Ni(II)-Aroylhydrazone Complexes as Catalyst Precursors Towards Efficient Solvent-Free Nitroaldol Condensation Reaction

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Abstract: The aroylhydrazone Schiff bases 2-hydroxy-(2-hydroxybenzylidene)benzohydrazide and (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide have been used to synthesize the bi- and tri-nuclear Ni(II) complexes $[Ni_2(L^1)_2(MeOH)_4]$ (**1**) and $[Ni_3(HL^2)_2(CH_3OH)_8] \cdot (NO_3)_2$ (**2**). Both complexes have been characterized by elemental analysis, spectroscopic techniques [IR spectroscopy and electrospray ionization-mass spectrometry (ESI-MS)], and single-crystal X-ray crystallography. The coordination behavior of the two ligands is different in the complexes: The ligand exhibits the keto form in **2**, while coordination through enol form was found in **1**. Herein, the catalytic activity of **1** and **2** has been compared with the nitroaldol condensation reaction under various conditions. Complex **2** exhibits the highest activity towards solvent-free conditions.

Keywords: Ni(II) complex; aroylhydrazone; X-ray structure; nitroaldol condensation

1. Introduction

The nitroaldol (Henry) reaction, a very useful and significant reaction, plays a vital role in the synthetic organic chemistry. It is widely used to build C–C bonds by the formation of β-nitroalcohols derived from coupling of a carbonyl compound with an alkyl nitro one with α- hydrogen atoms. The reaction takes place via construction of asymmetric centers (one or two) through the new C–C junction leading to optically active products. Inorganic metal complexes or inorganic/organic bases can catalyze this reaction [1–10]. The prepared functionalized β-nitroalcohols are known as important synthetic precursors, can be converted by nucleophilic displacement into other functionalities like α-hydroxy ketones, aldehydes, carboxylic acids, azides, sulphides, etc., of pharmaceutical significance [5–8], polyfunctionalized materials [11], and are used to generate compounds of biological importance such as 1,2-diaminoalcohol, [12] aminosugars, [13] nitroketones, [14] α,β-unsaturated nitro compounds [15], and many other important bifunctional compounds. The stereoselectivity nature of the Henry reaction was identified for the first time by Shibasaki et al. [16] using several chiral metal complexes [17–29] and chiral organocatalysts [20], exhibiting the growing interest in this field. The reaction has been studied using different conditions like homogeneous [5–8], heterogeneous [21–23], ionic liquids or supercritical media [24], materials of mesoporous nanocomposite [25], etc.

The design of the catalyst plays a crucial role in controlling the diastereo- and enantioselectivity of the products, leading to a serious task for researchers to search for efficient and selective catalysts from synthetic, economic, and environmental perspectives. Di and polynuclear metal complexes including coordination polymers can efficiently catalyze the nitroaldol reaction between aldehydes and nitroalkanes [26–28]. Solvent-free organic synthesis has received significant interest from the

chemist worldwide due to its advantage over chemical wastes in terms of sustainability and the requirements of green chemistry [29]. The use of solvent-free condition is also applied in the nitroaldol reaction [30,31]. Some nickel complexes showed good catalytic activity towards nitroaldol reactions under various conditions such as in homogeneous reaction states [32,33], under solvent-free microwave irradiation [25], in ionic liquids [34,35], or under heterogeneous [36–38] conditions. Aroylhydrazone Schiff bases form highly stable complexes with transition metals in various oxidation states, coordination numbers, and nuclearities, and can be tuned easily by changing different carbonyl derivatives [39–46].

In this study, we describe the synthesis and characterization of one dinuclear and one trinuclear Ni(II) complex derived from two different aroylhydrazones, and their activity as catalyst precursors towards nitroaldol (Henry) reactions to achieve desired functionalized products under different homogeneous catalytic reactions conditions. Solvent-free conditions are found most efficient in our catalytic system. This is probably due to more accessibility of substrate molecules to the metal centre under solvent-free condition than the presence of solvent molecule; 94%–97% yields are observed in our case, which is relatively higher than the yield found in other di or polynuclear catalytic system [26].

2. Results and Discussion

### 2.1. Syntheses and Characterizations

In this study, we have used two different aroylhydrazone Schiff bases, namely, 2-hydroxy-(2-hydroxybenzylidene)benzohydrazide (H_2L^1) and (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H_3L^2) [47,48], to synthesize two different (one dinuclear and one trinuclear) Ni(II) complexes. In the dinuclear complex [$Ni_2(L^1)_2(MeOH)_4$] (**1**), the ligand exhibits the enol form with the loss of all (two) acidic hydrogens whereas H_3L^2 undergoes coordination with the loss of two acidic hydrogens (out of three) and one remains protonated to form the trinuclear [$Ni_3(HL^2)_2(CH_3OH)_8$]·(NO_3)$_2$ (**2**) (Scheme 1). In both complexes, the phenolate oxygen at the ortho-position (from the aldehyde moiety of the ligand) forms a phenoxido bridge between two Ni(II) ions. Characterizations of **1** and **2** have been carried out by elemental analysis, spectroscopic methods (IR spectroscopy, ESI-MS), and X-ray diffraction (single crystal) techniques. Beside similar characteristic stretching signals of the ligand, a band at 1609 cm^{-1} appears in the IR spectrum of **2** that corresponds to the C=O stretching frequency [47,48]. The *m/z* value of **2** suggests the loss of two noncoordinate nitrate ions and one acidic proton from one of the two ligands present in **2** (see Experimental). The catalytic properties of **1** and **2** were investigated towards solvent-free nitroaldol condensation reaction and their activities were compared.

