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PAPER

Zinc(II) *ortho*-hydroxyphenylhydrazo-β-diketonate complexes and their catalytic ability towards diastereoselective nitroaldol (Henry) reaction†

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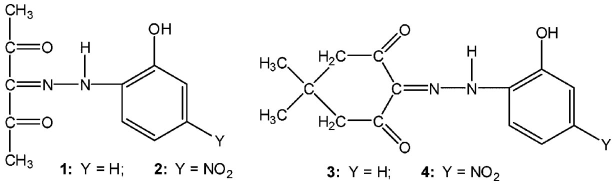
The zinc(II) complexes with *ortho*-hydroxy substituted arylhydrazo-β-diketonates $[Zn_2(CH_3OH)_2(\mu\text{-}L^1)_2]$ (**5**), $[Zn\{(CH_3)_2SO\}(H_2O)(L^2)]$ (**6**), $[Zn_2(H_2O)_2(\mu\text{-}L^3)_2]$ (**7**) and $[Zn(H_2O)_2(L^4)]\cdot H_2O$ (**8**) were synthesized by reaction of a zinc(II) salt with the appropriate hydrazo-β-diketone, $HO\text{-}2\text{-}C_6H_4\text{-}NHN{=}C\{C({=}O)CH_3\}_2$ (H_2L^1, **1**), $HO\text{-}2\text{-}O_2N\text{-}4\text{-}C_6H_3\text{-}NHN{=}C\{C({=}O)CH_3\}_2$ (H_2L^2, **2**), $HO\text{-}2\text{-}C_6H_4\text{-}NHN{=}\overline{CC({=}O)CH_2C(CH_3)_2CH_2C}({=}O)$ (H_2L^3, **3**) or $HO\text{-}2\text{-}O_2N\text{-}4\text{-}C_6H_3\text{-}NHN{=}\overline{CC({=}O)CH_2C(CH_3)_2CH_2C}({=}O)$ (H_2L^4, **4**). They were fully characterized, namely by X-ray diffraction analysis that disclosed the formation of extensive H-bonds leading to 1D chains (**5** and **6**), 2D layers (**7**) or 3D networks (**8**). The thermodynamic parameters of the Zn(II) reaction with H_2L^2 in solution, as well as of the thermal decomposition of **1–8** were determined. Complexes **5–8** act as diastereoselective catalysts for the nitroaldol (Henry) reaction. The *threo*/*erythro* diastereoselectivity of the β-nitroalkanol products ranges from 8 : 1 to 1 : 10 with typical yields of 80–99%, depending on the catalyst and substrate used.

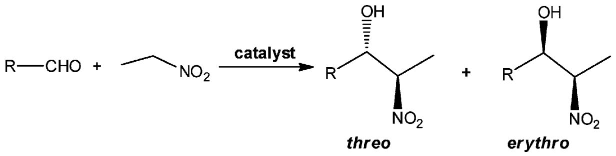
Introduction

Azoderivatives of β-diketones (ADB, Scheme 1) are versatile compounds[1] which can easily be prepared by diazotization with subsequent azo-coupling from cheap starting materials (aromatic amines and β-diketones), but their synthetic use in coordination chemistry has been underestimated notwithstanding their potentially rich chelating ability. In comparison with some widely used ligands, such as β-diketones or azocompounds, ADB have more coordinative possibilities, expecting to be able to chelate both "soft" and "hard" metal ions. The inclusion of the –OH group at the *ortho* position of the aromatic ring of phenylhydrazo-β-diketones creates a family of ADB (herein denoted by OHADB) that bears one further chelating arm and facilitates the complex formation[2] in comparison with analogous unsubstituted ADB[3] or related pentane-2,4-diones.[4] However, only several coordination compounds with such ligands are known, most of them being copper complexes.[2,5] To our knowledge, no examples of OHADB complexes with zinc(II) have been reported and hence the preparation of the first ones is a main aim of the current study.



Scheme 1 Schematic representations of the studied OHADB.

Even more underexplored is the application of OHADB complexes in catalysis (the use of copper(II)-OHADB complexes in some oxidation reactions has only been recently reported).[2] Hence, the exploration of the potential of the novel synthesized Zn(II)-OHADB complexes as catalysts constitutes another important task. In particular, we have selected the nitroaldol or Henry reaction[6,7] which consists of reacting an aldehyde with nitroalkane to give β-nitroalkanols (*threo* and *erythro*) (Scheme 2). It is one of the important carbon–carbon bond formation reactions and is known[6c–e] to be catalyzed by some zinc(II) complexes with N,O- or O,O-ligands.



Scheme 2 Formation of nitroaldols by the Henry reaction.

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The β-nitroalkanols obtained from this reaction are valuable starting materials for further synthesis of *e.g.* 1,2-amino alcohols or β-hydroxy acids.[6l] Usually this reaction is performed with homogeneous basic catalysts, such as alkali metal hydroxides, alkoxides or amines, with a rather good efficiency.[6a,b] However, the *threo*/*erythro* stereocontrol in the Henry reaction remains a challenging field, and efforts have been focused on the development of catalytic diastereo- or enantio-selective processes. In particular, it was found that heterobimetallic complexes with lanthanide BINOL (BINOL = 2,2′-dihydroxy-1,1′-binaphthyl) systems,[6f] a rhodium complex in the presence of a silyl ketene acetal,[6g] amberlyst A-21,[6h] benzyltrimethylammonium hydroxide,[6i] proazaphosphatranes,[6j] Mg–Al hydrotalcite,[6k,l] guanidines,[6m] cinchona alkaloid,[6n] Cu-bis(oxazoline)[6o] or Co-salen (salen = *N*,*N*′-bis(salicylidine)ethylenediamine) complexes[6p,q] are appropriate enantio-differentiating catalysts for the above transformation. In addition, zinc(II) containing compounds, *e.g.* Zn(II) dinuclear complexes[6c,d] or a mixture of $Zn(OTf)_2$ (OTf = triflate) and (+)-*N*-methylephedrine,[6e] also appear to catalyse such a reaction. However, yields and diastereoselectivities for most of the reported systems are rather moderate, and/or expensive components (*e.g.* metals such as Nb, La or Rd, chiral ligands or ionic liquids) are used. Therefore, the introduction of a cheap catalyst, containing *e.g.* zinc (a "green" metal), is of interest in this field.

