3	6	3.0	70	MeOH	56	86:14	18.6
4	3	8	3.0	70	MeOH	62	88:12	20.6
5	3	12	3.0	70	MeOH	73	85:15	24.3
6	3	24	3.0	70	MeOH	79	86:14	26.3
7	3	48	3.0	70	MeOH	87	85:15	29.0
8	3	48	1.0	70	MeOH	76	85:15	25.3
9	3	48	5.0	70	MeOH	80	80:20	26.6
10	3	48	3.0	70	THF	75	87:13	25.0
11	3	48	3.0	70	$H_2O$	70	82:18	23.3
12	3	48	3.0	70	CH <sub>3</sub> CN		—	
13	3	48	3.0	RT (20 °C)	MeOH	12	82:18	4.0
14	3	48	3.0	50	MeOH	76	84:16	25.3
15	3	48	3.0	100	MeOH	52	85:15	17.3
16	1	48	3.0	70	MeOH	78	84:16	26.0
17	2	48	3.0	70	MeOH	76	82:18	25.3
18	4	48	3.0	70	MeOH	82	81:19	27.3
19	Blank	48	_	70	MeOH	_	_	_
20	$Zn(NO_3)_2 \cdot 6H_2O$	48	3.0	70	MeOH	15	88:12	5.0
21	$H_2L1$	48	3.0	70	MeOH	_	_	_
22	$H_2L2$	48	3.0	70	MeOH	_	_	
23 <sup>e</sup>	3	48	3.0	70	MeOH	66	90:10	22.0

<sup>*a*</sup> Reaction conditions: 3.0 mol% of catalyst 3, benzaldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and methanol (2.0 mL). <sup>*b*</sup> Number of moles of β-nitroalkanol per 100 moles of aldehyde. <sup>*c*</sup> Calculated by <sup>1</sup>H NMR. <sup>*d*</sup> Number of moles of β-nitroalkanol per mole of the catalyst. <sup>*e*</sup> Nitropropane was used as a substrate.



Fig. 5 (A) Plot of  $\beta$ -nitroalkanol yield vs. time for the Henry reaction of benzaldehyde and nitroethane with 3 ( $\blacksquare$ ). (B) Kinetic profiles in six consecutive reaction cycles employing 3 as a catalyst.

Additionally, the filtrate solution, after the separation of the catalysts by filtration, was evaporated to dryness and the amount of zinc determined, being only between 0.012% and 0.022% of the amount used in the reaction, thus ruling out any significant leaching of the catalyst.

Although there are some reports on coordination polymers<sup>17</sup> which are catalytically active for this kind of reaction, the yields and selectivity are usually higher for our compounds as compared to other metal organic frameworks. The 3D zinc(II) framework with 1,3,5-tri(4-carboxyphenoxy)benzene, in the reaction of

4-nitrobenzaldehyde and nitroethane, leads to an overall yield of only 15% after 72 h of reaction time;<sup>17*a*</sup> with a 1,4-diazabicyclo[2.2.2]octane (DABCO) functionalized 3D-Zn MOF a yield of 34% after 120 h was obtained.<sup>17*b*</sup> Moreover, our catalyst **3** exhibits a marked higher yield (98% after 48 h) and selectivity towards the *syn* diastereoisomer (Table 2, *syn*: *anti* = 80:20) which was not reported for other cases. The overall yield (87%) with benzaldehyde in the presence of catalyst **3** is comparable with those obtained for other zinc amidoterephthalate coordination polymers.<sup>13</sup>

Entry	Aldehyde	Yield <sup>b</sup> (%)	Selectivity <sup>c</sup> (syn/anti)	TON
1	О2N-СНО	97	80:20	32.3
2	Н3СО-СНО	37	85:15	12.3
3	сі————————————————————————————————————	82	81:19	27.3
4	Н <sub>3</sub> С-СНО	63	85:15	21.0
5	Сно	67	86:14	22.3
6	но сно	81	81:19	27
7	CH <sub>3</sub> CHO	94	84:16	31.3
8	CH <sub>3</sub> CH <sub>2</sub> CHO	89	85:15	29.6

<sup>*a*</sup> Reaction conditions: 3.0 mol% of catalyst **3**, aldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and methanol (2.0 mL). <sup>*b*</sup> Number of moles of β-nitroalkanol per 100 moles of aldehyde. <sup>*c*</sup> Calculated by <sup>1</sup>H NMR. <sup>*d*</sup> Number of moles of β-nitroalkanol per mole of the catalyst.