2.2. General Description of the Crystal Structures

Crystals of [$Ni_2(L^1)_2(DMF)_4$] [$Ni_2(L^1)_2(DMF)_2(H_2O)_2$]·2DMF (**1A**) suitable for X-ray diffractions were obtained upon re-crystallization of **1** from DMF-water and slow evaporation of **2** from the methanolic solution, at ambient temperature. The crystallographic data are summarized in Table 1, representative molecular structures are displayed in Figures 1 and 2, and selected dimensions are presented in Table 2.

The asymmetric unit of the compound **1A** comprises a half unit of two different molecules and one solvent DMF. One half unit of one molecule contains the nickel(II) cation with one coordinated ligand, one DMF, and one water molecule. Another half consists of nickel(II) cation with one coordinated ligand and two DMF molecules. All the Ni(II) centers exhibit a distorted octahedral coordination environment. The structure of **1A** contains crystallographically generated inversion centres in the middle of the Ni1–Ni1^{i}or Ni2–Ni2^{ii} bonds, therefore in the heart of the respective Ni$_2$O$_2$ planes. The aroylhydrazones act as dianionic and tetradentate ONOO chelating equatorial ligands, binding to one of the Ni(II) centers via the enolate oxygen, the imino nitrogen, and the deprotonated phenolate oxygen, which is connected to other metal cation. Thus, the structure displays two μ-O bridges in each molecular unit, which connect the two nickel(II) centers. In the axial positions, there are two

DMF oxygens atoms in one unit and DMF and water in the other unit. The N−N bond distances of 1.385 (3) and 1.397 (3) Å for the coordinated ligand indicate their single bond hydrazino character. The O_{DMF}–Ni–O_{DMF} or O_{DMF}–Ni–O_{water} groups are nearly linear (170.47 (9)° and 172.52 (7)°) and in the $Ni_2(\mu\text{-}O)_2$ cores, the Ni–O–Ni angles are ca. 100°. The Ni–Ni contact distances are about 3.10 Å.
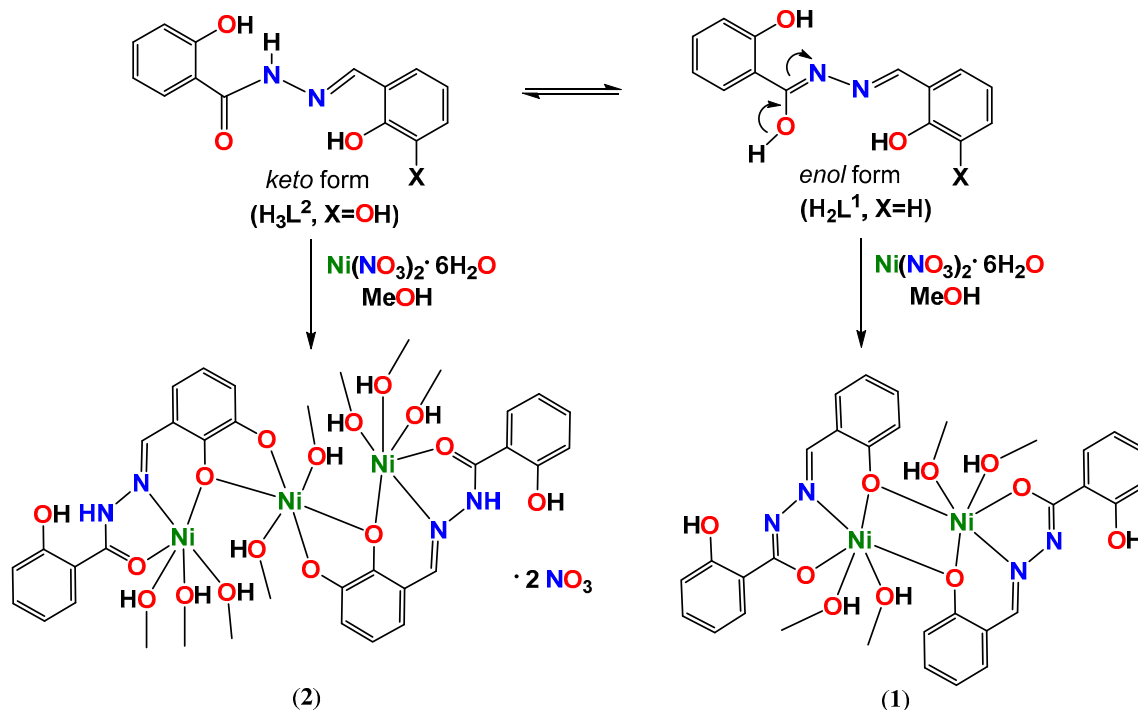

Scheme 1. Syntheses of **1** and **2**.