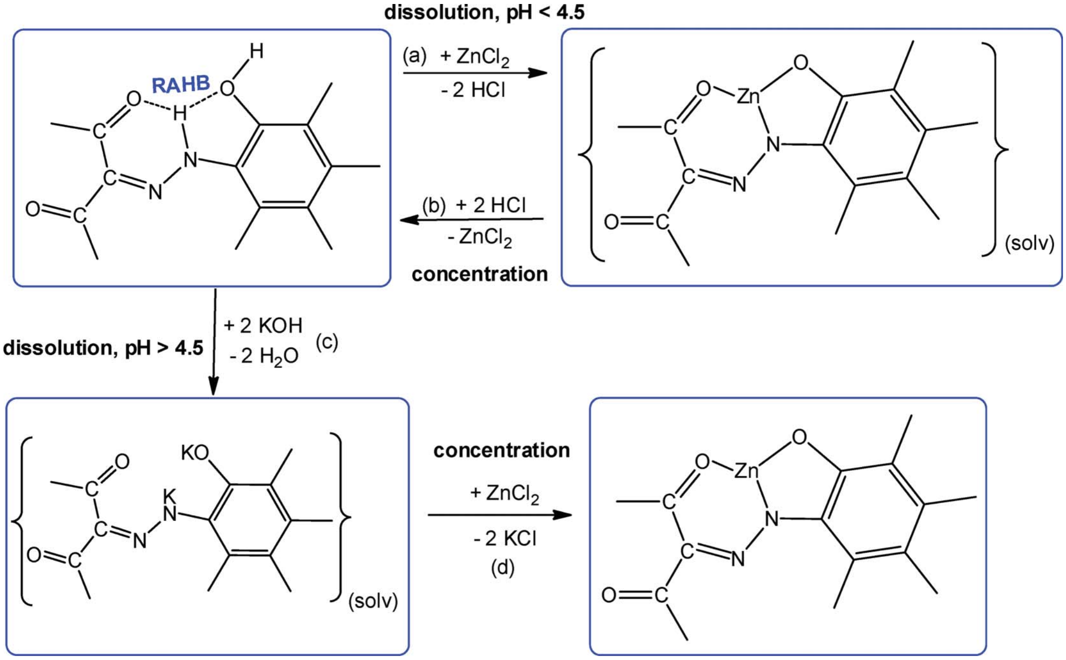
Thus, the main aims of the current work are as follows: (i) to synthesize the first complexes of OHADB with Zn(II) and study their properties including structural effects of substituents, and some physico-chemical parameters of complex formation and thermal decomposition; (ii) to study the catalytic activity and diastereoselectivity of the synthesized zinc(II) complexes in the nitroaldol reaction of nitroethane with various aldehydes.

Results and discussion

Synthesis and characterization of zinc(II) complexes with OHADB

The synthesis and characterization of the OHADB compounds 3-(2-hydroxyphenylhydrazo)pentane-2,4-dione (H_2L^1, **1**), 3-(2-hydroxy-4-nitrophenylhydrazo)pentane-2,4-dione (H_2L^2, **2**), 5,5-dimethyl-2-(2-hydroxyphenylhydrazo)cyclohexane-1,3-dione (H_2L^3, **3**) and 5,5-dimethyl-2-(2-hydroxy-4-nitrophenylhydrazo)cyclohexane-1,3-dione (H_2L^4, **4**) (Scheme 1) were reported earlier by us,[2] and hence will not be discussed (See Electronic Supplementary Information†).

Although Zn^{II} interacts with OHADB in solution,[3] simple solvent evaporation from the reaction mixture containing zinc nitrate and **1–4** gives a mixture of the starting materials, in contrast to the reactions of OHADB with copper(II) salts that lead to complexes that can be easily isolated from the reaction solution.[2,5a] The studied OHADB are known to have a difficult-to-destroy intramolecular resonance assisted N–H···O hydrogen bond (RAHB) linking one of the carbonyl groups to the NH-moiety of the hydrazo unit and further to the hydroxyl group of the aromatic part of the molecule,[2] thus hampering the coordination to metal ions (Scheme 3a). Apparently, upon concentration of the solution, the RAHB (destroyed by interaction with the solvent molecules) regains its structure (Scheme 3b). Clearly, to shift the overall process to the complex formation, one should remove the proton by addition of some base but this can lead to hydrolysis of Zn^{II} with its precipitation as a hydroxide. Hence, firstly one should quantitatively deprotonate the ligand and then add a Zn^{II} salt. Thus, the following procedure was used for the synthesis of the complexes: dissolution of the free ligand in a methanol–water (9 : 1 v/v) solution containing two equivalents of sodium (or potassium) hydroxide (Scheme 3c), followed by addition (after

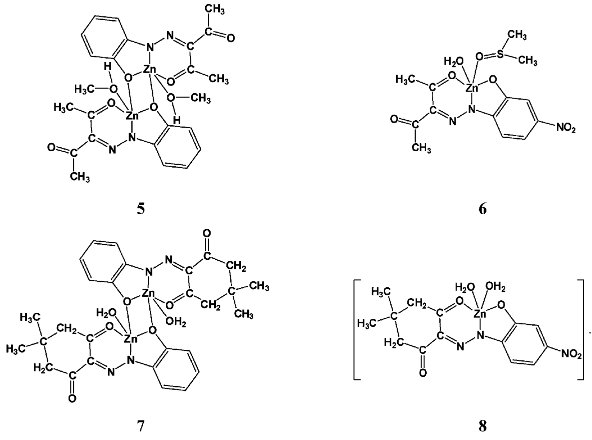


Scheme 3 Rupture of hydrogen bonds in OHADB and coordination to Zn^{II}.

5 min) of zinc(II) chloride and concentration of the reaction mixture (Scheme 3d).

General description of the X-ray crystal structures. Crystals suitable for X-ray diffraction analysis were obtained upon recrystallization from methanol for $[\mathrm{Zn_2(CH_3OH)_2(\mu\text{-}L^1)_2}]$ (**5**), dimethylsulfoxide for $[\mathrm{Zn\{(CH_3)_2SO\}(H_2O)(L^2)}]$ (**6**), and water–acetone (1 : 9, v/v) for $[\mathrm{Zn_2(H_2O)_2(\mu\text{-}L^3)_2}]$ (**7**) and $[\mathrm{Zn(H_2O)_2(L^4)}]\cdot\mathrm{H_2O}$ (**8**) (the schematic representations of their formulae are shown in Scheme 4). The ellipsoid plots of complexes **5–8** are depicted in Fig. 1, and representations of their polymeric networks are depicted in Figures S1 and S2 (Supporting Information).† Selected bonding parameters, H-bond distances and crystallographic data are given in Tables S1, S2 and experimental section, respectively.† The crystal structures of these complexes reveal 1D chains (**5** and **6**), 2D layers (**7**) or 3D networks (**8**). The geometries around the zinc ions in these complexes can be considered as distorted trigonal bipyramid with the axial sites occupied by the oxygen atoms of the chelating ligand. The disparity of the carbonyl moieties, one being coordinated to the metal and the other free, was confirmed and, accordingly, the C=O bond distances are longer in the former case (Table S1†).

