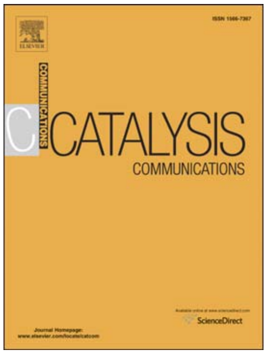

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A new cyclic binuclear Ni(II) complex as a catalyst towards nitroaldol (Henry) reaction

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Abstract

A new cyclic binuclear Ni(II) complex, $[Ni_2(H_2L)_2]\cdot 4MeOH$ (**1**), has been synthesized using the Schiff base *N'¹*,*N'³*-bis(2-hydroxybenzylidene)malonohydrazide (H_4L). The X-ray crystal structure of **1** shows that the ligand coordinates in the dianionic keto form (H_2L^{2-}) via mutual sharing of two Ni(II) ions. Complex **1** acts as a heterogeneous catalyst for the Henry reaction in water. A maximum conversion of *ca.* 93% was obtained under optimized conditions.

Keywords: binuclear Ni(II); X-ray structure; heterogeneous catalysis; Henry reaction.

1. Introduction

The nitroaldol (Henry) reaction, being discovered back in 1895 [1], as the coupling of a carbonyl with an alkyl nitro compound bearing α-hydrogen atoms, is a widely utilized method for the construction of carbon–carbon bonds and the preparation of β-nitroalcohols. The reaction can be catalyzed by inorganic/organic bases or metal complexes [2-9] and can be used as a tool for the syntheses of a variety of valuable building blocks of pharmaceutical significance [3-6]. Depending on the nature of the reactants, the reaction involves the formation of one or two asymmetric centres at the new carbon–carbon junction, where the optically active forms are useful intermediates in the synthesis of biologically active compounds [4] or polyfunctionalized materials [10]. The stereoselectivity of the reaction was first time reported by Shibasaki in 1992 [11] and a number of works have appeared in recent years [3-6], showing the current interest of the Henry reaction and its application. The reaction has been studied in homogeneous [3-6], heterogeneous [12-14], ionic liquids or supercritical fluids [15], mesoporous nanocomposite conditions [16], etc. However, the achievement of a good selectivity is still a challenge, and it is also important the search for new catalysts which can be prepared easily and are commercially cheap.

Ni(II) complexes play an important role in various homogeneous catalytic reactions, such as, tetralin oxidation [17], asymmetric aldol reaction [18], Mannich-type and Michael reactions [19] and alkene epoxidation [20], and can also exhibit interesting magnetic properties [21,22]. Some nickel compounds can also act as catalysts towards the Henry reaction under different conditions, namely in homogeneous systems [23], under solvent free microwave conditions [16] or in ionic liquids [24], and high activities (more than 90% yields) are found in a few cases [16,24].

On the other hand, hydrazone Schiff bases are useful and versatile pro-ligands for the synthesis of a huge variety of coordination compounds [25-30]. Though there is a number of Ni(II) complexes with hydrazone Schiff bases, it appears that they have not yet been explored for the catalytic Henry reaction. In this study, we report the synthesis, structure and catalytic activity towards this reaction in water of a new cyclic binuclear Ni(II) complex derived from the Schiff base *N'¹*,*N'³*-bis(2-hydroxybenzylidene)malonohydrazide [31].

2. Experimental

2.1. General Materials and Procedures

All the synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, i.e. without further purification or drying. $[Ni^{II}(O_2CMe)_2].4H_2O$ was obtained from Sigma-Aldrich and was used for the synthesis of complex **1**. *N′¹,N′³*-bis(2-hydroxybenzylidene)malonohydrazide was synthesized according to literature procedure [30]. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined with a Leica Gallen III instrument. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker Vertex 70 instrument in KBr pellets; wavenumbers are in cm^{-1}. The ^1H spectra were recorded at room temperature on a Bruker Avance II + 400.13 MHz (UltraShieldTM Magnet) spectrometer. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference.