A possible reaction mechanism for the Henry reaction catalyzed by **3** involves the activation of both the aldehyde and nitroethane by the metal centre (with deprotonation of the latter) and is followed by the formation of a C–C bond upon nucleophilic addition leading to the  $\beta$ -nitroalkanol.<sup>11a,12,13,18</sup> The proton abstraction from the nitroalkane ligand and the protonation of the C–C coupled species can be assisted by the ligand (with a carboxylate and an amide group) and also by methanol, thus possibly accounting for the good activity of our catalyst in the presence of methanol.

## Concluding remarks

We successfully isolated four zinc(II) coordination compounds derived from the 5-propionamidoisophthalic (H<sub>2</sub>L1) and 5-benzamidoisophthalic (H<sub>2</sub>L2) acids under various synthetic conditions. They exhibit 0D (1 and 2) and 1D (3 and 4) structures, due to the various coordination modes of the ligands. Single-crystal X-ray diffraction analyses reveal that the structures of 1 and 2 (also 3 and 4) are solvatomorphs with respect to the different numbers of water molecules present in the lattices. Complexes 1 and 2 have similar types of mononuclear structures but contain different numbers of non-coordinated water molecules. The coordination polymers 3 and 4 have helical and zig-zag type 1D polymeric structures, respectively. Their construction depends on the particular reaction conditions, which lead to significant differences in the coordination networks.

These complexes effectively catalyze the Henry reaction of nitroethane with various aldehydes producing the corresponding  $\beta$ -nitroalkanols in high yields. Among the four complexes studied here, complex 3 is the most active one. We have also proved the stability and recyclability of the catalysts. The *syn/anti* ratio of the nitroaldol products depends on various factors, such as the amount of catalyst, the electrophilicity of the substrates and the reaction conditions.

The above observations provide further evidence that simple Zn(u) complexes can be utilized as effective heterogeneous catalysts in the important type of reactions studied here. Further explorations on the use of this catalyst family in other organic transformations, as well as mechanistic investigations, are ongoing.

## Experimental

#### Materials and physical methods

The synthetic work was performed in open air atmosphere and at room temperature. All the chemicals were obtained from commercial sources and used as received. The infrared spectra (4000-400 cm<sup>-1</sup>) were recorded on a Bruker Vertex 70 instrument using KBr pellets; abbreviations: s = strong, m = medium, w = weak, bs = broad and strong, mb = medium and broad. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at ambient temperature on a Bruker Avance II + 300 (UltraShield™Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference; abbreviations: s = singlet, d = doublet, t = triplet, q = quartet. Carbon, hydrogen and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Electrospray mass spectra (ESI-MS) were obtained using an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80-105 V). Thermal properties were analyzed using a Perkin-Elmer Instrument system (STA6000) at a heating rate of 10 °C min<sup>-1</sup> under a dinitrogen atmosphere. Powder X-ray diffraction (PXRD) was conducted in a D8 Advance Bruker AXS (Bragg Brentano geometry) theta-2theta diffractometer, with copper radiation (Cu K $\alpha$ ,  $\lambda$  = 1.5406 Å) and a secondary monochromator, operated at 40 kV and 40 mA. A flat plate configuration was used and the typical data collection range was between  $5^{\circ}$  and  $40^{\circ}$ .

# Syntheses of 5-propionamidoisophthalic acid $(H_2L1)$ and 5-benzamidoisophthalic acid $(H_2L2)$

Both compounds were synthesized by similar two-step procedures.