Table 1. Crystal data and structure refinement details for complexes **1A** and **2**.

	1A	2
Empirical formula	$C_{20}H_{24}N_4NiO_{5.50}$	$C_{18}H_{26}N_3Ni_{1.50}O_{10}$
Formula Weight	467.14	532.48
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temperature/K	296 (2)	296 (2)
a/Å	12.766 (3)	9.114 (3)
b/Å	13.714 (4)	10.821 (3)
c/Å	14.344 (4)	13.221 (4)
α/°	84.87 (1)	71.721 (10)
β/°	63.594 (10)	83.309 (11)
γ/°	79.445 (9)	71.328 (10)
V (Å^3)	2211.2 (10)	1172.8 (6)
Z	4	2
D_{calc} (g cm^{-3})	1.403	1.508
μ(Mo Kα) (mm^{-1})	0.92	1.27
Rfls. collected/unique/observed	35885/8156/6683	10924/4209/2646
R_{int}	0.029	0.091
Final $R1$ [a], $wR2$ [b] ($I \geq 2\sigma$)	0.038, 0.108	0.093, 0.224
Goodness-of-fit on F^2	1.03	1.05

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR(F^2) = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

Compound **2** crystallizes in the triclinic $P\bar{1}$ space group. Its unit cell contains one molecule of the compound and two nitrate anions. Compound **2** is trinuclear with H_3L^2 coordinating to the Ni(II) cations in the dianionic $(HL^2)^{2-}$ form using both phenolate O atoms, the keto O atom, and the imine N

atom. The phenolate oxygen at the ortho position of the aldehyde moiety exhibits μ-O bridges with the other metal cation, which is located at the inversion centre. The asymmetric units of **2** contains half of the molecules, i.e., one and a half nickel cations, one $(HL^2)^{2-}$ ligand, four methanol molecules, and one nitrate anion. All the axial positions are occupied by methanol molecules. The terminal nickel cations exhibit distorted octahedral N1O5 coordination environment but the Ni(II) at center of inversion displays more regular octahedral geometry. The Ni–Ni contact distances are 3.764 Å, longer than the distances found in **1A**.

(a)   (b)
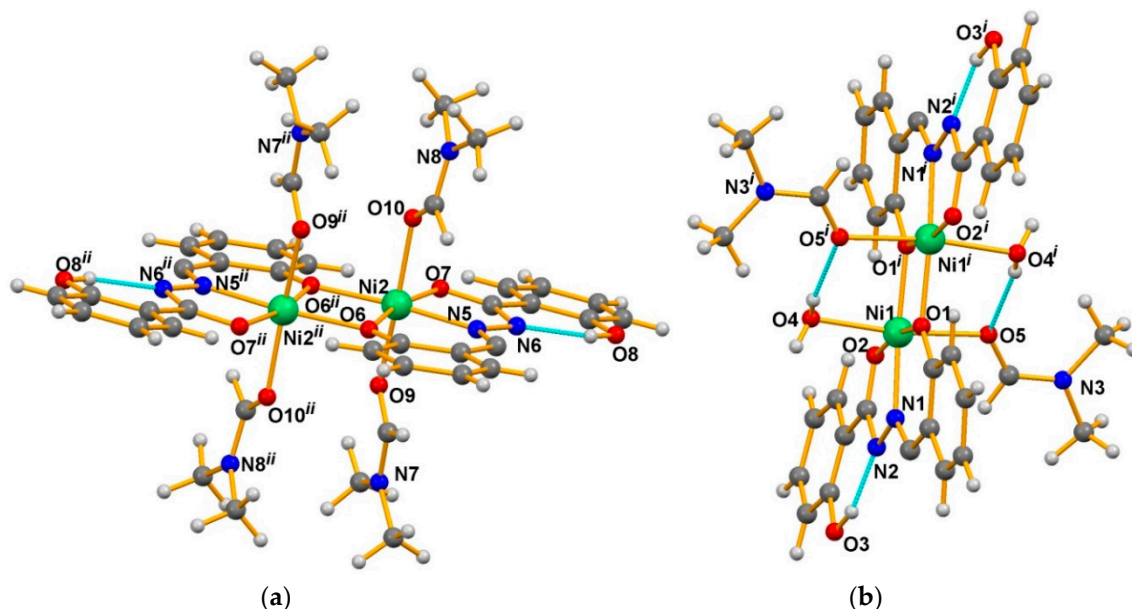
Figure 1. Molecular structure of compound **1A** with atom numbering scheme. (**a**) nickel(II) coordinated with two DMF, (**b**) nickel(II) coordinated with one DMF and one water molecule. Sky-blue doted lines represent hydrogen bonds. Symmetry codes (i) $-x, 1-y, 1-z$ (ii) $1-x, 2-y, 2-z$.
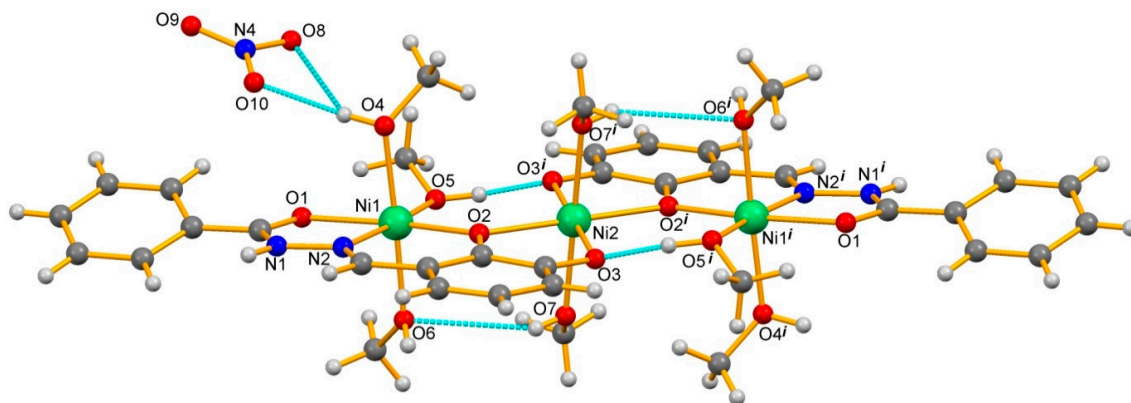
Figure 2. Molecular structure of compound **2** with atom numbering scheme. Sky-blue doted lines represent hydrogen bonds. Symmetry code (i) $1-x, 1-y, -z$.