Description of X-ray crystal structures of compounds 5 and 7. The complexes $[\mathrm{Zn_2(CH_3OH)_2(\mu\text{-}L^1)_2}]$ (**5**) and $[\mathrm{Zn_2(H_2O)_2(\mu\text{-}L^3)_2}]$ (**7**) crystallize as binuclear species, the former with two methanol and the latter with two water ligands (Scheme 4, Fig. 1, Tables S1 and S2†). In both structures, only half of the molecule is in the asymmetric unit, the metal is in a general position and an inversion centre is in the centre of a $\mathrm{Zn_2(\mu\text{-}O)_2}$ core. **1** and **3** act as dianionic N,O,O-tridentate ligands by means of the *ortho*-O atom (O1, upon deprotonation of the *ortho*-OH group) which bridges two zinc atoms, one of the nitrogen atoms (N1) of the hydrazone unit and



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Scheme 4 Schematic representations of **5–8**.

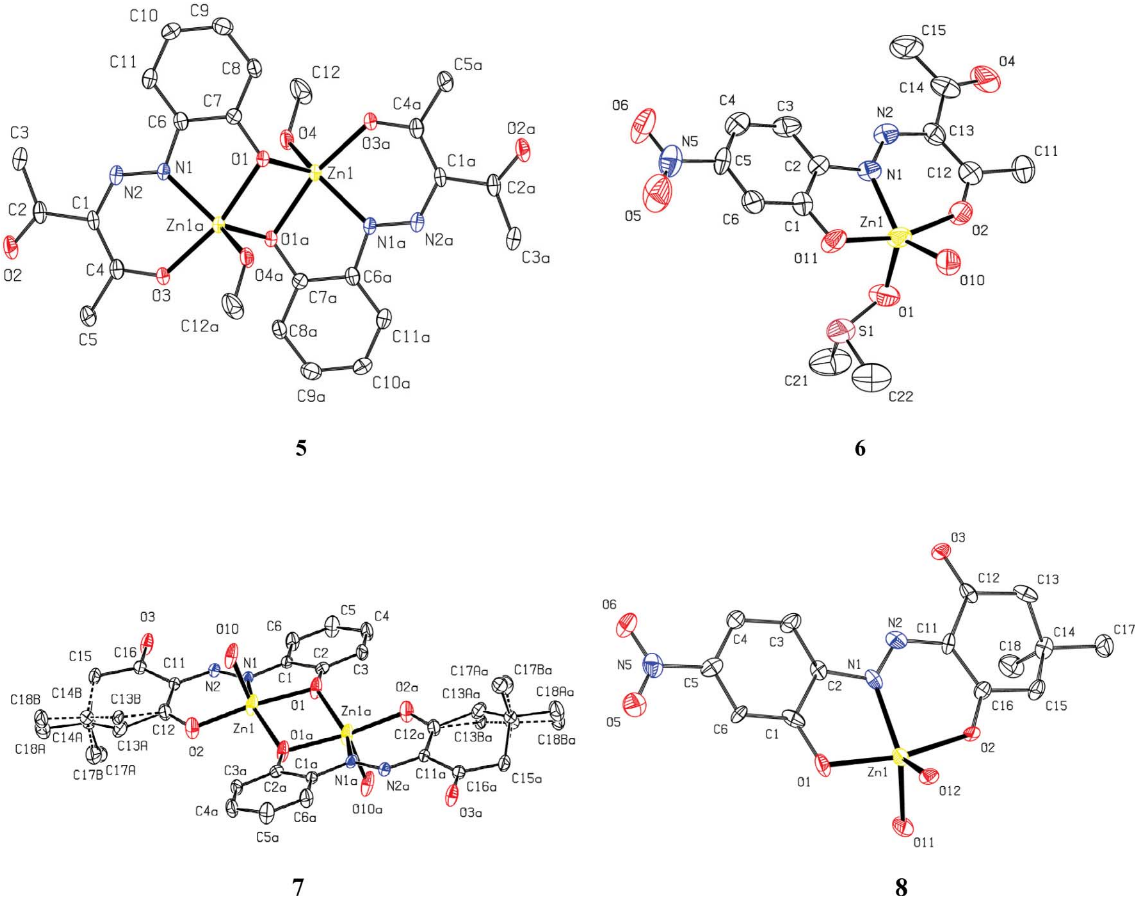

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Fig. 1 Ellipsoid plots with atom labelling scheme (ellipsoids are drawn at the 50% probability level) for complexes **5–8**. For **7**, the diagram shows the structure with disorder model (types A and B atoms). H atoms and crystallization H_2O molecule in **8** are omitted for clarity. Symmetry operators for generating equivalent atoms: $1 - x, 1 - y, 1 - z$ (**5**) and $1 - x, 1 - y, -z$ (**7**).

one oxygen atom from a carbonyl group. The pentacoordinated zinc(II) ions pertain to three different metallacycles: one *endo* ring of the $Zn_2(\mu\text{-}O)_2$ core, which is the central planar ring of the molecule, and two fused six- and five-membered *exo* metallacycles. The O–Zn–O angle in the central core is larger in **5** than in **7** (81.84(8)° and 77.78(9)°, respectively), while the Zn–O–Zn angle is smaller in **5** than in **7** (98.16(8)° and 102.22(9)°, respectively). The intramolecular Zn–Zn distance in **5** is considerably shorter than in **7** (3.0955(5) Å and 3.1551(5) Å, respectively), possibly due to the bulkiness of the β-diketone fragment of **3** in comparison with **1**. Moreover, the structure twisting in **5** is more evident than in **7**; while in **5** the angle between the plane defined by the $Zn(\mu\text{-}O)_2Zn$ core and that defined by the other coordinating atoms is of 49.69°. In **7**, that angle is only of 24.26°. Cooperative hydrogen bond networks are present in these complexes (Fig. S1†). In **5**, they involve infinite 1D chains of the zinc dimers connected by intermolecular O4–H4 · · · O2 interactions [Table S2†; *d* (D · · · A) 2.629(4) Å; ∠(D–H · · · A) 178(5) °], supported by less intense intermolecular C3–H3A · · · O1 contacts [*d* (D · · · A) 3.313(4) Å; ∠(D–H · · · A) 149°]. Other selected relevant interchain contacts are established between one hydrogen from the methyl ester moieties and the six-membered metallacycles of neighbouring chains [*d* (H3B · · · *centroid*) 2.88 Å; ∠(C3–H3B · · · *centroid*) 117°]. In **7**, however, the hydrogen bond network leads to 2D layers, since each coordinated water molecule is doubly bound to the free carbonyl of two vicinal neighbouring dimers. The shortest intermolecular Zn · · · Zn separation is of 6.8604(6) Å in **5** and 6.6632(7) Å in **7**.

