Accepted Manuscript

Synthesis, crystal structure and catalytic properties in the diastereoselective nitroaldol (Henry) reaction of new zinc(II) and cadmium(II) compounds

Raja Jlassi, Ahmed Khalladi, Houcine Naïli, Tobias Rüffer, Heinrich Lang, Walid Rekik

PII:	\$0277-5387(18)30709-5
DOI:	https://doi.org/10.1016/j.poly.2018.10.064
Reference:	POLY 13538
To appear in:	Polyhedron
Received Date:	5 September 2018
Accepted Date:	18 October 2018



Please cite this article as: R. Jlassi, A. Khalladi, H. Naïli, T. Rüffer, H. Lang, W. Rekik, Synthesis, crystal structure and catalytic properties in the diastereoselective nitroaldol (Henry) reaction of new zinc(II) and cadmium(II) compounds, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.10.064

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis, crystal structure and catalytic properties in the diastereoselective nitroaldol (Henry) reaction of new zinc(II) and cadmium(II) compounds

Raja Jlassi^a, Ahmed Khalladi^{a,b}, Houcine Naïli^a, Tobias Rüffer^b, Heinrich Lang^b and Walid Rekik^{a,*}

^a Laboratoire de physico-chimie de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, Université de Sfax, BP 1171, 3000 Sfax, Tunisie
 ^b Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Anorganische Chemie,

D-09107 Chemnitz, Germany

Abstract

The new complex $[Zn(im)_4](NO_3)_2$ (1) was synthesized and crystallographically characterized. In the solid state, 1 is built up by $[Zn(C_3H_4N_2)]^{2+}$ cations and NO_3^- anions interlinked by N-H···O hydrogen bonds which give rise to the formation of a 3D network.

Complex **1** and $[CdNa_2(\mu-L^2)]_n \cdot 6.34H_2O$ (**2**), (L = 2-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)terephthalate) were used as catalysts for the Henry reaction, and high yields were obtained under optimum conditions. Both **1** and **2** act as very efficient catalysts for the Henry reaction and convert nitroethane and aldehydes to β -nitroalcohols in yields of up to 89%. The threo/erythro diastereoselectivity depends on the choice of catalyst and also the selection of the reaction substrate, reaching values up to 89:11.

Keywords: Supramolecular chemistry; Crystal structure; Henry reaction; Diastereoselectivity

* Corresponding author: E-mail address: walid.rekik@fss.usf.tn

Walid REKIK, Tel. : +21697341185, Sfax Faculty of Sciences, Chemistry Department, Soukra Road km 3,5 - B.P. 1171, 3018 Sfax – Tunisia

1-Introduction

Imidazole ($C_3H_4N_2$) is an organic compound. It is considered as an alkaloid. Imidazole and its derivatives are heterocycles which can participate in the formation of complex ions. They form a ring structure with various substituents. This ring system is commonly found in several natural molecules, such as the amino acid histidine, coffee, purines or vitamin B12. In biology, imidazole is a pharmacophore with low toxicity. [1] Thus, the imidazole motif is present in important biological building blocks. Indeed, it is included in the formulation of many drugs, mainly anti-inflammatory, antifungal, antihypertensive and even anti-cancer drugs. [2-4] On the other hand, the Henry or nitroadol reaction is a main synthetic tool for the formation of a C-C bond. This reaction is composed of the combination of nitroalkane and aldehyde compounds, resulting in β -nitroalcohols. The Henry reaction is usually performed with homogeneous catalysis and can be catalyzed by either organic or inorganic bases, as well as metal complexes. [5–7] Hence, aldehydes or α -keto esters can be shifted to the corresponding nitroalcohols with apparently excellent enantio- and diastereoselectivity. [8–10] Yet, a high number of these catalysts are not selective and/or lead to lower yields. Threo/erythro stereocontrol in the Henry reaction is still considered as a challenging aspect.

Therefore, the procedure of the current work is as follows: (i) to synthesize the $[Zn(im)_4](NO_3)_2$ (1) complex; (ii) to determine its crystal structure; (iii) to observe the catalytic activity of 1 and $[CdNa_2(\mu-L^2)]_n.6.34H_2O$ (2) and to study their diastereoselectivity in the Henry reaction of nitroethane with several aldehydes.