Table 2. Selected bond distances (Å) and angles (°) in complexes **1A** and **2**.

			1A		
Ni1—N1	1.995 (2)	N1—Ni1—O1	89.97 (8)	N5—Ni2—O6	89.33 (8)
Ni1—O1	2.0231 (17)	N1—Ni1—O1^i	170.34 (8)	N5—Ni2—O6^{ii}	169.38 (8)
Ni1—O1^i	2.0256 (16)	O1—Ni1—O1^i	80.43 (7)	O6—Ni2—O6^{ii}	80.07 (8)
Ni1—O2	2.039 (2)	N1—Ni1—O2	78.97 (9)	N5—Ni2—O7	79.06 (8)
Ni1—O4	2.128 (2)	O1—Ni1—O2	168.93 (7)	O6—Ni2—O7	168.18 (8)
Ni1—O5	2.1753 (18)	O1^i—Ni1—O2	110.62 (7)	O6^{ii}—Ni2—O7	111.52 (8)
Ni2—N5	2.009 (2)	N1—Ni1—O4	95.68 (9)	N5—Ni2—O9	92.27 (8)
Ni2—O6	2.0342 (18)	O1—Ni1—O4	89.38 (8)	O6—Ni2—O9	93.83 (8)
Ni2—O6^{ii}	2.0488 (18)	O1^i—Ni1—O4	85.34 (8)	O6^{ii}—Ni2—O9	88.04 (8)
Ni2—O7	2.059 (2)	O2—Ni1—O4	92.13 (8)	O7—Ni2—O9	84.51 (8)
Ni2—O9	2.0975 (19)	N1—Ni1—O5	91.79 (8)	N5—Ni2—O10	92.08 (8)
Ni2—O10	2.1161 (19)	O1—Ni1—O5	90.17 (7)	O6—Ni2—O10	94.69 (8)
N1—N2	1.385 (3)	O1^i—Ni1—O5	87.23 (7)	O6^{ii}—Ni2—O10	89.24 (8)
N5—N6	1.397 (3)	O2—Ni1—O5	89.74 (8)	O7—Ni2—O10	88.00 (8)
O2—C8	1.276 (3)	O4—Ni1—O5	172.52 (7)	O9—Ni2—O10	170.47 (9)
O7—C28	1.267 (3)	Ni1—O1—Ni1^i	99.57 (7)	Ni2—O6—Ni2^{ii}	99.93 (8)
			2		
Ni1—O4	2.089 (7)	N2—Ni1—O5	170.5 (2)	O3—Ni2—O3^{iii}	180.0
Ni1—N2	1.991 (6)	N2—Ni1—O2	90.7 (2)	O3—Ni2—O2^{iii}	99.4 (2)
Ni1—O5	2.025 (6)	O5—Ni1—O2	98.7 (2)	O3^{iii}—Ni2—O2^{iii}	80.6 (2)
Ni1—O2	2.031 (5)	N2—Ni1—O1	78.7 (2)	O3—Ni2—O2	80.6 (2)
Ni1—O1	2.088 (6)	O5—Ni1—O1	91.9 (2)	O3^{iii}—Ni2—O2	99.4 (2)
Ni1—O6	2.092 (6)	O2—Ni1—O1	169.4 (2)	O2^{iii}—Ni2—O2	180.0
Ni2—O3	1.948 (6)	N2—Ni1—O4	87.6 (3)	O3—Ni2—O7	88.8 (3)
Ni2—O3^{iii}	1.948 (5)	O5—Ni1—O4	93.5 (3)	O3^{iii}—Ni2—O7	91.2 (3)
Ni2—O2^{iii}	2.108 (5)	O2—Ni1—O4	93.1 (2)	O2^{iii}—Ni2—O7	93.3 (2)
Ni2—O2	2.108 (5)	O1—Ni1—O4	86.8 (2)	O2—Ni2—O7	86.7 (2)
Ni2—O7	2.143 (8)	N2—Ni1—O6	91.9 (3)	O3—Ni2—O7^{iii}	91.2 (3)
Ni2—O7^{iii}	2.143 (8)	O5—Ni1—O6	86.7 (3)	O3^{iii}—Ni2—O7^{iii}	88.8 (3)
N1—N2	1.387 (8)	O2—Ni1—O6	88.8 (2)	O2^{iii}—Ni2—O7^{iii}	86.7 (2)
C1—O1	1.250 (9)	O1—Ni1—O6	91.3 (3)	O2—Ni2—O7^{iii}	93.3 (2)
-	-	O4—Ni1—O6	178.0 (3)	O7—Ni2—O7^{iii}	180.0
-	-	Ni1—O2—Ni2	125.2 (2)	-	-