*2.2. Synthesis of $[Ni_2(H_2L)_2]\cdot 4MeOH$ (**1**)*

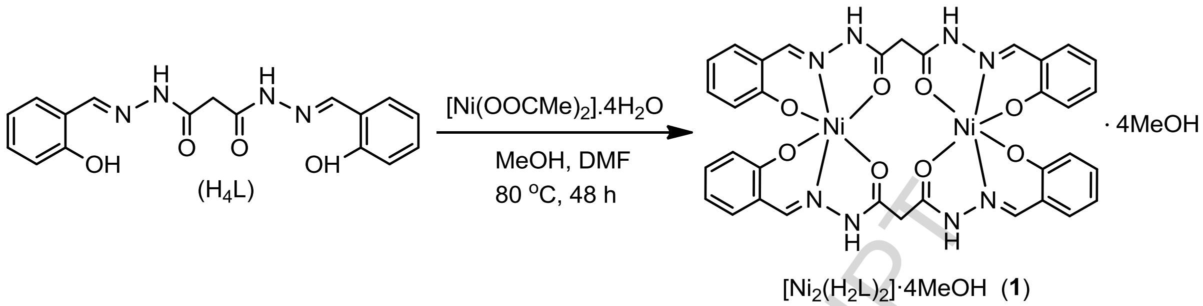
A mixture of 2 mL DMF solution of H_4L (7 mg, 0.02 mmol) and 5 mL methanolic solution of $[Ni^{II}(O_2CMe)_2]\cdot 4H_2O$ (5 mg, 0.02 mmol) was sealed in a capped glass vessel and heated to 80 °C for 48 h and, after subsequent gradual cooling to room temperature, good quality crystals were isolated by filtration, washed 3 times with methanol, and then dried open in air. This compound is insoluble in common organic solvents and water. Yield: 56% (based on Ni). Anal. calc. for $[Ni_2(H_2L)_2]\cdot 4MeOH$ (**1**) ($C_{38}H_{44}N_8Ni_2O_{12}$): C, 49.49; H, 4.81; N, 12.15 found: C, 49.26; H, 4.92; N, 12.02. IR (KBr; cm^{-1}): 3425 ν(OH), 1689 ν(C=N), 1303 ν(C–O)enolic, 1195 ν(N–N).

2.3. Catalytic activity studies

The catalytic study was performed in air under with the following conditions for each essay: to 1.0–5.0 mol% (0.1–0.5 μmol) of the catalyst precursor **1** (typically 1 mol %) contained in the reaction flask was added water (2 mL), nitroethane (2 mmol) and aldehyde (1 mmol), in that order. The reaction mixture was stirred for the required time at the particular temperature. After evaporation of the solvent, the residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR. The yield of the β-nitroalkanol product (relatively to the aldehyde) was established by ^1H NMR as reported previously [32]. A number of ^1H NMR analyses was performed in the presence of 1,2-dimethoxyethane as an internal standard, added to the $CDCl_3$ solution, to verify the adequacy of the procedure, giving 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 *syn* and *anti* isomers was also determined by ^1H NMR spectroscopy. In the ^1H 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 *syn* or *anti* isomers, respectively [32].

3. Results and discussion

In DMF-methanol, reaction of $[Ni^{II}(O_2CMe)_2]\cdot 4H_2O$ with the Schiff base *N′¹,N′³*-bis(2-hydroxybenzylidene)malonohydrazide (H_4L) at 80 ºC, upon cooling to room temperature, yields green crystals of $[Ni_2(H_2L)_2]\cdot 4MeOH$ (**1**) (Scheme 1). It is a binuclear cyclic Ni(II) compound where ligands, in the dianionic keto form (H_2L^{2-}), mutually share two Ni(II) ions. Complex **1** was characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. Its catalytic activity was studied towards the Henry reaction in water, under heterogeneous conditions.



Scheme 1: Synthesis of $[Ni_2(H_2L)_2]\cdot4MeOH$ (**1**).