2-Experimental

Preparation of $[Zn(im)_4](NO_3)_2(1)$

The compound $[Zn(im)_4](NO_3)_2$ was synthesized through the reaction of 2 mmol of imidazole, 2 mmol of $Zn(NO_3)_2$ ·H₂O and 50 ml of methanol. The solution was stirred for 10 min until there was complete dissolution of the reactants and then it was allowed to stand at room temperature. After a few days, green

prismatic crystals suitable for X-ray diffraction were obtained. IR data (cm⁻¹): N–H 1463, 1634; C–H 3014; S–O 1094, 1195; O–H 3356.

Preparation of $[CdNa_2(\mu-L^2)]_n.6.34H_2O$ (2)

The synthesis method of the complex $[CdNa_2(\mu-L^2)]_n.6.34H_2O$ has already been described in a previous report.[11]

Single-crystal data collection and structure determination

A suitable crystal of $[Zn(im)_4](NO_3)_2$ (1) was measured at 110 K with an Oxford Gemini S diffractometer. For data collection, cell refinement and data reduction, the software CrysAlisPro was used.[12a] The structure was solved by direct methods using SHELXS-2013 and refined by full-matrix least-squares procedures on F^2 using SHELXL-2013.[12b] All non-hydrogen atoms were refined anisotropically and all isotropically refined hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms. Selected crystallographic and structural refinement data of 1 are summarized in Table 1, while selected bond distances and angles, as well as data for the hydrogen bonds, are listed in Tables 2 and 3, respectively. The drawings were made with the Diamond program. [13]

General procedure for the catalytic activity studies

The combination of the solvent along with the catalyst in a phial resulted in an agitated solution. 1 mmol of aldehyde and 4 mmol nitroethane were mixed and stirred at room temperature for a convenient amount of time, then the solvent was evacuated. The dissolution of the deposit in DMSO-d₆ was analyzed by ¹H NMR spectroscopy. [14-16] The competence of the procedure was approved by running a blank ¹H NMR spectrum with 1,2-dimethoxyethane as an internal reference.

3. Results and discussion

Crystal structure of 1

In a previous work, we have reported that the polymeric structure of $[CdNa_2(\mu-L^2)]_n.6.34H_2O$ consists of infinite (1D) chains interlinked by H-bonds.[11] Contrary to **2**, the structural study of **1** shows

that it is built from $[Zn(im)_4)]^{2+}$ cations and (NO_3^-) anions, which are linked together through H-bonds to give a 3D network.

 $[Zn(im)_4](NO_3)_2$ crystallizes with monoclinic symmetry, in the centrosymmetric space group P2₁/c. The asymmetric unit of **1** contains one $[Zn(C_3H_4N_2)]^{2+}$ cation and two nitrate NO₃⁻ anions. The zinc(II) cation occupies a general position and it is coordinated by four nitrogen atoms belonging to four imidazole (im) groups (Fig. 1).

To determine the geometry around the zinc(II) ion of **1** the τ_4 parameter, introduced by Yang, Powel and Houser, is helpful.[17] This uses an empirical method based on bond angles to give a percentage of distortion to the ideal extremes, which are tetrahedral and square planar geometries. The calculated τ_4 parameter for **1** is 0.94, which demonstrates that the $[Zn(C_3H_4N_2)]^{2+}$ cation exhibits a tetrahedral geometry (T_d). The ZnN₄ tetrahedra are slightly distorted. Indeed, the Zn–N bond lengths are between 1.991(2) and 2.004(2) Å and the N–Zn–N angles vary from 103.93(9) to 114.74(8) ° (Table 2).

Within the imidazole group (im), which plays the role of a ligand, the C–C bonds are 1.348(4) and 1.353(4) Å in length, while the C–N distances are in the range 1.321(3)-1.384(3) Å. The C–C–N bond angles fall in the range $106.2(2)-109.4(2)^{\circ}$, while the C–N–C angles range from 105.6(2) to $108.0(2)^{\circ}$. These values for the different distances and angles are comparable to those observed in other compounds containing the same ligand. [18]

The nitrate anions compensate the positive charge of the organometallic cations to ensure the electrical neutrality of the molecule. Within the uncoordinated nitrate anions, the O-N-O angles vary from 119.6(2) to 120.7(2) ° and the N–O distances are between 1.246(3) and 1.259(3) Å (Table 2). These value ranges are in agreement with many studied structures involving free nitrate groups. [19–23] The NO₃⁻ anions are placed in the structure between the [Zn(im)₄]²⁺ cations in a manner such that they alternate along the [101] direction and form mixed layers parallel to the (bc) plane (Fig. 2).