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 2, -z + 2$; (iii) $-x + 1, -y + 1, -z$.

2.3. Catalytic Studies

The catalytic activity of complexes **1** and **2** for the nitroaldol (or Henry) reaction was evaluated using benzaldehydes and nitroethane as models (Scheme 2, Tables 3 and 4). An excess nitroethane was used to obtain maximum conversion of benzaldehydes into products.
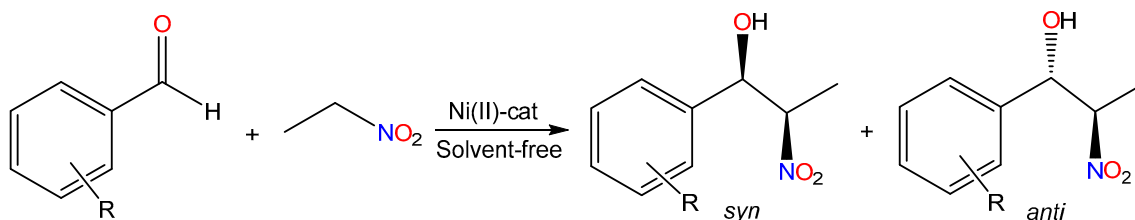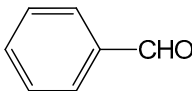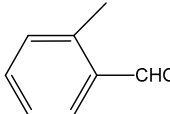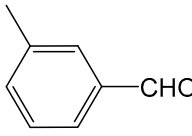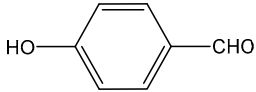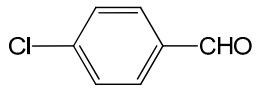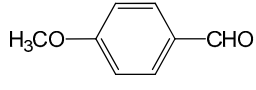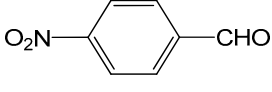

Scheme 2. Nitroaldol condensation reaction of nitroethane and benzaldehydes.

Table 3. Catalytic activity of **1** and **2** in the model nitroaldol condensation reaction [a] of nitroethane and benzaldehyde.

Entry.	Catalyst	Time (h)	Amount of Catalyst (mol%)	Temp. (°C)	Solvent	Yield or Conversion (%) [b]	Selectivity [c] syn: anti	TOF/h^{-1} [d]
1	**1**	24	1.0	ambient	-	86.6	70:30	3.6
2	**1**	24	1.0	ambient	H_2O	80.2	70:30	3.3
3	**1**	24	1.0	ambient	MeOH	72.2	64:36	3.0
4	**1**	24	1.0	ambient	MeCN	56.4	58:42	2.4
5	**2**	24	1.0	ambient	-	89.2	72:28	3.7
6	**2**	24	1.0	ambient	H_2O	82.4	70:30	3.4
7	**2**	24	1.0	ambient	MeOH	72.6	66:34	3.0
8	**2**	24	1.0	ambient	MeCN	58.0	60:40	2.4
9	**2**	24	1.0	40	-	90.8	72:28	3.8
10	**2**	24	1.0	60	-	94.0	77:23	3.9
11	**2**	24	1.0	75	-	90.6	76:24	3.8
12	Blank	24	–	60	-	-	-	-
13	Ni(OAc)$_2$	24	1.0	60	-	9	62:38	0.3
14	**2**	24	2.0	60	-	94.2	76:24	1.9
15	**2**	24	3.0	60	-	92.8	74:26	1.3
16	**2**	24	5.0	60	-	91.6	71:29	0.8
17	**2**	6	1.0	60	-	44.4	68:32	7.4
18	**2**	12	1.0	60	-	60.8	72:28	5.1
19	**2**	48	1.0	60	-	92.6	74:26	1.9

[a] Experimental conditions: Benzaldehyde (1 mmol); nitroethane (2 mmol); solvent (2 mL); [b] Determined using ^{1}H NMR analysis; [c] Molar ratios, calculated using ^{1}H NMR (see Figure S1 for entry 10); [d] Estimated as moles of *syn*- and *anti*-β-nitroethanol/mol of **1** or **2**, per hour.