Complex **1** crystallizes in the monoclinic space group $P2_1/c$ (Table S1), its unit cell containing one molecule of the compound and four molecules of methanol. The organic ligand, the dianionic keto form of the Schiff base N'^{1},N'^{3}-bis(2-hydroxybenzylidene)malonohydrazide (H_2L^{2-}), acts as a hexachelator to two Ni(II) centres to form a binuclear cyclic structure (Scheme 1, Figure 1). The Ni(II) centres present a distorted octahedral N_2O_4 geometry with quadratic elongations and angle variances of 1.024, 75.82^{o2} and 1.026, 61.50^{o2} for Ni1 and Ni2, respectively. For the coordination sphere of each metal cation every H_2L^{-2} ligand contributes with an imine nitrogen, a phenolate and a ketonic oxygen atom in such a way that the N atoms are in the axial positions and the equatorial sites are occupied by the O atoms, the chelation planes around the metals being almost perpendicular (89.46º for Ni1 and 85.59º for Ni2). Angles of 77.30º or 79.02º between the least-square planes of the five-membered metallacycles pertaining to every H_2L^{-2} ligand result from their folding at the methylene carbons C9 or C29, respectively. The structure features a 2D network by means of contact interactions involving the imine nitrogen atoms N22 and the phenolate oxygen atoms O21 of the complex molecule [*d*(D···A) 2.822(5) Å, ∠ (D–H···A) 167.7º] and also extensive interactions involving the methanol molecules (Figure S1 and Table S3).

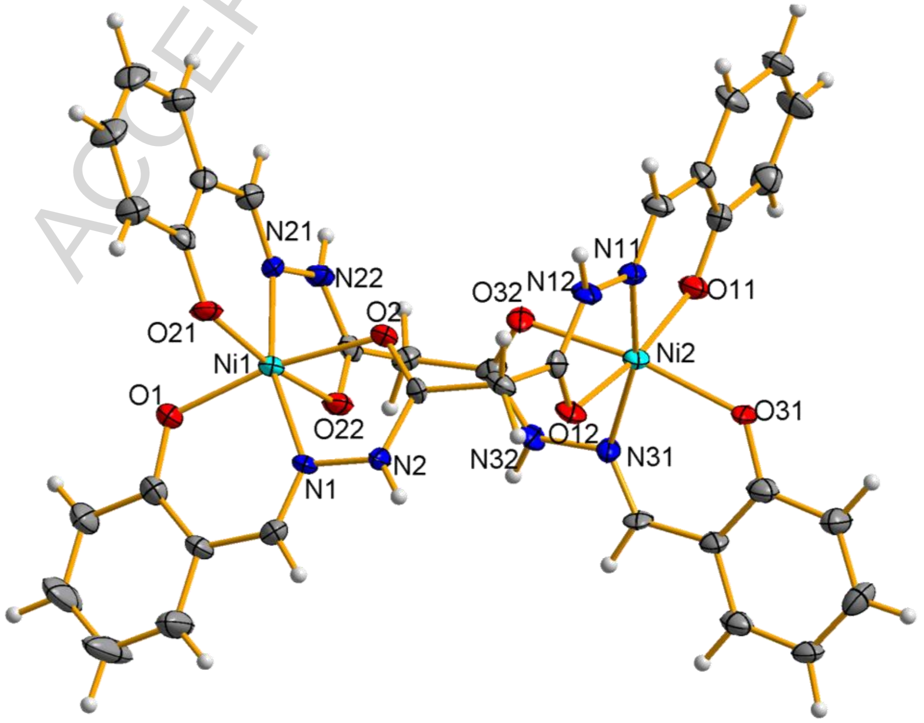
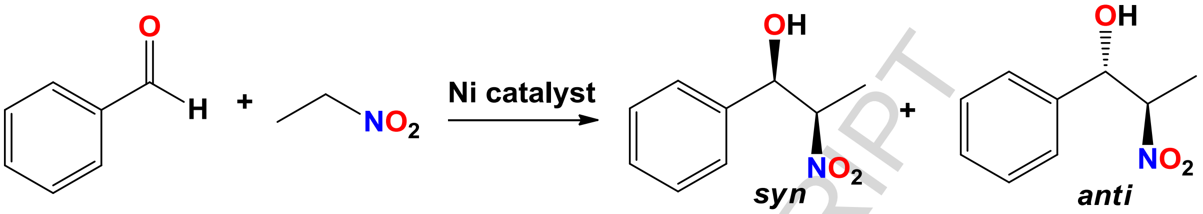


Figure 1: Molecular structure of **1** with atom numbering scheme (thermal ellipsoids are drawn at the 50% probability level). Methanol molecules were omitted for clarity.