The anions and cations are linked together by N-H···O hydrogen bonds. Indeed, each nitrate anion establishes two N-H···O hydrogen bonds with two complex cations to generate the three dimensional structure, cf. Fig. 3 and Table 3.

UV-vis spectra of the compounds

The UV-visible absorption spectra, shown in Fig. 4, of both compounds $[Zn(im)_4](NO_3)_2$ (1) and $[CdNa_2(\mu-L^2)]_n$ 6.34H₂O (2) in aqueous solution were recorded at room temperature away from direct measurements of absorbance using a UV-1650 spectrophotometer PL.

The absorption spectra of various mononuclear d^{10} group 12 complexes display bands assigned to metal centered, metal to ligand charge transfer (MLCT), charge transfer to solvent (CTTS), ligand to metal charge transfer (LMCT), intraligand (IL) and ligand to ligand charge transfer (LLCT) transitions, depending on the natures of the metal and the ligands. [24-29] In contrast to complexes with d^n (0 < n < 10) configurations, d^{10} and s^2 complexes cannot display ligand field (d-d) bands; instead the metal-centered bands are limited to interconfigurational nd \rightarrow (n+l)s or nd \rightarrow (n+l)p electronic transitions.

The electronic spectra recorded for both compounds show transitions at 206, 209 and 291 nm for **1** and 268 nm for **2**, which can be assigned to the $\pi \rightarrow \pi$ * transition of the C=N group and the aromatic ring of the ligand. The peaks appearing at 351 and (415/473 nm) for complexes **1** and **2**, respectively, represent ligand-to-metal charge-transfer (LMCT) transitions corresponding to N-Zn for compound **1** and N-Cd for **2**; the peaks can also be associated with an $n \rightarrow \pi$ * transition or electron transitions of the hydrazo to the enol-azo form for compound **2**. [30–33]

Complexes 1 and 2 show only charge transfer transitions, which can be assigned to a charge transfer from the ligand to the metal and vice versa, since no d-d transition are expected for d^{10} Zn(II), Cd(II) complexes. [34]

Catalytic activity of 1 and 2 in the Henry reaction

The catalytic behavior of the synthesized catalysts **1** and **2** has been tested in the Henry reaction (Scheme 1). The reaction proceeded at room temperature using different solvents, such as protic methanol, water and aprotic MeCN.

Initially, the nitroaldol (Henry) reaction was carried out in MeCN for 24 h, giving yields of 25.2 and 22.9 % for catalysts **1** and **2**, respectively. The use of MeOH shows a better performance and leads to different yields (79 % for catalyst **1** and 47.5 % for catalyst **2**) and enhances the selectivity compared to that obtained with MeCN (Table 4, entries 1-4). Probably, this difference is due to the protic character of MeOH. The latter will provide a H⁺ proton which is necessary for the mechanism of the reaction to give the nitroaldol product. In addition, the degree of solubility of the reactants and products in methanol improved the yield. The course of the reaction in water was one of the desired advantaged to be examined; a higher yield (43.3 and 35.9 %, for **1** and **2**, Table 4, entries 5 and 6) in comparison with MeCN and a lower yield than the reaction in MeOH were observed. The effectiveness of the solvent can be consequently classified in this order: MeOH > H₂O > MeCN.

It is also concluded from entries 1, 3 and 5 of Table 4 that the precursor $[Zn(im)_4](NO_3)_2$ (1) is the best catalyst (having the best yields with the three solvents). A blank reaction was tested as well, as using simple pre-salts, in both cases no product was recognized (Table 4, entries 7-9), which provides further evidence that the reaction requires the presence of a catalyst to occur.