Description of X-ray crystal structures of compounds 6 and 8. The monomeric complexes $[Zn\{(CH_3)_2SO\}(H_2O)(L^2)]$ (**6**) and $[Zn(H_2O)_2(L^4)]\cdot H_2O$ (**8**) are formed by coordination of the dianions $(L^2)^{2-}$ and $(L^4)^{2-}$, respectively (Scheme 4, Fig. 1). In the structure of **6**, the neighbouring zinc units are positioned in relative proximity to each other (Zn · · · Zn separation of 5.060 Å) as a result of their linkage *via* strong H-bonds (Fig. S2 and Table S2†) between one of the hydrogen water molecules of one unit and the coordinated phenolate oxygen of a vicinal one [*d*(D · · · A) of 2.542(6) Å], and are further assembled *via* slightly weaker hydrogen bonds involving the other hydrogen of the coordinated water molecule and the uncoordinated carbonyl oxygen moiety [*d*(D · · · A) of 2.687(8) Å]. These interactions give rise to the generation of infinite 1D chains. The units of **8**, however, display multiple H-bonds also involving the crystallization water molecule (Fig. S2†) thus leading to the formation of a 3D network. As a result of such contacts, the Zn · · · Zn distance in **8** is the shortest one found in this work [4.835(3) Å]. It is also noteworthy to mention that both **6** and **8** have two labile ligands (water and dimethylsulfoxide) which can be of significance for their catalytic application (see below).

Complex formation in solution and thermal decomposition. The constant of complex formation in solution is an important parameter for various applications,[3] and we have evaluated it for the reaction of Zn^{II} with **2** by pH-metric titration of a mixture of zinc(II) nitrate and **2**, in aqueous ethanol solution, using the Martell–Chaberek method[8a] and well known relationships for thermodynamic functions[8b] (details are given in Supporting Information, Tables S4 and S5†). The stability constant is found to be $\log k = 9.86 \pm 0.04$ (Table S3†), showing that the zinc(II) complex with L^2 is less stable in solution than that with pentane-2,4-dione ($\log \beta = 17.6$).[4a] The negative values of $\Delta G°$ (−56.3 kJ mol^{-1}) and $\Delta H°$ (−31.8 kJ mol^{-1}) (Table S4†) indicate that the complexation is spontaneous and is mainly contributed by the enthalpy factor. The positive entropy change (82.1 J mol^{-1} K^{-1}) conceivably relates to the abstraction of Zn^{II}-coordinated water molecules during the reaction, *i.e.* with the increase of the number of free molecules in the system. By comparing the results obtained herein with those of previous works,[5] we can conclude that the studied metal ions form complexes with L^2 in ethanol–water solution with the following general order of complex stability: $Fe^{III} > Cu^{II} > UO_2^{+2} > Ni^{II} > Co^{II} > Mn^{II} > Zn^{II} > Cd^{II}$.

The thermal decomposition of **1–4** and their zinc(II) complexes was investigated by DTG-DTA thermogravimetric analysis (Fig. S3, Table S5†). Upon heating of **1–4**, no thermal decomposition occurs until 194 °C, then a sharp mass loss appears at *ca.* 194–320 °C. All the complexes decompose in several stages (Fig. S3†), the first of them (in the *ca.* 90–250 °C range) being apparently connected to elimination of the coordinated or hydrated solvent molecules.

Catalytic activity of the complexes 5–8 in the Henry reaction

In this second part of the work, we have tested the catalytic activity of the Zn^{II} complexes **5–8** for the Henry reaction (Scheme 2). The optimization of the reaction conditions (temperature, reaction time, amount of catalyst, solvent) was carried out in a model nitroethane–benzaldehyde system with complex **6** as the catalyst precursor (Scheme 2, Table 1). The products were mixtures of β-nitroalkanol diastereoisomers (*threo* and *erythro* forms, with predominance of the former) according to ^1H NMR analysis (see Experimental), and high yields up to 99% (based on the aldehyde) were achieved at room temperature. Nitromethane is also a substrate, undergoing a high conversion into the nitroaldol (99% yield after 5 h reaction catalyzed by **6**; entry 34, Table 1).

Control reactions were carried out in the absence of catalyst **6** but in the presence of $ZnCl_2$, $Zn(NO_3)_2$ or free ligand **2** (entries 23–32, Table 1). No nitroaldol reaction between benzaldehyde and nitroethane takes place in the absence of the metal complex, even in the presence of zinc chloride or zinc nitrate (entries 32, 23, 24, respectively). The use of free ligand **2** (metal-free conditions) leads, after an extended reaction time of 48 h, to a yield of 60% of the β-nitroalkanol (entry 31), which, however, is substantially lower than those obtained in the presence of our Zn^{II} complexes, in a shorter time (*e.g.* 98% for **6**, 24 h—entry 6 and Fig. S4†). The systems exhibit (Table 1) diastereoselectivity towards the *threo* isomer, typically leading to *threo*/*erythro* molar ratios in the 80 : 20–70 : 30 range using nitroethane as substrate. This selectivity is usually higher than those reported for most of other systems (Table 2).[6,7] The stereochemical control of the two newly generated carbon centres is difficult, in particular due to the easy epimerization of the nitro-substituent on the carbon chain,[7u,v] but some *enantio*-differentiating catalysts can overcome this difficulty.[7w,x] Our catalysts have the advantages of being rather cheap and easy-to-prepare. In our systems, the stereoselectivity decreases significantly after *ca.* 24 h (entries 1–7, Table 1) whereas the yield does not increase appreciably after this time (entries 6 and 7, Table 1; Fig. S4†), which, thus, was chosen as the typical one for most of the experiments, namely those discussed below.

Table 1 Optimization of the parameters of the Henry nitroaldol reaction between benzaldehyde and nitroethane with **6** as the catalyst precursor[a]