Table 4. Solvent-free nitroaldol condensation of different aldehydes and nitroethane catalyzed by **2** [a].

Entry	Substrate	Yield or Conversion (%) [b]	syn: anti ratio [c]	TOF/h^{-1} [d]
1	⬡—CHO	94.0	77:23	3.9
2	⬡(CH$_3$)—CHO	60.8	72:28	2.5
3	⬡(CH$_3$)—CHO	56.4	70:30	2.3
4	HO—⬡—CHO	74.0	76:24	3.1
5	Cl—⬡—CHO	88.4	74:26	3.7
6	H_3CO—⬡—CHO	70.2	70:30	2.9
7	O_2N—⬡—CHO	97.0	80:20	4.0
8	CH$_3$CHO	66.6	72:28	2.8
9	CH$_3$CH$_2$CHO	78.2	74:26	3.2

[a] Experimental conditions: Catalyst **2**, 1.0 mol%, aldehyde (1 mmol), nitroethane (2 mmol), 24 h, 60 °C; [b] Determined using ^{1}H NMR analysis (see Experimental); [c] Molar ratio, calculated using ^{1}H NMR; [d] Estimated as moles of *syn*- and *anti*-β-nitroethanol/mol of **2**, per hour.

The selectivity for the β-nitroethanol products was 100% for all the experiments (the only compounds found besides *syn-* and *anti-* β-nitroethanols were non-reacted substrates).

Trinuclear complex **2** showed a higher activity than the dinuclear one, at the same temperature and under similar conditions (Table 3). Consequently, the reaction conditions (temperature, reaction time, amount of catalyst, and type of solvent) were optimized using a model nitroethane-benzaldehyde system with catalyst **2** (Table 3). Thus, the optimal experimental conditions found are exhibited in entry 10 of Table 3, leading to a β-nitroethanol yield of 94% (TOF = 3.9 h^{-1}) and a good selectivity *syn*:*anti* (77:23).

A blank test was performed with neat benzaldehyde and nitroethane in the absence of any metal catalyst, at 60 °C. No β -nitroalkanol was detected after 24 h of reaction time (entry 12, Table 3). The nitroaldol reaction also did not occur appreciably (9% yield of nitroethanol) by using $Ni(OAc)_2$ instead of the catalyst precursor 1 or 2 (entry 13, Table 3).

To determine the catalytic performance of **2** in the nitroaldol condensation reaction, a series of aromatic and aliphatic aldehydes were selected to screen as starting materials (Table 4). In general, the reactivity of the substituted benzaldehydes is less than benzaldehyde itself, possibly the presence of steric hindrance. In the case of substituted aromatic aldehydes having electron-withdrawing substituents in para-position, higher yields (entries 5 and 7, Table 4) are obtained, which may be attributed to the higher electrophilicity of the substrate compared to the aldehydes bearing electron-donating moieties. A maximum yield of 97% with a *syn: anti* diastereoselectivity ratio of 80:20 was observed for the aldehyde, which is para-nitro-substituted (entry 7, Table 4). For the aliphatic aldehydes, acetaldehyde and propionaldehyde (entries 8 and 9, Table 4), a maximum of 78.2% yield was obtained for propionaldehyde (entry 9, Table 4) with a *syn: anti* diastereoselectivity ratio of 74:26.

The catalytic activity of compound **2** was also compared in the reactions using various substituted aromatic aldehydes with different nitroalkanes, producing the corresponding β-nitroalkanols (Scheme 3), leading to yields ranging from 38% to 94% (Table 5).
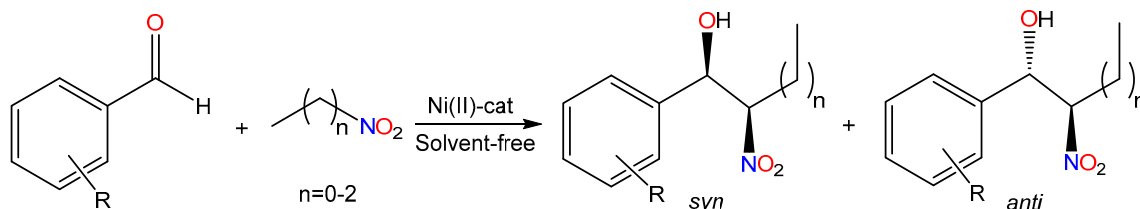
Scheme 3. Nitroaldol condensation reaction of various aldehydes and different nitroalkanes.

**Table 5.** Solvent-free nitroaldol condensation of different aldehydes and nitroalkanes catalyzed by **2** [a].

Entry	Aldehyde	Nitroalkane	Yield or Conversion /% [b]	*syn: anti* ratio [c]	TOF/h^{-1} [d]
1		nitromethane	94.2	-	3.9
2	CHO	nitroethane	94.0	77:23	3.9
3		nitropropane	54.2	68:32	2.5
4		nitromethane	56.6	-	2.3
5		nitroethane	44.4	66:34	1.8
6		nitropropane	38.4	58:42	1.6

[a] Experimental conditions: Catalyst **2**, (1.0 mol%), aldehyde (1 mmol), nitroalkane (2 mmol), 24 h, 60 °C; [b] Determined using ^{1}H NMR analysis (see Experimental); [c] Molar ratio, determined using ^{1}H NMR; [d] Estimated as moles of *syn*- and *anti*-β-nitroethanol/mol of **2**, per hour.