In the first step, dimethyl-5-aminoisophthalate (2.09 g, 10.0 mmol) and NEt<sub>3</sub> (1.51 g, 15.0 mmol) were placed in a round bottom flask and then dry dichloromethane (30 mL) was added. After cooling in an ice bath followed by dropwise addition of acid chloride [propionyl chloride (1.10 g, 12.0 mmol) for H<sub>2</sub>L1 or benzoyl chloride (1.68 g, 12.0 mmol) for H<sub>2</sub>L2], the reaction mixture was stirred overnight at room temperature. Upon removal of the solvent under reduced pressure a white

solid was obtained. 20 mL of water were then added to the white solid which was then extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulfate; subsequent removal of the solvent gave the methyl ester of compound  $H_2L1$  or  $H_2L2$ .

In the second step, the isolated ester (2.65 g, 10.0 mmol for the methyl ester of H<sub>2</sub>L1/3.13 g, 10.0 mmol for the methyl ester of H<sub>2</sub>L2) and NaOH (0.8 g, 20.0 mmol) were dissolved in 20 mL of MeOH : water (4 : 1). The reaction mixture was refluxed for 4 h at 80 °C, after which the solvent was removed under reduced pressure. 10 mL of water were added and the solution was acidified (pH = 2) with dilute HCl solution. The obtained white solid product H<sub>2</sub>L1 or H<sub>2</sub>L2 was removed by filtration and washed with water until total removal of the acid. Yield: 62% (1.47 g) for H<sub>2</sub>L1 and 81% (2.31 g) for H<sub>2</sub>L2.

Characterization details for H<sub>2</sub>L1: anal. calcd for C<sub>11</sub>H<sub>11</sub>NO<sub>5</sub> (M = 237.21): C, 55.70; H, 4.67; N, 5.90. Found: C, 55.11; H, 4.50; N, 4.72. FT-IR (KBr, cm<sup>-1</sup>): 3387 (s), 3208 (s), 3101 (m), 2973 (m), 2634 (w), 2511 (w), 1719 (s), 1693 (s), 1642 (m), 1563 (m), 1389 (m), 1300 (m), 1255 (s), 1199 (s), 1079 (w), 940 (w), 918 (w), 779 (m), 680 (m); <sup>1</sup>H-NMR (CD<sub>3</sub>OD): 8.43–8.42 (2H, d, Ar–H), 8.31 (1H, s, Ar–H), 2.40–2.37 (2H, q, –CH<sub>2</sub>), 1.20–1.15 (3H, t, –CH<sub>3</sub>); MS (ESI): m/z: 260.1 [M + Na]<sup>+</sup>.

Characterization details for  $H_2L2$ : anal. calcd for  $C_{15}H_{11}NO_5$ (M = 285.25): C, 63.16; H, 3.89; N, 4.91. Found: C, 63.14; H, 3.60; N, 4.82. FT-IR (KBr, cm<sup>-1</sup>): 3532 (mb), 2849 (w), 2571 (w), 1719 (s), 1645 (m), 1566 (s), 1436 (s), 1385 (m), 1348 (w), 1254 (s), 913 (w), 757 (w), 710 (m), 694 (m), 665 (m), 602 (w), 544 (w); <sup>1</sup>H-NMR (DMSO- $d_6$ ): 10.612 (1H, s, -NH), 8.70 (2H, s, Ar–H), 8.24 (1H, d, Ar–H), 8.02–8.002 (2H, d, Ar–H), 7.51–7.62 (3H, m, Ar–H); <sup>13</sup>C-NMR (DMSO- $d_6$ ): 167.01, 166.3, 140.3, 134.7, 132.3, 132.09, 128.8, 128.2, 125.4, 125.2, MS (ESI): m/z: 308.1 [M + Na]<sup>+</sup>.