Entry	Catalyst	Time (h)	Amount of catalyst (mol%)	T (°C)	Solvent	Yield (%)[b]	Selectivity *threo*/*erythro*[c]	TOF[d]
1	**6**	0.5	3.01	20	MeOH	32	78 : 22	22
2	**6**	1	3.01	20	MeOH	43	78 : 22	14
3	**6**	3	3.01	20	MeOH	48	78 : 22	5.4
4	**6**	5	3.01	20	MeOH	55	77 : 23	3.6
5	**6**	10	3.01	20	MeOH	68	76 : 24	2.3
6	**6**	24	3.01	20	MeOH	98	76 : 24	1.4
7	**6**	48	3.01	20	MeOH	98	70 : 30	0.7
8	**6**	24	0.03	20	MeOH	24	67 : 33	37
9	**6**	24	0.27	20	MeOH	35	72 : 28	5.3
10	**6**	24	0.82	20	MeOH	90	72 : 28	4.6
11	**6**	24	1.37	20	MeOH	94	73 : 27	2.9
12	**6**	24	5.48	20	MeOH	97	76 : 24	0.7
13[e]	**6**	24	3.01	20	—	82	71 : 29	1.1
14	**6**	24	3.01	20	THF	13	71 : 29	0.2
15	**6**	24	3.01	20	DMF	99	80 : 20	1.4
16	**6**	24	3.01	20	CH_3CN	82	74 : 26	1.1
17	**6**	24	3.01	20	MeOH+H_2O (1.5/0.1 v/v)	73	71 : 29	1.0
18	**6**	24	3.01	20	MeOH+H_2O (1.0/0.5 v/v)	71	71 : 29	1.0
19	**6**	5	3.01	20	MeOH	55	72 : 28	3.6
20	**6**	5	3.01	50	MeOH	74	72 : 28	4.9
21	**6**	5	3.01	80	MeOH	82	70 : 30	5.5
22	**6**	0.5	3.01	80	MeOH	55	58 : 42	37
23[f]	$ZnCl_2$	48	3.01	20	MeOH	—	—	—
24[f]	$Zn(NO_3)_2$	48	3.01	20	MeOH	—	—	—
25[f]	**2**	0.5	3.01	20	MeOH	11	77 : 23	7.0
26[f]	**2**	1	3.01	20	MeOH	16	76 : 24	5.2
27[f]	**2**	3	3.01	20	MeOH	18	77 : 23	1.9
28[f]	**2**	5	3.01	20	MeOH	29	77 : 23	1.9
29[f]	**2**	10	3.01	20	MeOH	35	76 : 24	1.2
30[f]	**2**	24	3.01	20	MeOH	57	76 : 24	0.8
31[f]	**2**	48	3.01	20	MeOH	60	77 : 23	0.4
33[f]	Blank	48	—	20	MeOH	—	—	—
34[g]	**6**	5	3.01	20	MeOH	99	—	6.6

[a] Reaction conditions: 0.03–5.48 mol% (0.27–54.8 μmol) of catalyst precursor (typically 3.01 mol%), methanol (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol). [b] Determined by ^1H NMR analysis (see Experimental). [c] Calculated by ^1H NMR. [d] TOF (h^{-1}) was estimated as moles of products (*threo*- and *erythro*-β-nitroalkanol)/mol of catalyst per hour. [e] Methanol (solvent)-free conditions, using nitroethane as solvent (2 mL). [f] For comparison purposes. [g] Nitromethane was used as substrate.

The rise of the catalyst amount greatly enhances the product yield from 24 to 97% for the respective amounts of 0.03 and 5.48 mol% of catalyst **6**, but with a decrease of the overall TOF from 37 to 0.7 (entries 8–12, Table 1). In general, **6** is highly effective even at low catalyst loadings, *e.g.* for 8.2 μmol *i.e.* 0.82 mol % *vs.* substrate loading, a TOF of 4.6 h^{-1} with an yield of 90% were reached (entry 10), what is an excellent result if compared with other zinc catalysts described in the literature, where 5–20 mol % loadings were commonly used to reach yields and selectivities comparable with ours (Table 2).[6c,7b,c]

Further, we examined the effect of solvents (entries 6 and 13–18, Table 1). THF falls below all the others, giving only 13% total yield which conceivably relates to the low solubility of **6** in this solvent. In all the other tested solvents, the yields are comparable and almost quantitative for MeOH and DMF (entries 6 and 15). If the nitroethane reagent was used as solvent (solvent-free conditions, entry 13) a lower but still considerable yield (82%) was achieved. The use of mixed methanol–water solvents disfavour the reaction (entries 17, 18), which relates with other data on nitroaldol reactions.[7d] The polar solvents DMF or MeOH facilitate the formation of *threo*-diastereomers (entries 6 and 15). On the other hand, increasing the temperature in the 20–80 °C range improves the yield of β-nitroalkanol from 55 to 82% for 5 h reaction time (entries 19–21).

The reactions of a variety of *para*- or *ortho*-substituted aromatic and aliphatic aldehydes with nitroethane (Table 3; **6** was used as the catalyst precursor) were also studied and shown to provide the respective β-nitroalkanols with yields ranging from 28 to 99% and with selectivities up to *ca.* 90% for either the *threo* or the *erythro* isomer. The nature of substrates greatly influences the yields and selectivities. Thus, for aryl aldehydes, those bearing electron-withdrawing groups exhibit higher reactivities compared

Table 2 Comparison of activities of catalysts towards the Henry reaction using aldehyde and nitroethane or nitromethane

Catalyst[a]	Solvent	Aldehyde	Yield (%)	Selectivity *threo*/*erythro*	Reference
6	MeOH	Benzaldehyde	98	76 : 24	This work
La/Na/amide[b]	THF	Benzaldehyde	48	72 : 28	[6h]
Nd/Na/amide[c]	THF	Benzaldehyde	85	92 : 8	[6h]
$[\{Rh(C_5Me_5)Cl\}_2(\mu\text{-}Cl)_2]$[d]	—	Benzaldehyde	24	60 : 40	[6i]
Copper(II) Schiff base[e]	CH_2Cl_2	Benzaldehyde	92	60 : 40	[7p]
Guanidine-ionic liquid[f]	—	Benzaldehyde	14	50 : 50	[7o]
Mg:Al hydrotalcite	THF	Benzaldehyde	62	40 : 60	[6n]
Zn Brucine[g]	THF	Benzaldehyde	80	55 : 45	[7o]
Zn-Fam Catalyst[h]	THF	Benzaldehyde	90	nd[n]	[7p]
Phenoxide substituted Cu complexes[i]	THF	Benzaldehyde	75	nd[n]	[7d]
Zn-ethylenediamine[j]	CH_3OH	Benzaldehyde	40	nd[n]	[7r]
Zn-guanidines[k]	CH_3CN	2-methylpropanal	90	nd[n]	[7s]
Dentrimer[l]	THF	*p*-$(NO_2)(C_6H_4CHO)$	94	46 : 54	[7t]
Triethylamine	THF	*p*-$(NO_2)(C_6H_4CHO)$	85	43 : 57	[7t]
DIPEA[m]	THF	*p*-$(NO_2)(C_6H_4CHO)$	95	44 : 56	[7t]

[a] Composition is given in Table S7, see Supporting information.† [b] Lanthanum ($La(O^iPr)_3$)/sodium source/amide ligand heterobimetallic catalyst. [c] Neodymium ($Nd(O^iPr)_3$)/sodium source/amide ligand heterobimetallic catalyst. [d] Rh complex in the presence of a silyl ketene acetal. [e] Chiral binuclear Cu(II) Schiff base complexes. [f] 1,1,3,3-tetramethyl guanidine (TMG)-based ionic liquid. [g] Brucine-derived aminoalcohol. [h] Ferrocenyl-substituted aziridinylmethanol (Fam) was used as a catalyst with Zn. [i] Phenoxide substituted Cu complexes. [j] Mono ethylenediamine Zn complex. [k] Zn(II) with chiral guanidine ligands. [l] Tertiary amines dendritically encapsulated within a flexible peptidic shell. [m] *N*,*N*-diisopropyl ethylamine. [n] nd: not determined, because nitromethane was used as substrate.

to those having electron-donating moieties (entries 6 and 7 *vs.* 2–5, Table 3), which relates with the increased electrophilicity of the substrate with the former substituents. In the case of 2,4,6-trimethylbenzaldehyde, no selectivity and a low yield are observed, probably due to steric hindrance, whereas 2-methylbenzaldehyde shows a high selectivity (75% for *threo* isomer) with a good yield (85%) (entry 5, Table 3).

