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Graphical Abstract



The Henry reaction catalyzed by Ni^{II} and Cu^{II} complexes bearing arylhydrazones of acetoacetanilide

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Abstract

The new nickel coordination polymer $[Ni(HL^1)(CH_3OH)_2]_n$ (1) and co-crystal H_3L^1 ·DMF (2) were obtained by reaction of $NiCl_2 \cdot 2H_2O$ with 2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene) hydrazineyl)benzoic acid (H_3L^1) in the presence and absence of triethylamine, respectively, in a mixture of methanol and dimethylformamide (DMF) (20:1, v/v). Reaction of $CuCl_2 \cdot 2H_2O$ with H_3L^1 in the presence of 2,2'-(methylazanediyl)*bis*(ethan-1-ol) (HR) in methanol yields $[Cu(HR)_2(H_2L^1)_2]$ (3), whereas treatment of this copper salt with sodium 2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl)benzenesulfonate (NaH_2L^2) in a mixture of acetone and water (10:1, v/v) produces $[Cu(HL^2)(H_2O)_2] \cdot 2(H_2O) \cdot \{(CH_3)_2C=O\}$ (4). Compounds 1–4 were characterized by IR and ESI-MS spectroscopies, elemental and X-ray crystal structural analyses, and tested as catalyst for the Henry reaction of aliphatic and aromatic aldehydes with nitroethane in different solvents such as acetonitrile, methanol or water. Good yields (up to 87%) and diasteroselectivities (*syn/anti* 77:23) were observed in the reactions catalyzed by **3** in water.

Keywords: Ni^{II} and Cu^{II} complexes; arylhydrazones of acetoacetanilide; Henry reaction

1. Introduction

The Henry (nitroaldol) reaction describes the catalytic coupling of a nucleophilic nitro alkane with an electrophilic aldehyde or ketone to produce a highly synthetically useful β -nitroalcohol (Scheme 1) [1]. The prepared functionalized β -nitroalcohols represent important synthetic building blocks that have been used in the syntheses of 2-amino alcohols, nitroalkenes, α -nitroketones,

pharmaceutical substances, etc. [1-6]. Both deasterioselectivity and yield of β -nitroalcohols are strongly depending on used catalysts. Up to now, many homogeneous catalysts, such as amberlyst A-21 [7], cinchona alkaloid [8], alkali metal hydroxides, alkoxides or amines [7,9], a rhodium complex in the presence of a silvl ketene acetal [10], heterobimetallic complexes with lanthanide BINOL (BINOL = 2,2'-dihydroxy-1,1'-binaphthyl) systems [11], Mg-Al hydrotalcite [12,13], guanidines [14], benzyltrimethylammonium hydroxide [15], proazaphosphatranes [16], Cubis(oxazoline) [17] or Co-salen (salen = N,N'-bis(salicylidine)ethylenediamine) complexes [18,19] Zn(II) dinuclear complexes [20,21] or a mixture of $Zn(OTf)_2$ (OTf = triflate) and (+)-Nmethylephedrine [22], Zn(II)-1,3,5-triazapentadienato [23], etc. were used in the Henry reaction aldehydes nitroalkanes. Most of these suffer between and methods from some disadvantages/limitations, such as relatively high catalyst amount, long reaction time, toxic solvents, narrow substrate scope, low reaction temperatures, use of additives, multistep synthetic procedures for catalyst preparation, etc. Thus, the development of readily available, highly deasteriostereoselective and cheaper catalysts for Henry reaction with a broad range of aldehyde substrates is still highly desirable.



Scheme 1. The Henry (nitroaldol) reaction.