Complex **1** acts as a catalyst for the heterogeneous Henry reaction of nitroethane and benzaldehyde (Scheme 2) which was studied under various conditions (Table 1).



Scheme 2: Henry reaction of nitroethane and benzaldehyde.

Table 1. Catalytic activity of **1** in the Henry reaction[a]

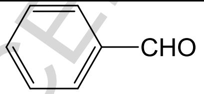
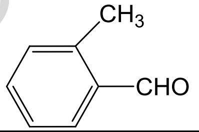
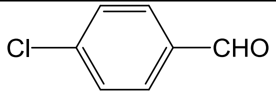
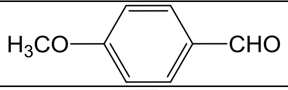
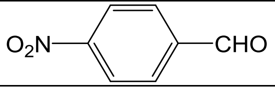
Entry	Catalyst	Time (h)	Amount of catalyst (mol%)	Temp. (ºC)	Solvent	Yield (%) [b]	Selectivity [c] *syn* : *anti*	TOF[d]
1	**1**	24	1.0	20	H_2O	84	70:30	3.5
2	**1**	24	1.0	20	MeOH	73	63:37	3.0
3	**1**	24	1.0	20	MeCN	54	54:46	2.3
4	**1**	24	1.0	40	H_2O	88	72:28	3.7
5	**1**	24	1.0	60	H_2O	93	72:28	3.9
6	**1**	24	1.0	80	H_2O	86	75:25	3.6
7	Blank	24	–	60	H_2O	–	–	–
8	$Ni(OAc)_2$	24	1.0	60	H_2O	7.1	62:38	0.3
9	**1**	24	2.0	60	H_2O	92	72:28	1.9
10	**1**	24	3.0	60	H_2O	92	72:28	1.3
11	**1**	24	5.0	60	H_2O	91	70:30	0.8
12	**1**	6	1.0	60	H_2O	42	65:35	7.0
13	**1**	12	1.0	60	H_2O	57	70:30	4.7
14	**1**	48	1.0	60	H_2O	92	72:28	1.9
15 [e]	**1**	24	1.0	40	H_2O	90	64:36	3.8
16[f]	**1**	24	1.0	40	H_2O	91	66:34	3.8

[a]Reaction conditions: 1.0–5.0 mol% (0.1–0.4 µmol) of catalyst precursor (typically 1 mol%), solvent (H_2O, MeOH, MeCN) (2 mL), nitroethane (2 mmol) and benzaldehyde (1 mmol). [b]Determined by ^1H NMR analysis (see Experimental). [c]Molar ratio, calculated by ^1H NMR (see ESI). [d]TOF (h^{-1}) was estimated as moles of products (*syn*- and *anti*-β-nitroalkanol)/mol of catalyst per hour. [e]In presence of 0.25 eqv. K_2CO_3 solution. [f]In presence of 0.25eqv. Et_3N solution.

The use of protic solvents (e.g. water or MeOH) usually provides better results than aprotic ones (e.g. acetonitrile) [4,33-34], what is also observed in our case (Table 1, entries 1–3). At room temperature (20 °C), the highest yield (84%) and selectivity (*syn* : *anti* = 70:30) are obtained in water (entry 1). Thus, water was chosen as the sole solvent for further studies. To establish the optimized conditions, the variations of temperature (20 – 80 °C), catalyst amount (1–5 mol %) and reaction time (6–48 h) were applied. At 60 °C, for 24 h reaction time, with 1 mol % loading of catalyst **1**, the highest yield of 93 % with the good *syn* : *anti* molar ratio of 72:28 was achieved (entry 5). Calculation for entry 5 is given in ESI (Figure S2). The variation (1–5 mol %) of the catalyst amount (entries 5, 9–11) resulted in only a smaller or negligible effect on the yield and selectivity. Thus, 1 mol % loading is the typical value. Control (blank) experiments were carried out in the absence of any metal catalyst or in the presence of a simple Ni(II) salt, $[Ni(OAc)_2]\cdot 4H_2O$. In the former case (entry 7) no nitroaldol coupling product was detected, whereas, with $[Ni(OAc)_2]\cdot 4H_2O$ a low product yield (7%) was obtained (entry 8). The effect of a small amount of base was also examined at 40 °C (entries 15 and 16), but only minor changes in the yield and selectivity were detected.