The linear aliphatic aldehydes (entries 10–14, Table 3) lead to higher selectivities for the *erythro* diasteroisomer than the aromatic ones, and the highest yield (99%), within the aliphatic aldehydes, is observed for the shortest ones (entries 10, 11). Furthermore, the diastereoselectivity towards the *threo* isomer and the yield are markedly improved in PhCH=CHCHO relative to $PhCH_2CH_2CHO$ (entries 8 and 9), the conjugation of the aldehyde group with the aromatic phenyl ring in the former possibly playing a role.

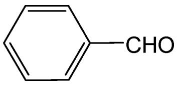
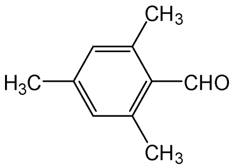
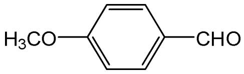
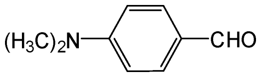
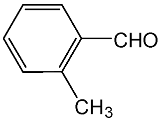
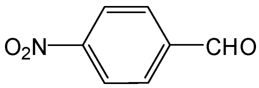
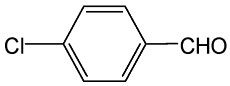
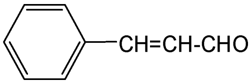
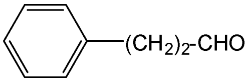
For comparison, all the synthesized Zn-OHADB complexes were tested as catalysts in the Henry addition of nitroethane and benzaldehyde (Table 4). All the catalysts preferentially produce the *threo* isomer, with variable degrees of diastereoselectivity, and high yields of the β-nitroalkanol mixture. The activities of the monomeric complexes **6** and **8** are similar (product yields up to 97%, Table 4, entries 2 and 4) and higher than those of the dinuclear ones **5** and **7** (entries 1 and 3, Table 4). The lowest activity of catalyst **7** may be accounted for by its lower solubility, since the related complex **5**, with a higher solubility, leads to an higher yield of β-nitroaldol. The higher *erythro*-selectivity of **7** in comparison with **5** is in accord with an earlier study where the selectivity could be promoted by steric hindrance within the bicyclic transition state using heterobimetallic complexes with a rare earth metal.[7e,f] Under solvent-free conditions, the decrease in the β-nitroalkanol yield compared to what achieved in methanol points out the possible role of the protic solvent to facilitate the proton transfer in the nitroaldol reaction (see below).

A noteworthy aspect of the Henry reaction is the possible involvement of metallic complexes with different nuclearities. For example, Cu-catalyzed reactions are known to proceed with involvement of monometallic forms of the active species,[7g–m] whereas Zn-catalyzed reactions can involve either mononuclear[6s] or di- or polynuclear[6c,e] complexes. However, considering the higher efficiency of the mononuclear zinc complexes, in our case the reaction is supposed to proceed with the participation of such a type of compound. This is corroborated by the ESI-MS$^+$ detection, in the reaction medium, of monomeric species formed upon dissociation of the Zn-OHADB dimers **5** and **7**. The data suggest that the same Zn-OHADB Lewis acid centre activates both nitroethane (increasing its acidity) and aldehyde (increasing its electrophilic character), as shown in the proposed Scheme 5. In fact, both intermediates with benzaldehyde (**a**) and benzaldehyde + nitroethane (**b** or derived **c** or **d**) were detected. The OHADB ligand can function as a Brønsted base, promoting the deprotonation of the acidic nitroethane with formation of the reactive nitronate species (**c**) (step 2) which adds to the ligated benzaldehyde *via* a nucleophilic intramolecular attack with formation of a C–C bond to give an intermediate with a β-nitroalkanol (**d**) (step 3).[7b,x] The deprotonation of nitroalkane and the C–C bond formation are crucial, and the Lewis acid and Brønsted base interactions of the zinc centre with the substrates allow a high efficiency of the overall process.[7b] Subsequently, another benzaldehyde coordinates, leading (step 4) to the formation of the intermediate (**e**) (which was also detected by ESI-MS$^+$). Release of the β-nitroalkanol (step 5) would complete the catalytic cycle. The linear plot of ln[benzaldehyde] *vs.* time (Table S6, Figure S5†) indicates a first-order dependence and thus supports the proposed mechanism. The reaction was also monitored by UV-vis spectroscopy (Figure S6 and S7†) but the results were not conclusive.

Conclusions

We have achieved simple and effective syntheses of mono- and dinuclear 5-coordinate zinc(II) complexes with OHADB ligands,

Table 3 Henry reaction of various aldehydes and nitroethane with catalyst **6**[a]

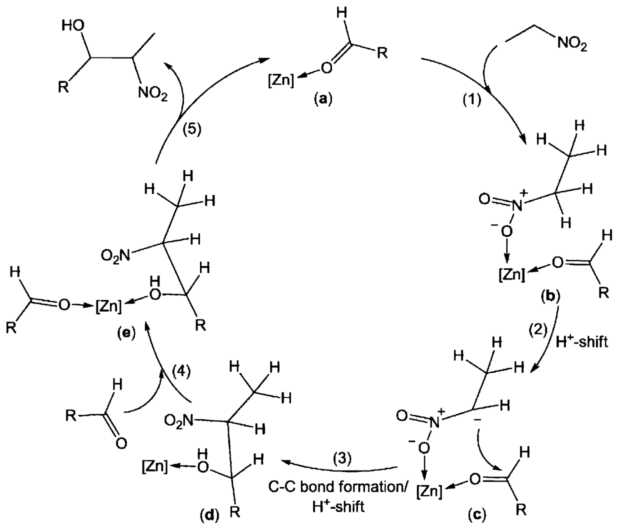
Entry	Substrate	Yield (%)[b]	Selectivity *threo*/*erythro*[c]
1		98	70 : 30
2		34	50 : 50
3		32	75 : 25
4		28	77 : 23
5		85	75 : 25
6		96	63 : 37
7		89	79 : 21
8		89	89 : 11
9		66	10 : 90
10	CH_3CH_2CHO	99	9 : 91
11	$CH_3(CH_2)_2CHO$	99	34 : 66
12	$CH_3(CH_2)_3CHO$	92	25 : 75
13	$CH_3(CH_2)_4CHO$	86	14 : 86
14	$CH_3(CH_2)_5CHO$	83	10 : 90

[a] Reaction conditions: 3.01 mol% of catalyst **6**, methanol (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol), reaction time: 24 h. [b] Determined by ^1H NMR analysis (see Experimental). [c] Calculated by ^1H NMR.