After identifying the best solvent (methanol) and the best catalyst (precursor 1), further steps were taken for optimization and to study the influence of other parameters, such as the quantity of catalyst used. Indeed, entries 10, 11 and 12 (Table 4) show that increasing the amount of the catalyst improves the yield, but does not have a great influence on the diastereoselectivity. It was found that the ideal amount of catalyst for the reaction is 3 mol%.

Also, the effect of temperature was investigated (Table 4, entries 17-18). The yield increased from 71.8 % (at room temperature) up to 94.9 % at 35 °C, without a significant increase upon further heating. As a result, we obtained an optimum yield of 95.1% by heating to 45 °C. It turns out that one can save time by

increasing the temperature to give a better yield. However, the stereoselectivity is maintained without any recorded influence.

In addition, a reduction in the reaction time led to a remarkable decrease in yield (Table 4, entries 15 and 1.6) Carrying out the reaction for different times indicated that the best yields correspond to 15h (71.8%) and 48h (90.7%) durations. It is concluded that the time taken for the reaction has a significant effect on its yield.

It is also believed that, beside the different parameters for the reaction optimization, the reaction substrates have a significant effect. The use of substrates other than benzaldehyde (Table 5) concluded that aromatic aldehydes with electron withdrawing substituents are more reactive to the Henry reaction than those with electron donating substituents; a similar result was reported for the same reaction catalyzed by zinc(II). [35-42] The position of the substituent on the aromatic ring has a definite influence on the activity of a catalyst, probably due to steric hindrance.

Remarkably, good results have been obtained using catalyst 1 with substrates such as aliphatic aldehydes, acetaldehyde (CH_3CHO) as well as propionaldehyde (CH_3CH_2CHO), with high yields and diastereoselectivity values.

Regarding the values of the selectivity, from the results that have been registered for all the tests carried out, it is noted that the reaction selectively promotes the formation of the threo product rather than the erythro product.

4. Conclusions

Two new hybrid materials, $[Zn(im)_4](NO_3)_2$ (1) and $[CdNa_2(\mu-L^2)]_n \cdot 6.34H_2O$ (2), have been prepared and fully characterized. The single-crystal XRD shows that complex 1 is centrosymmetric and adopts a 0D structure built of $[Zn(C_3H_4N_2)]^{2+}$ cations and $(NO_3)^-$ anions which are linked together via N–H···O hydrogen bonds. While, in previous work we have successfully used

(2-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)terephthalate) (L) as a chelating ligand, bearing

 β -diketone fragments as well as carboxyl groups, to obtain a 1D metal-organic Cd^{II} complex polymer.

Furthermore, the present study discloses the catalytic application of 1 and 2 in the heteregeneous oxidation of the Henry reaction, showing that both catalysts act as active precursors. Both complexes 1 and 2 are effective catalysts for the addition of nitroethane to various aldehydes, producing the corresponding β -nitroalcohols with high yields and diastereoselectivities.

Appendix A. Supplementary data

CCDC 1585201 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

REFERENCES

[1] OECD (2003). Screening Information Dataset Imidazole. CAS No. 288-32-4. UNEP Publications.

[2] L. Shargel, A.H. Mutnick, P.F. Souney, L.N. Swanson, (2006).

Dans Comprehensive Pharmacy Review, 6eme ed. Philadelphia: Lippincott Williams & Wilkins.

[3] T. Castaño, A. Encinas, C. Pérez, A. Castro, N.E. Campillo, C. Gil, Bioorg. Med. Chem. 16 (2008) 6193.

[4] R.G. Bogle, G.S. Whitley, S.C. Soo, A.P. Johnstone, P. Vallance, Br. J. Pharmacol. 111 (1994) 1257.

[5] A. Dhakshinamoorthy, M. Opanasenko, J. Čejka, H. Garcia, Adv. Synth. Catal. 355 (2013) 247.

- [6] A.G. Doyle, E.N. Jacobsen, Chem. Rev. 107 (2007) 5713.
- [7] F.A. Luzzio, Tetrahedron. 57 (2001) 915.
- [8] C. Palomo, M. Oiarbide, A. Laso, Eur. J. Org. Chem. (2007) 2561.
- [9] J. Boruwa, N. Gogoi, P.P. Saikia, N.C. Barua, Tetrahedron: Asymm. 24 (2006) 3315.