To examine the catalytic potential scope of **1** in the Henry reaction, a series of aldehydes were screened as starting materials (Table 2). With one exception (see below), substituted benzaldehydes react less effectively than benzaldehyde itself, possibly on account of steric effects. Nevertheless, electron-withdrawing substituents in *para*-position of the substituted aromatic aldehydes lead to higher yields (entries 3–5) than those that are obtained with the electron-donor *ortho*-methyl substituent (entry 2). However, the steric effect associated to the *ortho* position can also play a role. The highest yield (97%) and high diastereoselectivity (*syn : anti* ratio of 74:26) was obtained for the nitro-substituted aldehyde (entry 5). Aliphatic aldehydes, such as acetaldehyde and propionaldehyde (entries 6 and 7), have also been used as substrates. A maximum of 71% conversion was obtained in the case of propionaldehyde (entry 7) with a *syn : anti* ratio of 71:29.

Table 2. Henry reaction of various aldehydes and nitroethane with catalyst **1**[a]

Entry	Substrate	Yield (%)[b]	*syn* : *anti* ratio[c]	TOF[d]
1		93	72:28	3.9
2		64	70:30	2.7
3		91	73:27	3.8
4		82	68:32	3.4
5		97	74:26	4.0
6	CH_3CHO	64	70:30	2.7
7	CH_3CH_2CHO	71	71:29	2.9

[a] Reaction conditions: 1.0 mol% of catalyst **1**, H_2O (2 mL), nitroethane (2 mmol) and aldehyde (1 mmol), reaction time: 24 h, reaction temperature: 60 °C . [b] Determined by ^1H NMR analysis (see Experimental). [c] Molar ratio, calculated by ^1H NMR.). [d] TOF (h^{-1}) was estimated as moles of products (*syn*- and *anti*-β-nitroalkanol)/mol of catalyst per hour.

In comparison with other heterogeneous nickel catalysts (Table 3), our system, with the advantage of using water, leads to yields that are similar to those reported for heterogeneous Ni–Al (Ni:Al=3:1) hydrotalcites when using ionic liquids [24] or for Ni-hydroxyapatite under microwave irradiation to promote the reaction [16].

Table 3. Comparison of activities of various Ni catalysts towards the Henry reaction.

Catalyst	Solvent/Temp/Time	Aldehyde	Yield (%)	Selectivity (*syn:anti*)	Ref.
1	Water/60 °C/24 h	benzaldehyde	93	72:28	This study
1	Water/60 °C/24 h	4-nitrobenzaldehyde	97	74:26	This study
Mixed salt $(H_2DABCO)[Ni(H_2O)_6](SeO_4)_2$[a]	MeOH/20 °C/24 h	benzaldehyde	37	53:47	23
Ni–Al (Ni:Al=3:1) HT[b]	Ionic liquids/60 °C/ 6 h	4-nitrobenzaldehyde	93	Not determined	24
Ni-Hap[c]	Microwave assisted 160 W / 1 min	benzaldehyde	96	Not determined	16
Ni-Hap[c]	Microwave assisted 160 W / 1 min	4-nitrobenzaldehyde	97	Not determined	16

[a]DABCO = 1,4-diazabicyclo[2.2.2]octane ; [b]HT = hydrotalcites; [c]HAp = Hydroxyapatite , $[Ca_{10}(PO_4)_6(OH)_2]$.