Table 4 Catalytic activity of various Zn(II)-OHADB complexes in the Henry reaction[a]

Entry	Catalyst	Solvent	Yield (%)[b]	Selectivity *threo*/*erythro*[c]	TOF[d]
1	**5**	MeOH	81	75 : 25	1.9
2	**6**	MeOH	98	70 : 30	1.4
3	**7**	MeOH	71	55 : 45	1.8
4	**8**	MeOH	99	75 : 25	1.6
5[e]	**5**	—	97	75 : 25	2.3
6[e]	**6**	—	82	71 : 29	1.1
7[e]	**7**	—	10	54 : 46	0.3
8[e]	**8**	—	83	67 : 33	1.3

[a] Reaction conditions: catalyst precursor: **5** (1.75 mol%), **6** (3.00 mol%), **7** (1.61 mol%), **8** (2.60 mol%), methanol (2 mL), nitroethane (4 mmol) and benzaldehyde (1 mmol), reaction time: 24 h. [b] Determined by ^1H NMR, based on the starting benzaldehyde. [c] Calculated by ^1H NMR (see Experimental). [d] TOF (h^{-1}) was estimated as moles of products (*threo*- and *erythro*-β-nitroalkanol)/mol of catalyst per hour. [e] Methanol (solvent)-free conditions, using nitroethane as solvent (2 mL).



Scheme 5 Proposed catalytic cycle for the Henry reaction catalyzed by the complexes **5–8**. [Zn] = Zn(L) (L = η^2 or η^3-L); **a**, **b** (or **c** or **d**) and **e** were detected by ESI-MS(+) [m/z = 437 (and 455 for the corresponding complex with ligated H_2O), 513 and 619, respectively, for the case of catalyst **6**].

which appear to be the first reported examples of Zn-OHADB complexes. Their structure and nuclearity are dependent on substituents in the β-diketone and aromatic parts of the OHADB ligands. The complexation process in solution is spontaneous, exothermic and entropically favourable, but in the solid state the formation of strong ligand hydrogen bonds leads to extensive 1D chains (**5** and **6**), 2D layers (**7**) or 3D networks (**8**).

The Zn-OHADB complexes are effective catalysts for the addition of nitroethane to various aldehydes producing the corresponding β-nitroalkanols in high yields and diastereoselectivities. The *threo*/*erythro* diastereoselectivity of the nitroaldol products can be controlled over a considerably wide range, depending on the catalyst, the substrates and experimental conditions. Comparison of the activities of the Zn-OHADB complexes with those of other catalysts indicates that the former have a promising potential towards the Henry diastereoselective transformation, being, to our knowledge, among the most active and diasteroselective ones so far reported for the nitroaldol reaction under mild conditions.

Experimental section

General comments

All the synthetic work was performed in air and at room temperature. All the chemicals were obtained from commercial sources and used as received. The infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000 MX instrument in KBr pellets. The ^1H and ^{13}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. Carbon, hydrogen, and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Electrospray mass spectra (ESI-MS) were run with 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 with a Perkin-Elmer Instrument system (STA6000) at a heating rate of 10 °C min^{-1} under a dinitrogen atmosphere.

The acidity of the solutions was measured using an I-130 potentiometer with an ESL-43-07 glass electrode and an EVL-1M3.1 silver–silver chloride electrode. To maintain the required pH, a commercial volumetric concentrate of HCl (pH 1–2) and an ammonium acetate buffer solution (pH 3–10) were used. In aqueous solutions of the salts, the concentrations of metal ions were determined by atomic absorption spectroscopy.[9a] The pH-metric titration of mixtures of reagent solutions with $ZnCl_2$ were carried out in aqueous-ethanol solution with consideration of the Bates correction[9b] at temperatures of 298 ± 0.5, 308 ± 0.5, and 318 ± 0.5 K. A constant temperature was maintained within ± 0.5 K by using an ultrathermostat (Neslab 2 RTE 220).

Preparation of Zn complexes and their characterization

To 50 mL of a methanol–water (9 : 1 v/v) solution of **1–4** (0.2 mmol), 0.4 mmol KOH were added and dissolved. After 5 min, 0.2 mmol $ZnCl_2$ were added. The mixture was stirred under solvent refluxing for 5 min and then left for slow solvent evaporation. The solid (greenish–grey **5**, dark red **6** and **8**, or orange **7**) was filtered off after 5 d, washed with a small amount of methanol and dried in air. Crystals suitable for X-ray diffraction analysis were obtained upon recrystallization from methanol (**5**), dimethylsulfoxide (**6**) and water–acetone (1 : 9 v/v) (**7** and **8**) (41, 47, 44 and 58% yields, respectively, based on Zn).

$[Zn_2(CH_3OH)_2(\mu\text{-}L^1)_2]$ **5**: Greenish–grey powder soluble in acetone, methanol, ethanol, acetonitrile, dimethylformamide and DMSO. Anal. Calcd for $C_{24}H_{28}N_4O_8Zn_2$ (M = 631.24): C, 45.66; H, 4.47; N, 8.87. Found: C, 45.15; H, 4.18; N, 8.80. IR, cm^{-1}: 1629 ν(C=O), 1595 ν(C=O), 1521 ν(C=N). MS (ESI): *m/z*: 632 $[M+H]^+$. ^1H NMR (300.13 MHz, DMSO-d_6), δ: 2.16 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.00–7.63 (4H, Ar–H). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6), δ: 27.96 (CH_3), 30.72 (CH_3), 113.89 (C_{Ar-H}), 114.73 (C_{Ar-H}), 115.61 (C_{Ar-H}), 119.28 (C_{Ar-H}), 127.07 (C=N), 132.99 ($C_{Ar-NZn-N}$), 140.97 (C_{Ar-OZn}), 187.70 and 197.13 (C=O).

$[Zn\{(CH_3)_2SO\}(H_2O)(L^2)]$ **6**: Red powder soluble in acetone, methanol, ethanol, acetonitrile, dimethylformamide and DMSO. Anal. Calcd for $C_{13}H_{17}N_3O_7SZn$ (M = 424.74): C, 36.76; H, 4.03; N, 9.89. Found: C, 36.45; H, 3.98; N, 9.74. IR, cm^{-1}: 1655 ν(C=O), 1628 ν(C=O), 1600 ν(C=N). MS (ESI): *m/z*: 426.0 $[M+H]^+$. ^1H NMR (300.13 MHz, CD_3OD), δ: 2.21 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 7.21–7.72 (3H, Ar–H). $^{13}C\{^1H\}$ NMR (75.468 MHz, CD_3OD), δ: 25.23 (CH_3), 30.85 (CH_3), 38.11 ($2CH_3$), 109.91 (C_{Ar-H}), 114.22 (C_{Ar-H}), 115.71 (C_{Ar-H}), 134.28 (C=N), 135.12 (C_{Ar-NO_2}), 139.01 ($C_{Ar-NZn-N}$), 144.01 (C_{Ar-OZn}), 189.10 and 197.33 (C=O).