**Synthesis of 1.** A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (25.0 mg, 0.084 mmol) and H<sub>2</sub>L1 (20.0 mg, 0.084 mmol) was dissolved in 5 mL of DMF and methanol (1:1). A white precipitate was obtained when the mixture was stirred at room temperature for 30 min. The precipitate was dissolved by adding 0.5 mL of 28% aqueous ammonia solution, and the resulting mixture was sealed in an 8 mL glass vessel and heated at 75 °C for 48 h. Subsequent gradual cooling to room temperature (0.2 °C min<sup>-1</sup>) afforded needle-like colorless crystals. Yield: 81% (based on Zn). Anal. calcd for C<sub>11</sub>H<sub>17</sub>NO<sub>9</sub>Zn (M = 372.62): C, 35.46; H, 4.60; N, 3.76; found: C, 35.63; H, 4.21; N, 3.42. FT-IR (KBr, cm<sup>-1</sup>): 3447 (bs), 3316 (bs), 2979 (m), 2941 (w), 1637 (s), 1584 (s), 1363 (s), 1242 (m), 1217 (m), 1104 (w), 1080 (m), 901 (m), 774 (s), 735 (s).

**Synthesis of 2.**  $Zn(NO_3)_2 \cdot GH_2O$  (25.0 mg. 0.084 mmol) and  $H_2L1$  (20.0 mg. 0.084 mmol) were dissolved in DMF:1,4dioxane (1:1). A white precipitate was obtained after adding 0.2 mL of 28% aqueous ammonia solution to this reaction mixture. The precipitate was dissolved upon addition of additional 0.5 mL of 28% aqueous ammonia solution. The resulting mixture was sealed in a capped glass vessel and heated to 75 °C for 48 h. Subsequent gradual cooling to room temperature (0.2 °C min<sup>-1</sup>) afforded colorless crystals. Yield: 65% (based on Zn). Anal. calcd for  $C_{11}H_{21}NO_{11}Zn$  (M = 408.66): C, 32.33; H, 5.18; N, 3.43; found: C, 32.13; H, 5.21; N, 3.18. FT-IR (KBr, cm<sup>-1</sup>): 3355 (bs), 2976 (m), 2932 (w), 1681 (s), 1625 (s), 1567 (s), 1408 (s), 1362 (s), 1271 (s), 1209 (m), 1128 (m), 1073 (m), 902 (m), 773 (s), 731 (s).

Synthesis of 3. A mixture of  $Zn(NO_3)_2 \cdot 6H_2O$  (20.7 mg. 0.07 mmol) and  $H_2L2$  (20.0 mg. 0.07 mmol) was dissolved in DMF and MeOH (1:1). A white precipitate was obtained after adding 0.5 mL of 28% aqueous solution of  $NH_4OH$  to this reaction mixture. The precipitate was dissolved upon addition of additional 0.4 mL of 28% aqueous solution of  $NH_4OH$ . The resulting mixture was sealed in a 8 mL glass vessel and heated at 80 °C for 48 h. It was subsequently cooled to room temperature (0.2 °C min<sup>-1</sup>), affording plate-like colorless crystals. Yield: 74% (based on Zn). Anal. calcd for  $C_{15}H_{13}NO_7Zn$  (M = 384.63): C, 46.84; H, 3.41; N, 3.64; found: C, 46.23; H, 3.21; N, 3.42. FT-IR (KBr, cm<sup>-1</sup>): 3421 (s), 3327 (bs), 3168 (s), 1643 (s), 1579 (s), 1494 (m), 1427 (s), 1338 (s), 1278 (s), 910 (m), 781 (s), 819 (m), 771 (s), 732 (s).