- [10] C. Palomo, M. Oiarbide, A. Mielgo, Angew. Chem. Int. Ed. 43 (2004) 5442.
- [11] R. Jlassi, A.P.C. Ribeiro, G.A.O. Tiago, J. Wang, M.S. Krawczyk, L.M.D.R.S. Martins, H. Naïli,
- A.J.L. Pombeiro, W. Rekik, Inorg. Chim. Acta. 471 (2018) 76.
- [12] a) CrysAlisPro, Agilent Technologies, Version 1.171.37.31 (release 14-01-2014 CrysAlis171.NET)

(compiled Jan 14 2014,18:38:05), Agilent Technologies; b) G.M. Sheldrick, Acta Cryst. A64 (2008)112.

- [13] K. Brandenburg, Diamond version 2.0 Impact GbR, Bonn Germany (1998).
- [14] H. Naïli, F. Hajlaoui, T. Mhiri, T.C.O. Mac Leod, M.N. Kopylovich, K.T. Mahmudov, A.J.L.Pombeiro, Dalton Trans. 42 (2013) 399.
- [15] M.N. Kopylovich, T.C.O. Mac Leod, K.T. Mahmudov, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Dalton Trans. 40 (2011) 5352.
- [16] M.N. Kopylovich, A. Mizar, M.F.C. Guedes da Silva, T.C.O. Mac Leod, K.T. Mahmudov, A.J.L. Pombeiro, Chem. Eur. J. 19 (2013) 588.
- [17] L. Yang, D.R. Powell, R.P. Houser, Dalton Trans. (2007) 955.
- [18] A. Derbel, T. Mhiri, M. Graia, Acta. Cryst. E71 (2005) 1185.
- [19] I. Turel, N. Bukovec, M. Goodgame, D.J. Williams, Polyhedron. 16 (1997) 1701.
- [20] D. Wu, Y. Zhao, H. Ye, G. Wu, Acta Crystallogr. E66 (2010) 1568.
- [21] G.-Q. Guo, J.-H. Deng, J. Chen, Acta Crystallogr. E66 (2010) 1415.
- [22] T. Rosu, E. Pahontu, M. Reka-Stefana, D.-C. Ilies, R. Georgescu, S. Shova, A. Gulea, Polyhedron.31 (2012) 352.
- [23] S. Ilhan, H. Temel, J. Mol. Struct. 891 (2008) 157.
- [24] A.B.P, Lever. Inorganic Electronic Spectroscopy; Elsevier: Amsterdam. (1984).
- [25] C. Kutal. Coord. Chem. Reu. 99 (1990) 213.
- [26] C.K. Jorgenson. Oxidation Numbers and Oxidation States; Springer: New York. (1969) 128.
- [27] K.L. Stevenson, J.L. Braun, D.D. Davis, K.S. Kurtz, R.I. Sparks, Inorg. Chem. 27 (1988) 3472.

[28] (a) M.E. Koutek, W.R. Mason, Inorg. Chem. 19 (1980) 648. (b) M.M. Savas, W.R. Mason, Inorg. Chem. 26 (1987) 301.

- [29] D.J. Jr. Casadonte, D.R. McMillin, J. Am. Chem. Soc. 109 (1987) 331.
- [30] C. Reichardt, Chem. Rev. 94 (1994) 2319.
- [31] A. Airine, E. Rusu, D. Dorohoi, Spectrosc. Lett. 34 (2001) 65.
- [32] A.S. Klymchenko, A.P. Demchenko, Chem. Phys. Lett. 418 (2006) 223.
- [33] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. (1983) 48.
- [**34**] R.M. Silverstein, Spectrophotometric identification of organic compounds, 4th edn. John Wiley, New York. (1981).
- [**35**] O. Kammoun, W. Rekik, T. Mhiri, T. Bataille, K.T. Mahmudov, M.N. Kopylovich, H. Naïli, J. Organomet. Chem. 136 (2013) 741.
- [36] K.T. Mahmudov, M.N. Kopylovich, M. Haukka, G.S. Mahmudova, E.F. Esmaeila, F.M. Chyragov, A.J.L. Pombeiro, J. Mol. Struct. 108 (2013) 1048.
- [37] N.Q. Shixaliyev, A.M. Maharramov, A.V. Gurbanov, V.G. Nenajdenko, V.M. Muzalevskiy, K.T.
- Mahmudov, M.N. Kopylovich, Catal. Today. 76 (2013) 217.
- [38] A.G. Doyle, E.N. Jacobsen, Chem. Rev. 107 (2007) 5713.
- [39] F.A. Luzzio, Tetrahedron. 57 (2001) 915.
- [40] F. López, A.J. Minnaard, B.L. Feringa, Acc. Chem. Res. 40 (2007) 179.
- [41] A.H. Hoveyda, A.W. Hird, M.A. Kacprzynski, Chem. Commun. (2004) 1779.
- [42] A. Dhakshinamoorthy, M. Opanasenko, J. Cejka, H. Garcia, Adv. Synth. Catal. 355 (2013) 247.