$[Zn_2(H_2O)_2(\mu\text{-}L^3)_2]$ **7**: Orange powder soluble in acetone, methanol, ethanol, acetonitrile, dimethylformamide and DMSO. Anal. Calcd for $C_{28}H_{32}N_4O_8Zn_2$ (M = 683.4): C, 49.21; H, 4.72; N, 8.20. Found: C, 49.09; H, 4.73; N, 8.10. IR, cm^{-1}: 1592 ν(C=O), 1567 ν(C=O), 1503 ν(C=N). MS (ESI): *m/z*: 684 $[M+H]^+$. ^1H NMR (300.13 MHz, DMSO-d_6), δ: 1.04 (s, 6H, CH_3), 2.36 (s, 2H, CH_2), 2.49 (s, 2H, CH_2), 6.46–7.51 (4H, Ar–H). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6), δ: 20.10 (CH_3), 30.70(CH_3), 51.28 (CH_2), 51.81 (CH_2), 38.9 (C_{ipso}), 114.50 and 119.74 (C_{Ar-H}), 129.89 ($C_{Ar-NZn-N}$), 130.43 (C=N), 140.11 (C_{Ar-OZn}), 185.31 and 192.89 (C=O).

$[Zn(H_2O)_2(L^4)]\cdot H_2O$ **8**: Red powder soluble in acetone, methanol, ethanol, acetonitrile, dimethylformamide and DMSO. Anal. Calcd for $C_{14}H_{19}N_3O_8Zn$ (M = 422.7): C, 39.78; H, 4.53; N, 9.94. Found: C, 39.45; H, 4.47; N, 9.87. IR, cm^{-1}: 1655 ν(C=O), 1637 ν(C=O), 1604 ν(C=N). MS (ESI): *m/z*: 406 $[M-H_2O + H]^+$. ^1H NMR (300.13 MHz, DMSO-d_6), δ: 1.03 (s, 6H, CH_3), 2.40 (s, 2H, CH_2), 2.49 (s, 2H, CH_2), 7.25–7.60 (3H, Ar–H). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6), δ: 28.16 (CH_3), 30.69 (CH_3), 51.60 (CH_2), 51.92 (CH_2), 38.77 (C_{ipso}), 108.32, 112,92 and 114.30 (C_{Ar-H}), 131.82 (C=N), 146.24 (C_{Ar-NO_2}), 147.63 ($C_{Ar-NZn-N}$), 162.57 (C_{Ar-OZn}), 187.73 and 193.37 (C=O).

X-ray structure determinations

The X-ray quality single crystals of complexes **5–8** were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 150 K or 298 K (**6**), (Table 5). Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[10a] on all the observed reflections. Absorption corrections were applied using SADABS.[10a] Structures were solved by direct methods by using the SHELXS-97 package[10b] and refined with SHELXL-97.[10c] Calculations were performed using the WinGX System-Version 1.80.03.[10d] All hydrogens were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. There was some disorder in the structure of **7** with carbon atoms C13, C14, C17 and C18 having inadequate thermal parameters. The occupancies of the disordered carbon atoms (in Fig. 1 notations A and B represent the disordered positions of those atoms) were determined by using the "free variable" (FVAR) option in SHELXL software,[10c] which means that occupancy was allowed to vary during the refinement. A value of 0.41 as an average for FVAR was obtained and the *R*-value improved in 10%. CCDC 797547–797550 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 5 Crystal data and structure refinement details for **5–8**

	5	**6**	**7**	**8**
Formula unit	$C_{24}H_{28}Zn_2N_4O_8$	$C_{13}H_{17}ZnN_3O_7S$	$C_{28}H_{32}Zn_2N_4O_8$	$C_{14}H_{19}ZnN_3O_8$
Formula weight (g mol^{-1})	631.24	424.73	683.32	422.69
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P 21/c
a (Å)	8.0218(4)	8.782(6)	6.8688(3)	6.5844(11)
b (Å)	8.8006(3)	10.621(9)	9.8233(5)	15.743(3)
c (Å)	10.3280(5)	10.703(9)	11.9184(6)	16.287(3)
α (°)	93.178(2)	115.83(2)	106.825(2)	90.00
β (°)	103.423(3)	106.16(2)	105.369(3)	96.006(10)
γ (°)	111.763(2)	90.23(3)	95.625(2)	90.00
Z	1	2	1	4
Volume (Å^3)	650.53(5)	854.0(12)	728.81(6)	1679.0(5)
D_c (g cm^{-3})	1.611	1.652	1.557	1.672
μ (Mo-Kα) (mm^{-1})	1.899	1.602	1.701	1.513
Reflections collected	6173	4652	4919	8485
Unique reflections	2320	2859	2601	2936
R_{int}	0.0415	0.0813	0.0283	0.1851
Final $R_1{}^a$, w$R_2{}^b$ ($I \geq 2\sigma$)	0.0337, 0.0734	0.0603, 0.0797	0.0359, 0.0819	0.1032, 0.2737
GOF on F^2	0.969	0.839	1.049	1.086

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $wR_2 = [\Sigma [w(F_o{}^2 - F_c{}^2)^2] / \Sigma [w(F_o{}^2)^2]]^{1/2}$

Catalytic activity studies

A typical reaction was carried out under air as follows: to 0.03–5.48 mol% (0.27–54.8 μmol) of catalyst precursor (typically 3.01 mol%) contained in the reaction flask were added methanol (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol), in that order. The reaction mixture was stirred for the required time at room temperature and air atmospheric pressure. After evaporation of the solvent, the residue was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR. The yield of β-nitroalkanol product (relatively to the aldehyde) was established typically by taking into consideration the relative amounts of these compounds, as given by ^{1}H NMR and previously reported.[7] The adequacy of this procedure was verified by repeating a number of the ^{1}H NMR analyses in the presence of 1,2-dimethoxyethane as internal standard, added to the DMSO-d_6 solution, which gave yields similar to those obtained by the above method. Moreover, the internal standard method also confirmed that no side products were formed. The ratio between the *threo* and *erythro* isomers was also determined by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra, the values of vicinal coupling constants (for the β-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 *threo* or *erythro* isomers, respectively.[6l,7a] For monitoring the reaction along the time, samples were withdrawn at specific time intervals and analysed by ^{1}H NMR, UV-vis and ESI-MS. The UV-vis spectra during the reaction were run in the 200–700 nm range. The ESI-MS equipped with an ionspray source in positive ion mode detected species in the m/z range of 100 to 1000. Control experiments were performed under the same reaction conditions but in the absence of any of the Zn-OHADB catalysts, in the presence of $ZnCl_2$, $Zn(NO_3)_2$ or free ligand **2** (metal free).

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