Arylhydrazones of active methylene compounds (AHAMC) and their complexes have attracted much attention due to their useful properties such as catalysts, molecular switches, sensors, liquid crystals, etc. [24]. Ln, Fe^{III}, Zn^{II}, Cu^{II}, Ni^{II}, Sn^{II/IV}, Co^{II} and UO₂^{II} complexes of AHAMCs have already been applied as catalysts for C–C coupling of aldehydes with nitroalkanes [25]. Now, we herein report the use of [Ni(HL¹)(CH₃OH)₂]_n (1), H₃L¹·DMF (2) [Cu(HR)₂(H₂L¹)₂] (3) and [Cu(HL²)(H₂O)₂]·2(H₂O)·{(CH₃)₂C=O} (4) (H₃L¹ = 2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl)benzoic acid, NaH₂L² = 2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene) hydrazineyl)benzenesulfonate, HR = 2,2'-(methylazanediyl)*bis*(ethan-1-ol)) as the homogenous catalysts for the Henry reaction of aliphatic and aromatic aldehydes with nitroethane to afford β -nitroalcohols in high yields in water at room temperature.

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. H_3L^1 and NaH_2L^2 were synthesized according to the reported procedure [25g,26]. The ¹H NMR spectra were

recorded at room temperature on a Bruker Avance II + 400 (UltraShieldTM Magnet) spectrometer operating at 400 MHz for proton. The chemical shift is reported in ppm using tetramethylsilane as the internal reference. Elemental analyses (C, H, and N) were performed on a Finnigan EA 1112 instrument. 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 0 to 1200 in methanol solution. The compounds were observed in the positive or negative mode (capillary voltage = 80–105 V).

2.2. Synthesis

2.2.1. Synthesis of 1 and 2

0.1 mmol (33 mg) of H_3L^1 were dissolved in 20 mL of methanol-dimethylformamide (20:1 v/v) mixture, then 0.1 mmol (28 mg) of NiCl₂·2H₂O and 0.1 mL of triethylamine (in the case of 1) were added and the system was stirred for 10 min. After *ca*. 3 d at room temperature, yellow (brown in the case of 1) crystals precipitated which were then filtered off and dried in air.

1: Yield, 55 %. Calcd. for $C_{19}H_{21}N_3NiO_6$ (*Mr* = 446.09): C 51.16, H 4.75, N 9.42; found C 51.07, H 4.63, N 9.36. MS (ESI, positive ion mode), *m/z*: 383.02 [*Mr*-2CH₃OH+H]⁺. IR (KBr): 3458 (br) v(OH), 3008 v(NH), 1676 (s) v(C=O), 1592 v(C=N) cm⁻¹.

2: Yield, 70 %. Calcd. for C₂₀H₂₂N₄O₅ (Mr = 398.42): C 60.29, H 5.57, N 14.06; found C 60.22, H 5.49, N 14.01. MS (ESI, positive ion mode), m/z: 326.20 [Mr-DMF+H]⁺. IR (KBr): 3434 v(H₂O), 3241 v(NH), 1696 and 1662 v(C=O), 1599 v(C=N) cm⁻¹.

2.2.2. Synthesis of 3

0.1 mmol (33 mg) of H_3L^1 were dissolved in 15 mL of methanol, then 0.1 mmol (17 mg) of $CuCl_2 \cdot 2H_2O$ and 0.1 mmol (12 mg) of 12,2'-(methylazanediyl)*bis*(ethan-1-ol) were added and the system was stirred for 10 min. After *ca*. 2 d at room temperature, greenish crystals precipitated which were then filtered off and dried in air.

3: Yield, 57 %. Calcd. for $C_{44}H_{54}CuN_8O_{12}$ (*Mr* = 950.51): C 55.60, H 5.73, N 11.79; found C 55.53, H 5.67, N 11.72. MS (ESI, positive and negative ion modes), *m/z*: 150.54 $[Cu(C_{10}H_{26}N_2O_4)^{2+}]$ and 324.30 $[H_2L^1]^-$. IR (KBr): 3401, 3384 and 3372 (br) v(OH), 3211 v(NH), 1669 (s) v(C=O), 1600 v(C=N) cm⁻¹.