Figure captions

Figure 1: Asymmetric unit of 1.

Figure 2: View down the b axis of the crystal structure of compound 1

Figure 3: Ball-and-stick model of a selected part of the 3D network formed by 1 in the solid state due to

intermolecular hydrogen bonds, indicated by green coloured dashed bonds.

Figure 4: Absorption spectra of compounds 1 and 2

Scheme 1. Formation of nitroaldols by the Henry reaction.

Table 1. Crystallographic data for 1.

	•		
	Empirical formula	$[Zn(im)_4](NO_3)_2$	
	Formula weight (g/mol)	461.72	
	Temperature (K)	100 K	
	Crystal system	Monoclinic	
	Space group	$P2_{1/C}$	
	$a(\mathbf{A})$	17,1186(7)	
	$h(\Lambda)$	6.0185(3)	
	$b(\mathbf{A})$	16 7568(0)	
	$\mathcal{C}(\mathbf{A})$	100.211(5)	
	p()	109.211(3)	
	$V(A^3)$	18/4.08(16)	
	Z	4	
	Calculated density (g cm ⁻³)	1.636	
	λ (MoK α) (Å)	0.71073	
	Measured reflections	7834	
	Independent reflections	3291	
	Reflections $[I > 2\sigma(I)]$	2832	
	θ range for data collection (°)	2.951-24.995	
	F (000)	944	
	Number of parameters	262	
	$R_1 [I > 2\sigma(I)]$	3 52%	
	$wR_{2}\left[L > 2\sigma\left(L\right)\right]$	6.98%	
	GOOF	1 090	
-	3001	1.090	

distanc	es (Å)	angles (°)
	Tetrahe	edral ZnN4	
Zn(1)-N(1)	1.999(2)	N(1)-Zn(1)-N(2)	103.93(9)
Zn(1)-N(2)	2.004(2)	N(3)-Zn(1)-N(2)	105.58(8)
Zn(1)-N(3)	1.983(2)	N(3)-Zn(1)-N(4)	114.61(9)
Zn(1)-N(4)	1.991(2)	N(4)-Zn(1)-N(1)	106.11(8)
		N(3)-Zn(1)-N(1)	114.74(8)
		N(4)-Zn(1)-N(2)	111.43(8)
	Liga	$nd HL^1$	
N(1)-C(1)	1.324(3)	C(1)-N(1)-C(3)	105.6(2)
N(1)-C(3)	1.384(3)	C(2)-C(3)-N(1)	109.4(2)
N(7)-C(1)	1.336(3)	C(1)-N(7)-C(2)	108.0(2)
N(7)-C(2)	1.369(3)	C(3)-C(2)-N(7)	106.2(2)
N(2)-C(4)	1.321(3)	N(2)-C(4)-N(8)	111.1(2)
N(2)-C(6)	1.380(3)	C(4)-N(2)-C(6)	105.6(2)
N(8)-C(4)	1.333(3)	C(6)-C(5)-N(8)	106.9(2)
N(8)-C(5)	1.355(3)	C(4)-N(8)-C(5)	107.7(2)
N(3)-C(7)	1.325(3)	C(7)-N(3)-C(9)	105.7(2)
N(3)-C(9)	1.378(3)	C(8)-C(9)-N(3)	109.2(2)
N(9)-C(7)	1.336(3)	C(7)-N(9)-C(8)	108.0(2)
N(9)-C(8)	1.360(3)	C(9)-C(8)-N(9)	106.4(2)
N(4)-C(10)	1.326(3)	C(10)-N(4)-C(12)	106.0(2)
N(4)-C(12)	1.377(3)	C(11)-C(12)-N(4)	108.7(2)
N(10)-C(10)	1.326(3)	C(10)-N(10)-C(11)	108.1(2)
N(10)-C(11)	1.363(3)	N(4)-C(10)-N(10)	110.7(2)
D(1)-N(5)	1.246(3)	O(1)-N(5)-O(2)	120.0(2)
D(2)-N(5)	1.259(3)	O(2)-N(5)-O(3)	120.0(2)
D(3)-N(5)	1.259(3)	O(1)-N(5)-O(3)	120.1(2)
D(4)-N(6)	1.251(3)	O(4)-N(6)-O(5)	120.7(2)
D(5)-N(6)	1.252(3)	O(5)-N(6)-O(6)	119.75(19)
D(6)-N(6)	1.257(3)	O(4)-N(6)-O(6)	119.6(2)
C(2)-C(3)	1.348(4)		
C(5)-C(6)	1.351(4)		
C(8)-C(9)	1.351(4)		
C(11)-C(12)	1.353(4)		
D(6)-N(6) C(2)-C(3) C(5)-C(6) C(8)-C(9) C(11)-C(12)	1.252(3) $1.257(3)$ $1.348(4)$ $1.351(4)$ $1.351(4)$ $1.353(4)$	O(4)-N(6)-O(6)	119.6(2