In general, the yield of β-nitroalkanol decreased in the order of nitromethane > nitroethane > 1-nitropropane for both aldehydes, and the same molecular size dependent behavior was found for the

aldehydes (Table 5). A proposed catalytic cycle promoted by Ni(II) centre is presented in Scheme 4 showing the reaction pathway towards the formation of the β-nitroalkanols.
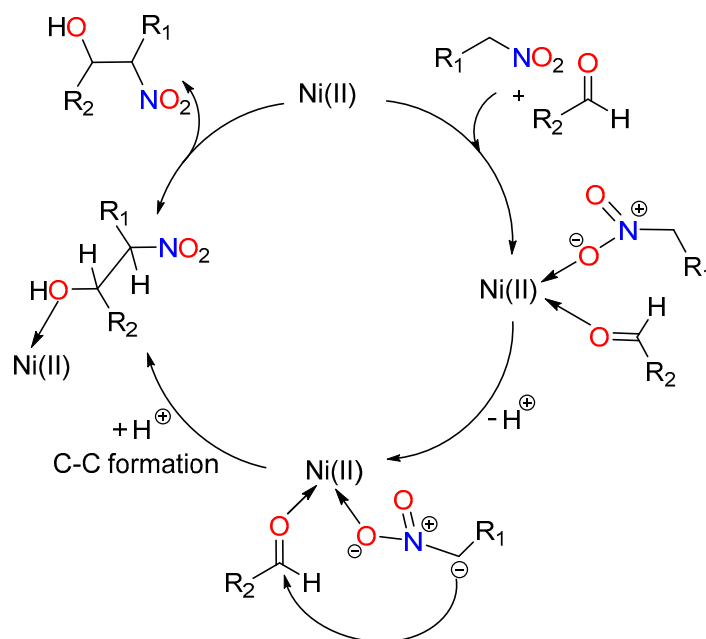
Scheme 4. Proposed catalytic cycle for the β-nitroalkanol formation in the Ni(II) catalyzed nitroaldol reaction.

3. Materials and Methods

The syntheses for this study were performed in air and reagents and solvents (commercially available) that were used as received, without further purification. The metal source for the synthesis of complexes was $Ni(NO_3)_2 \cdot 6H_2O$. Elemental analyses (C, H, and N) were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker Vertex 70 instrument in KBr pellets (Bruker Corporation, Ettlingen, Germany); wavenumbers are in cm^{-1}. The ^{1}H NMR spectra were recorded on a Bruker Avance II + 400.13 MHz (UltraShieldTM Magnet) spectrometer at room temperature. The internal reference was tetramethylsilane. The chemical shifts are reported in ppm in the ^{1}H NMR spectra. Mass spectra were recorded in a Varian 500-MS LC Ion Trap Mass Spectrometer (Agilent Technologies, Amstelveen, The Netherlands) equipped with an electrospray (ESI) 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 carried out from *m/z* 100 to 1200 in methanol solution. The compounds were observed in the positive and negative mode (capillary voltage = 80–105 V).

3.1. Syntheses of the Pro-Ligand H_2L

The aroylhydrazone pro-ligand 2-hydroxy-(2-hydroxybenzylidene)benzohydrazide (H_2L^1) and (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H_3L^2) (Scheme 1) were prepared by a reported method [47,48] upon condensation of the 2-hydroxybenzohydrazine with 2-hydroxybenzaldehyde or 2,3-dihydroxybenzaldehyde.

3.2. Synthesis of the Nickel(II) Complexes

- Synthesis of $[Ni_2(L^1)_2(MeOH)_4]$ (**1**)

First, 0.26 g (1.01 mmol) of H_2L^1 was dissolved in 25 mL of methanol, and $Ni(NO_3)_2 \cdot 6H_2O$ (0.32 g, 1.10 mmol) were added to it. The resultant mixture was stirred for 15 min at 50 °C; a dark green solution was obtained. The dark green solution was then filtered, and the solvent was allowed to

evaporate slowly. After 1 d, a green microcrystalline powder was obtained, washed 3 times with cold methanol, and dried in open air.

Yield: 0.293 g (78%, with respect to Ni(II)). Anal. Calcd for (**1**) $C_{32}H_{36}N_4Ni_2O_{10}$: C, 50.97; H, 4.81; N, 7.43. Found: C, 50.93; H, 4.78; N, 7.39. IR (KBr; cm^{-1}): 3416 ν(OH), 1609 ν(C=N), 1254 ν(C–O) enolic and 1154 ν(N–N). ESI-MS(+): *m/z* 753 [**1**+H]$^+$ (100%).