2.2.3. Synthesis of 4

0.1 mmol (38 mg) of NaH₂L² were dissolved in 15 mL of acetone-water (15:1 ν/ν) mixture, then 0.1 mmol (17 mg) of CuCl₂·2H₂O was added and the system was stirred for 5 min. After *ca*. 3 d at room temperature, brown crystals precipitated which were then filtered off and dried in air.

4: Yield, 49 %. Calcd. for C₁₉H₂₇CuN₃O₄S (Mr = 553.04): C 41.26, H 4.92, N 7.60; found C 41.22, H 4.87, N 7.55. MS (ESI, positive ion mode), m/z: 423.90 [Mr-4H₂O-{(CH₃)₂C=O}+H]⁺. IR (KBr): 3420 (s, br) v(OH), 3175 v(NH), 1639(s) v(C=O), 1598 v(C=N) cm⁻¹.

2.3. Crystal structure determination

X-ray diffraction patterns of 1–4 were collected using a Bruker SMART APEX-II CCD area detector equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. Absorption correction was applied by SADABS [27,28]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using Bruker's SHELXTL-97 [29]. All non-hydrogen atoms were refined anisotropically. The details of the crystallographic data, selected bond distances and angles for 1–4 are summarized in Tables S1-S3. Crystallographic data for the structural analysis has been deposited to the Cambridge Crystallographic Data Center (CCDC 1839644 for 3, 1833022 for 2, 1839643 for 3, and 1839645 for 4). Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or <u>www.ccdc.cam.ac.uk/data_request/cif</u>).

2.2. Catalytic activity studies

To a 10 mL vial were added the catalyst (1.0–6.0 mol%) and 2 mL solvent (CH₂Cl₂, MeCN or MeOH) and the solution was stirred for 2 min at room temperature. Then, the aldehyde (1 mmol) and nitroethane (4 mmol) were added and the resulting transparent homogeneous solution was stirred at room temperature for the appropriate time. The solvent was removed under reduced pressure and the resulting mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford the Henry reaction product (isolated yield) [30]. The analytical data of the obtained β -nitroalcohols are in good agreement with literature [31,32]. The *syn/anti* diastereoselectivity of the β -nitroalcohols was determined by ¹H NMR spectroscopy (in CDCl₃) based on the vicinal coupling constants of the products between the α -N–C–H and the α -O–C–H [30–34].

3. Results and discussion

3.1. Synthesis and characterization of 1-4

Both ligands, 2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl)benzoic acid (H_3L^1) and sodium 2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzenesulfonate (NaH_2L^2) , were reported earlier by some of us [25g,26]. Reaction of NiCl₂·2H₂O with 2-(2-(1,3-H_3L^1 in the presence and absence of triethylamine, in a mixture of methanol and dimethylformamide (DMF) (20:1, v/v) leads to $[Ni(HL^1)(CH_3OH)_2]_n$ (1) and H_3L^1 ·DMF (2), respectively (Scheme 2). It has already been proved that the coordination ability of AHAMC can be improved by addition of a base to reaction mixture for a weakening of the resonance assisted hydrogen bond (RAHB) in these ligands (Scheme 2) [24d,s]. Thus, only Fe(III)-AHAMC or Cu(II)-AHAMC complexes can be obtained by direct reaction of metal salts with AHAMC [24s]. In order to obtain other metal complexes of AHAMC ligands the base should be used for destroy strong RAHB system (Scheme 2). Due to the strong coordination ability of the used auxiliary ligand, 2,2'-(methylazanediyl)*bis*(ethan-1-ol) (HR), the reaction of CuCl₂·2H₂O with H₃L¹ in the presence of HR in methanol yields [Cu(HR)₂(H₂L¹)₂] (**3**), which compoused by [Cu(HR)₂]²⁺ complex cation and two anionic moieties [(H₂L¹)⁻]₂ (Scheme 2).