Table 2. Selected bond distances (Å) and angles (°) for 1.

N9-H9A $O3^i$ 0.860 2.0676(1) 2.0138(1) 167.796(4) N8-H8A $O2^n$ 0.860 2.0481(1) 2.8416(1) 153.062(4) N7-H7A $O4$ 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10A $O6^{iti}$ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: $i = 1$ - x , $-y$, 1 - z . $ii = x$, -1 . 5 - y , $-1/2$ + z . $iii = -x$, 1.5 + y , 0.5 - z .	N9-H9AQ3 ⁱ 0.860 2.0676(1) 2.0138(1) 167.796(4) N8-H8AQ2 ⁱⁱ 0.860 2.0481(1) 2.8416(1) 153.062(4) N7-H7AQ4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: <i>i</i> = 1-x, -y, 1-z. <i>ii</i> = x, -1.5-y, -1/2+ z. <i>iii</i> = -x, 1.5 + y, 0.5 - z.	N9-H9AO3 ⁱ 0.860 2.0676(1) 2.0138(1) 167.796(4) N8-H8AO2 ⁱⁱ 0.860 2.0481(1) 2.8416(1) 153.052(4) N7-H7AO4 0.860 2.0329(1) 2.855(1) 159.788(4) N10-H1OAO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.		D-H	Н…А	D····A	D-H····A
N8-H8AO2 ⁱⁱ 0.860 2.0481(1) 2.8416(1) 153.062(4) N7-H7AO4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z. Image: constant of the symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	N8-H8AO2 ⁱⁱ 0.860 2.0481(1) 2.8416(1) 153.062(4) N7-H7AO4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+z. iii = -x, 1.5 + y, 0.5 - z. Image: codes: code: cod: code: code: code: code: code: cod: code: cod	N8-H8AO2 ⁱⁱ 0.860 2.0481(1) 2.8416(1) 153.062(4) N7-H7AO4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z. Image: constant of the symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	N9-H9A····O3 ⁱ	0.860	2.0676(1)	2.0138(1)	167.796(4)
N7-H7AO4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+z. iii = -x, 1.5 + y, 0.5 - z.	N7-H7AO4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	N7-H7AO4 0.860 2.0329(1) 2.8555(1) 159.788(4) N10-H10AO6 ⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	N8-H8A…O2 ⁱⁱ	0.860	2.0481(1)	2.8416(1)	153.062(4)
N10-H10A···O6 ⁱⁱⁱ 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	<u>N10-H10AO6ⁱⁱⁱ</u> 0.860 <u>1.9454(1)</u> <u>2.7907(1)</u> <u>167.252(4)</u> <u>Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.</u>	NIO-HIOAOG ^{III} 0.860 1.9454(1) 2.7907(1) 167.252(4) Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	N7-H7A…O4	0.860	2.0329(1)	2.8555(1)	159.788(4)
Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	Symmetry codes: i = 1-x, -y, 1-z. ii = x, -1.5-y, -1/2+ z. iii = -x, 1.5 + y, 0.5 - z.	N10-H10A…O6 ⁱⁱⁱ	0.860	1.9454(1)	2.7907(1)	167.252(4)
RAND	CEPTER MANUSCRIN	A CORDER OF THE OPTIME	Symmetry codes: $i = 1$	x, -y, 1-z. ii =	x, -1.5-y, -1/2+x	z. $iii = -x, 1.5 + y$	y, 0.5 - z.
			Symmetry coues. t = 1	x, -y, 1-z. <i>u</i>			