**Synthesis of 4.** A mixture of  $Zn(NO_3)_2 \cdot 6H_2O$  (25.0 mg, 0.084 mmol) and  $H_2L2$  (24.0 mg, 0.084 mmol) was dissolved in 3 mL of DMF and 1,4-dioxane (1:1). A white precipitate was obtained when the mixture was stirred at room temperature for 1 h. The precipitate was dissolved by adding 0.6 mL of 28% aqueous ammonia solution, and the resulting mixture was sealed in an 8 mL glass vessel and heated at 75 °C for 24 h. Subsequent gradual cooling to room temperature (0.2 °C min<sup>-1</sup>) afforded needle-like colorless crystals. Yield: 73% (based on Zn). Anal. calcd for  $C_{15}H_{17}NO_9Zn$  (M = 420.66): C, 42.83; H, 4.07; N, 3.33; found: C, 42.23; H, 4.21; N, 3.12. FT-IR (KBr, cm<sup>-1</sup>): 3332 (bs), 1643 (s), 1550 (s), 1491 (m), 1429 (s), 1367 (s), 1286 (m), 1259 (m), 1105 (w), 1029 (w), 777 (s), 733 (s).

#### Procedure for the Henry reaction catalyzed by the Zn-complexes

In a typical reaction, a mixture of aldehyde (1.0 mmol), nitroethane (0.3 mL, 4.0 mmol) and Zn-catalyst (3 mol%, 11.2 mg for 1, 12.2 mg of 2, 11.5 mg of 3 and 12.6 mg of 4) was placed in a capped glass vessel, and then 2 mL of MeOH were added into it. The mixture was heated at 70 °C for 48 h, and subsequently quenched by centrifugation and filtration at room temperature. The filtrate was evaporated in vacuum to give the crude product. The residue was dissolved in DMSO- $d_6$ and analyzed by <sup>1</sup>H NMR. The yield of the  $\beta$ -nitroalkanol product (relatively to the aldehyde) was established typically by taking into consideration the relative amounts of these compounds, as given by <sup>1</sup>H NMR and previously reported.<sup>12,13,19</sup> The syn/anti selectivity was calculated on the basis of <sup>1</sup>H-NMR spectra which is presented in Fig. S7 (ESI<sup>†</sup>). In the <sup>1</sup>H NMR spectra, the values of vicinal coupling constants (for the  $\beta$ -nitroalkanol products) between the α-N-C-H and the α-O-C-H protons identify the isomers, being J = 7-9 or 3.2-4 Hz for the syn or anti isomers, respectively.19

In order to perform the recycling experiment, first we washed the used catalyst with methanol and dried it at room temperature. It was then used for the nitroaldol reaction as described above.

#### Crystal structure determination

X-ray quality crystals of the compounds (1–4) were immersed in cryooil, mounted in a nylon loop and measured at room temperature.

#### Paper

Intensity data were collected using a Bruker AXS-KAPPA APEX-II PHOTON 100 diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda$  0.71073) radiation. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART<sup>20</sup> software and refined using Bruker SAINT<sup>20a</sup> on all the observed reflections. Absorption corrections were applied using SADABS.<sup>20a</sup> Structures were solved by direct methods by using the SHELXS-97 package<sup>20b</sup> and refined using SHELXL-97.<sup>20b</sup> Calculations were performed using the WinGX System-Version 1.80.03.<sup>20c</sup> The hydrogen atoms attached to carbon atoms and to the nitrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation;  $U_{iso}(H)$  were defined as  $1.2U_{eq}$  of the parent nitrogen atoms or the carbon atoms for phenyl and methylene residues, and  $1.5U_{eq}$  of the parent carbon atoms for the methyl groups. The hydrogen atoms of coordinated water molecules were located from the final difference Fourier map and the isotropic thermal parameters were set at 1.5 times the average thermal parameters of the belonging oxygen atoms; their positions were restrained by using DFIX and DANG. Least square refinements using anisotropic thermal motion parameters for all the nonhydrogen atoms and isotropic ones for the remaining atoms were employed. In compound 2, the ethyl group was structurally disordered over two orientations and were refined with the use of PART instruction; the occupancy was refined to a ratio of 0.66 and 0.34. Crystallographic data are summarized in Table S1 (ESI<sup>†</sup>) and selected bond distances and angles are presented in Table S3 (ESI<sup>+</sup>). CCDC 1040066-1040069 for 1-4.

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