A monomeric complex $[Cu(HL^2)(H_2O)_2] \cdot 2(H_2O) \cdot \{(CH_3)_2C=O\}$ (4) was obtained by reaction of CuCl₂·2H₂O with NaH₂L² in a mixture of acetone and water (10:1, v/v) (Scheme 2). The compounds 1–4 are characterized by ESI-MS, IR spectroscopy, elemental analysis and single crystal X-ray diffraction (see Tables S1-S3, Fig.). In the IR spectrum of 1, the v(NH), v(C=O) and v(C=N) signals appear at 3008, 1676 and 1592 cm⁻¹, respectively, values that are significantly shifted in relation to the corresponding signals of H₃L¹ [3240 v(NH), 1696 and 1663 v(C=O), 1599 v(C=N) cm⁻¹] [26], whereas same groups in 2 have similar signals at 3241 v(NH), 1696 and 1662 v(C=O), 1599 v(C=N) cm⁻¹. In the IR spectrum of 3, the v(NH) and v(C=O) signals are also significantly shifted: 3211 v(NH) and 1669 (s) v(C=O) cm⁻¹. The IR spectrum of 4 shows v(NH) and v(C=O) vibrations at 3175 and 1639 cm⁻¹ respectively, which significantly shift in relation to the corresponding signals of NaH₂L² [2925 v(NH) and 1669 v(C=O) cm⁻¹)] [25g]. Fragmentation peaks in mass spectra of the compounds can be related as follows: 383.02 [*Mr*-2CH₃OH+H]⁺ (for 1), 326.20 [*Mr*-DMF+H]⁺ (for 2), 150.54 [Cu(C₁₀H₂₆N₂O₄)²⁺] and 324.30 [H₂L¹]⁻ (for 3) and 423.90 [*Mr*-4H₂O-{(CH₃)₂C=O}+H]⁺ (for 4). The elemental analyses are consistent with the proposed formulations, which are also supported by X-ray crystallography (Fig.).

In 1, the nickel ion has a distorted octahedral coordination geometry with the chelating hydrazone ligands occupying the four equatorial positions and the apical sites being engaged with the methanol molecules (Fig.). The molecular structure of 2 contains two RAHB systems as well as an intramolecular six-membered hydrogen-bonded ring. The asymmetric unit of 3 comprises one anionic $(H_2L^1)^-$ molecular with two RAHB systems and half of the $[Cu(HR)_2]^{2+}$ complex cation, which both units are gathered by intermolecular hydrogen interactions (Fig.).



Scheme 2. Synthesis of 1–4.





Fig. Crystal structures of 1–4 with partial atom numbering scheme. H-bond interactions are shown as dashed blue lines.

3.2. Catalytic activity of 1-4 in the Henry reaction

Initially, 1, 2, 3, 4, NiCl₂: $2H_2O$, CuCl₂: $2H_2O$, H_3L^1 and NaH₂L² were screened in a model Henry reaction between benzaldehyde and nitroethane in different solvents (dichloromethane, acetonitrile and methanol) at room temperature and the results are listed in Table 1. Of these catalysts, 3 was found to be the best for this reaction, affording the expected β -nitroalcohol product in 66% yield with syn : anti = 73:27 in water after 24 h (Table 1, entry 25), what can eventually be associated to the ionic character of this compound. No C-C coupling reaction between nitroethane and benzaldehyde takes place in solvent-free conditions as well as in dichloromethane, acetonitrile and methanol in the absence of catalysts (1-3) or metal salts (entries 1-5, 8). NiCl₂· 2H₂O, CuCl₂· 2H₂O, H_3L^1 and $N_3H_2L^2$ lead to the yield of β -nitroalcohols of 4–39 % in 24 h (entries 6,7, 9–16), what is substantially lower than those obtained in the presence of complexes 1-3 in water (43-66 %, entries 19, 25 and 28). Thus, **3** and water were chosen as the catalyst and sole solvent, respectively, for further studies. The increase of reaction time from 0.5 h to 24 h led to higher conversion (entries 1–6, Table 2), however the 4 h appears to be the optimal reaction time. To optimize the catalyst loading, the reaction was carried out with different amounts of the catalyst and we found that 4 mol % of the catalyst was required to give the best results (Table 2, entry 10). We have also attempted to optimize the reaction by varying the temperature from 20°C to 75°C, which the yield of β -nitroaldols insignificantly increase (from 79 to 85 %) and diasteroselectivity drops from syn : anti = 74:26 to 72:28 in high temperature (Table 2, entries 10, 13–15). Furthermore, optimized reaction condition was applied for solvent-free conditions (Table 2, entry 16), which provides low yield (41 %).