Entry	Catalyst	Time,	Amount of	Temp.	Solvent	Yield,	Selectivity ^c
-		(h)	catalyst (mol%)	(°C)		(%) ^b	threo/ erythro
1	1	24	2.0	20	MeCN	25.2	58:42
2	2	24	2.0	20	MeCN	22.9	52:48
3	1	24	2.0	20	MeOH	79.3	77:23
4	2	24	2.0	20	MeOH	47.5	60:40
5	1	24	2.0	20	H ₂ O	43.3	66:44
6	2	24	2.0	20	H ₂ O	35.9	63:37
7	Blank	24	_	20	MeOH	-	-
8	$Zn(NO_3)_2$	24	1.0	20	MeOH	-	-
9	Cd(CH ₃ COO) ₂	24	1.0	20	MeOH	-	-
10	1	24	1.0	20	MeOH	70.2	77:23
11	1	24	3.0	20	MeOH	88.2	82:18
12	1	24	4.0	20	MeOH	88.8	82:18
13	1	5	3.0	20	MeOH	50.2	76:24
14	1	10	3.0	20	MeOH	69.3	76:24
15	1	15	3.0	20	MeOH	71.8	82:18
16	1	48	3.0	20	MeOH	90.7	82:18
17	1	15	3.0	35	MeOH	94.9	82:18
18	1	15	3.0	45	MeOH	95.1	85:15

Table 4. Henry nitroaldol reaction between benzaldehyde and nitroethane with 1 and 2 as catalyst precursors.^a

^a Reaction conditions: 1.0–4.0 mol% (0.1–0.4 μmol) of catalyst precursor (typically 2 mol%), solvent (MeOH, THF, MeCN) (2 mL), nitroethane (4 mmol) and benzaldehyde (1 mmol). ^b Determined by ¹H NMR analysis (see Experimental). ^c Calculated by ¹H NMR.

Entry	Substrate	Yield (%) ^b	threo/erythro ratio ^c
 1	Сно	84.1	84:16
2	02N-СНО	89.7	89:11
3	Н ₃ СО-СНО	84.3	80:20
4	сі—	73.3	72:28
5	СН3	71.7	70:30
6	SO ₃ Na	68.6	67:33
7	но	77.9	79:21
8	СН3СНО	93.0	98:2
0 0	CHICHICHO	02.8	03.7

Table 5: Henry	reaction of vari	ous aldehydes an	nd nitroethane w	/ith catalyst 1. ^a
----------------	------------------	------------------	------------------	-------------------------------

^a Reaction conditions: 3.0 mol% of catalyst **5**, MeOH (2 mL), nitroethane (4 mmol) and benzaldehyde (1 mmol), reaction time: 15h. ^b Determined by ¹H NMR analysis (see Experimental). ^c Calculated by ¹H NMR

CCC



















Both the 0D coordination complex $[Zn(im)_4](NO_3)_2]$ (1) and 1D coordination polymer $[CdNa_2(\mu L^{2}$]_n:6.34H₂O (2), where (L) is (2-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)terephthalate), have been successfully synthesized and characterized by IR and UV-vis absorption spectroscopies and single-crystal X-ray diffraction. Furthermore, 1 and 2 were used as catalysts in the Henry reaction with uni nitroethane and aldehydes. The diastereoselectivities of the products were determined using ¹H NMR spectroscopy.