Since recycling of a catalyst is one of the most significant advantages of heterogeneous catalysis, we checked the reusability of **1** up to three cycles (Table 4). The catalyst could be easily recovered by direct filtration. It almost retained its initial activity in the Henry reaction between benzaldehyde and nitroethane, showing comparable yields and diastereoselectivities (Table 4). The stability of the catalyst was confirmed by IR spectroscopy (Figure S3, ESI), powder XRD (Figure S4, ESI) and elemental analysis before and after the catalytic reaction.

Table 4. Recycling of catalyst **1** in the Henry reaction[a] using benzaldehyde and nitroethane.

Entry	Catalytic cycle	Yield (%)[b]	*syn : anti* ratio[c]
1	1	93	72:28
2	2	91	72:28
3	3	90	70:30

[a]Reaction conditions: 1.0 mol% of catalyst **1**, H_2O (2 mL), nitroethane (2 mmol) and benzaldehyde (1 mmol), reaction time: 24h. [b]Determined by ^1H NMR analysis (see Experimental). [c]Molar ratio, calculated by ^1H NMR.

The reaction can occur at the solid–liquid interface of water droplets [34] via a previously reported mechanism [11,16], where the catalyst **1** behaves as a Lewis acid to activate both nitroethane (by increasing its Brönsted acidity upon coordination by the nitro group) and aldehyde (by increasing its electrophilic character upon coordination by the CHO group), whereas the hydrazone Schiff base (eventually assisted by water [35]) acts a Brönsted base to facilate the deprotonation of the acidic nitroethane. The formed reactive nitronate species then adds to the ligated benzaldehyde via a nucleophilic intramolecular attack resulting in C–C coupling and thus yielding the β-nitroalkanol as proposed in other cases [11].

4. Conclusion

The Schiff base N'^{1},N'^{3}-bis(2-hydroxybenzylidene)malonohydrazide (H_4L) leads to a stable cyclic binuclear Ni(II) complex (**1**), where each ligand in the dianionic keto form acts as a hexachelator to the two Ni(II) centres. This complex shows a high activity towards heterogeneous Henry reaction in water. At optimized conditions (60°C, 1 mol % catalyst loading, 24 h), a maximum conversion of 92.7 % with a *syn*:*anti* selectivity ratio of 76:24 is achieved.

The catalytic activity of Ni(II)-Schiff base complexes had not yet been explored for that reaction, and thus this study opens such a possibility and shows that complexes of that type can operate effectively in the presence of water, without needing any added organic solvent or ionic liquid, or microwave irradiation. Further modifications of the Schiff base ligand and complex structure deserve to be explored to reach a higher selectivity and yield.

Acknowledgement

Authors are grateful to the Foundation for Science and Technology (FCT) (project PEst-OE/QUI/UI0100/2013), Portugal, for financial support. M.S. acknowledges the FCT, Portugal for a postdoctoral fellowship (SFRH/BPD/86067/2012). The authors are thankful to the Portuguese NMR Network (IST-UL Centre) for access to the NMR facility.

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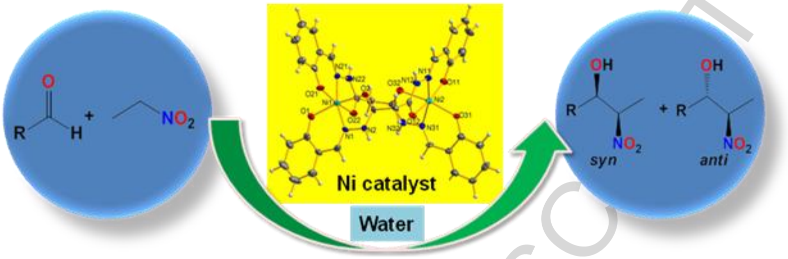
Graphical Abstract



Highlights

- A new cyclic binuclear Ni(II) complex, $[Ni_2(H_2L)_2]\cdot 4MeOH$ (**1**), has been synthesized
- The ligand coordinates in the dianionic keto form via mutual sharing of two Ni(II)
- Complex **1** acts as a heterogeneous catalyst for the Henry reaction in water