Table 1. Catalyst screening and optimization.					
Entry	Catalyst	Solvent	Yield, % ^c	Selectivity, syn/anti ^d	
1 ^b	Blank	No solvent	_		
2		MeCN	-	—	
3	Blank	MeOH	-	_	
4		H ₂ O	-	_	
5		MeCN	-	_	
6	NiCl ₂ ·2H ₂ O	MeOH	4	60:40	
7		H ₂ O	9	60:40	
8		MeCN	-	_	
9	CuCl ₂ ·2H ₂ O	MeOH	7	60:40	
10		H ₂ O	11	61:39	
11		MeCN	5	59:41	
12	H_3L^1	MeOH	26	59:41	
13		H ₂ O	35	60:40	
14		MeCN	9	57:43	
15	NaH_2L^2	MeOH	27	60:40	
16		H ₂ O	39	60:40	
17		MeCN	17	62:38	
18	1	MeOH	34	65:35	
19		H ₂ O	43	70:30	
20		MeCN	6	59:41	
21	2	MeOH	26	60:40	
22		H ₂ O	37	61:39	
23		MeCN	39	70:30	
24	3	MeOH	52	72:28	
25		H ₂ O	66	73:27	
26		MeCN	32	62:38	
27	4	MeOH	49	66:34	
28]	H ₂ O	63	70:30	

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^a Reaction conditions: catalyst precursor: NiCl₂·2H₂O, CuCl₂·2H₂O, H₃L¹, NaH₂L², **1**, **2**, **3** and **4** (1.0 mol%), acetonitrile, methanol or H₂O (2 mL), nitroethane (4 mmol) and benzaldehyde (1 mmol), reaction time: 24h, reaction temperature: 20 °C. ^b Solvent-free conditions, using nitroethane as solvent (2 mL), ^c Determined by ¹H NMR, based on the starting benzaldehyde. ^d Calculated by ¹H NMR (see Experimental).

Fable 2	. Optimiz	zation of the Henry react	ion condition	catalyzed by	3 . ^{<i>a</i>}
Entry	Time, h	Amount of catalyst, mol%	Temp., °C	Yield, % ^b	Selectivity,
1	0.5	4.0	20	39	74:2

Entry	Time, n	Amount of catalyst, mor%	Temp., C	r leid, %	Selectivity, syn/anti
1	0.5	4.0	20	39	74:26
2	1	4.0	20	55	74:26
3	2	4.0	20	67	74:26
4	4	4.0	20	79	74:26
5	6	4.0	20	79	75:25
6	24	4.0	20	79	75:25
7	6	1.0	20	66	73:27
8	6	2.0	20	72	74:26
9	6	3.0	20	76	75:25
10	6	4.0	20	79	75:25
11	6	5.0	20	80	75:25
12	6	6.0	20	80	75:25
13	6	4.0	35	82	73:27
14	6	4.0	55	84	73:27
15	6	4.0	75	85	72:28
16 ^d	6	4.0	20	41	74:26

^a Reaction conditions: 1.0–6.0 mol% of catalyst precursor (typically 5.0 mol%), H₂O (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol). ^b Isolated yields after column chromatography. ^c Determined by ¹H NMR. ^d Solvent-free conditions, using nitroethane as solvent (2 mL).