- Synthesis of $[Ni_2(L^1)_2(DMF)_4]$ $[Ni_2(L^1)_2(DMF)_2(H_2O)_2]\cdot2DMF$ (**1A**)

The green microcrystalline powder of **1** was dissolved in DMF and few drops of water was added. After *ca.* 3 d, nice green crystals were isolated from the solution. Isolated compound was washed 3 times with cold methanol and kept in open air for drying. The crystals are insoluble in common organic solvents.

Anal. Calcd for (**1A**) $C_{80}H_{96}N_{16}Ni_4O_{22}$: C, 51.42; H, 5.18; N, 11.99. Found: C, 51.39; H, 5.16; N, 11.93. IR (KBr; cm^{-1}): 3403 ν(OH), 1608 ν(C = N), 1258 ν(C–O) enolic and 1157 ν(N–N).

- Synthesis of $[Ni_3(HL^2)_2(CH_3OH)_8]\cdot(NO_3)_2$ (**2**)

First, 0.28 g, 1.02 mmol of H_3L^2 was dissolved in 25 mL of methanol and 0.58 g, 2.0 mmol of $Ni(NO_3)_2\cdot6H_2O$ were added to it. The resultant mixture was stirred for 15 min at 50 °C to obtain a dark green solution. A clear solution was obtained by filtering the mixture and the solvent was then allowed to evaporate slowly. After 1 d, green X-ray quality single crystals were isolated. The isolated compound was then washed 3 times with cold methanol and dried in open air.

Yield: 0.394 g (74%, with respect to Ni(II)). Anal. Calcd for (**2**) $C_{36}H_{52}N_6Ni_3O_{20}$: C, 40.60; H, 4.92; N, 7.89. Found: C, 40.54; H, 4.88; N, 7.85. IR (KBr; cm^{-1}): 3386 ν(OH), 2964 ν(NH), 1603 ν(C=O), 1387 ν(NO$_3^-$) and 1068 ν(N–N). ESI-MS(-): *m/z* 939 [**2**-2(NO$_3$)-H]$^-$ (100%).

3.3. X-ray Measurements

Single crystals of complexes **1A** and **2** appropriate for X-ray diffraction analysis were immersed in cryo-oil, mounted in Nylon loops, and measured at 296 K. A Bruker AXS PHOTON 100 diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation was used to collect the intensity data. Data collections were recorded using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART [49] software and the data were refined using Bruker SAINT [49] on all the observed reflections. Absorption corrections were done using SADABS [49]. Structures were solved by direct methods by applying SIR97 [50] and refined with SHELXL2014 [51]. Calculations were carried out using WinGX v2014.1 [52]. All non-hydrogen atoms were refined anisotropically. Those H-atoms bonded to carbon were placed in the model at geometrically calculated positions and refined using a riding model. $U_{iso}(H)$ were defined as $1.2U_{eq}$ of the parent carbon atoms for phenyl and methyne residues and $1.5U_{eq}$ of the parent carbon atoms for the methyl groups. Least square refinements were employed with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms.

3.4. Catalytic studies

All catalytic tests were run under atmospheric ambiance under with the following conditions for each essay: 1.0–5.0 mol% (0.1–0.5 µmol) of the catalyst precursor **1** or **2** (usually 1 mol%) under solvent-free condition contained 2 mmol of nitroethane and 1 mmol of aldehyde, in that order, or added solvent (2 mL) for reaction in a particular solvent. The reaction mixture was stirred at the particular temperature for the required duration. The solvent was then evaporated, the residue was dissolved in CDCl$_3$, and analyzed by ^{1}H NMR. In the case of solvent-free conditions, the reaction mixture was dissolved in CDCl$_3$ and analyzed by ^{1}H NMR. A previously reported method was employed to determine the yield of the β-nitroalkanol product (relatively to the aldehyde) by ^{1}H NMR [47,48]. To verify the adequacy of the procedure, a number of ^{1}H NMR analyses were performed in the presence

of 1,2-dimethoxyethane as an internal standard, added to the CDCl$_3$ solution, giving yields similar to those obtained by the above method. Moreover, the internal standard method also confirmed the absence of other side products formed. The ratio between the syn and anti isomers was also determined by ^{1}H NMR spectroscopy. The values of vicinal coupling constants (for the β-nitroalkanol products), in the ^{1}H NMR spectra, 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 [53,54].

4. Conclusions

Binuclear and trinuclear aroylhydrazone Ni(II) complexes in two different tautomeric forms (enol and keto) [Ni$_2$(L^1)$_2$(MeOH)$_4$] (**1**) and [Ni$_3$(HL^2)$_2$(CH$_3$OH)$_8$]·(NO$_3$)$_2$ (**2**), where H$_2$L^1 = 2-hydroxy(2-hydroxybenzylidene)benzohydrazide, and H$_3$L^2 = (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide, have been synthesized and fully characterized. They act as efficient catalysts for the solvent-free Henry reaction of β-nitroalkanols formation with excellent yields and diastereoselectivity. The avoidance of a solvent, either organic or ionic liquid, in this reaction brings a number of benefits render it a safer, more economical, and environmentally benign C–C coupling process.

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