In order to check the substrate scope of this C–C coupling reaction catalyzed by 3 with the optimized conditions mentioned above, the reactions were carried out using various substrates. The results are summarized in Table 3. A wide range of aromatic aldehydes participate well in this reaction affording the corresponding β -nitroalcohols in moderate to good yields (65–87%) and moderate diasteroselectivities (*syn* : *anti* = 72:28 – 75:25). The aromatic aldehydes with *para* electron-withdrawing substituents show better yield than those with electron-donating substituents (entries 1–7). It is noting that *ortho*-substituted aromatic aldehydes such as 2-nitrobenzaldehyde and 2-methylbenzaldehyde, which are considered as sterically hindered substrates also provided admirable yields of β -nitroalcohols (entries 8 and 9). Whereas, 2,4,6-trimethylbenzaldehyde decreases the yield and diasteroselectivity of β -nitroalcohols (entry 10). When aliphatic aldehydes propionaldehyde, butyraldehyde and pentanal were chosen as substrates the reaction was much effective (Table 2, entries 11–13).

Entry	Substrate	Yield, % ^b	Selectivity, <i>syn/anti^c</i>
1	4-(Dimethylamino)benzaldehyde	67	73:27
2	4-Methoxybenzaldehyde	74	73:27
3	4-Methylbenzaldehyde	76	74:26
4	Benzaldehyde	79	74:26
5	4-Bromobenzaldehyde	81	74:26
6	4-Chlorobenzaldehyde	82	74:26
7	4-Nitrobenzaldehyde	84	75:25
8	2-Nitrobenzaldehyde	82	73:27
9	2-Methylbenzaldehyde	79	73:27
10	2,4,6-trimethylbenzaldehyde	65	72:28
11	Propionaldehyde	87	75:25
12	Butyraldehyde	86	75:25
13	Pentanal	85	75:25

Table 3. Henry reaction of nitroethane with various aldehydes catalyzed by 3.^a

^a Reaction conditions: 5.0 mol% of catalyst **3**, H₂O (2 mL), nitroethane (4 mmol) and aldehyde (1 mmol), reaction time: 4 h. ^b Isolated yields after column chromatography. ^c Determined by ¹H NMR.

In comparison to other reported catalysts, such as lanthanide/sodium amide systems (48–85%) [11], copper(II) complexes (70–77%) with amidoterephthalate [35], pyrrolidine-based organocatalyst (67%) [36], scorpionate complex [NiCl{SO₃C(pzPh)₃}] (pz = pyrazolyl; 31.5% yield for benzadehyde) [1q], 2-((*E*)-(((1*S*)-quinolin-4-yl(5-vinylquinuclidin-2-yl)methyl)imino) methyl) phenol (72) [37], (*S*)-2-((2-(hydroxydiphenylmethyl)pyrrolidin-1-yl)methyl)-6-(trifluoromethyl) phenol (81) [43], etc. our complex **3** shows high catalytic performance in the C–C coupling of both aliphatic and aromatic aldehydes with nitroethane.

4. Conclusions

Four new compounds, Ni^{II}-coordination polymer (1), co-crystal (2), Cu^{II}-ionic (3) and Cu^{II}mononuclear (4) complexes containing dicarboxylic- or sulfonic functionalized arylhydrazones of acetoacetanilide have been synthesized by variation of reaction condition and structurally characterized. All compounds have been tested as homogeneous catalysts for the addition of nitroethane to aliphatic or aromatic aldehydes producing the corresponding β -nitroalkanols (Henry reaction). Ionic complex **3** was found to be the efficient catalyst for this C–C coupling reaction in water (green solvent), producing β -nitroalcohols with good yields (65–87%) and diastereoselectivities (*syn/anti* 75:25–72:28).

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Highlights

- ▶ Ni^{II} and Cu^{II} complexes bearing arylhydrazones of acetoacetanilide
- \blacktriangleright Ionic Cu^{II} complex shows high catalytic activity in Henry reaction
- ► The catalytic activity depends on the nature of solvents, and water was chosen as green solvent