Synthesis and Catalytic Activity of Novel Ni–N Complexes¹

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Abstract—A series of nickel complexes with 1,3-xylylenediamine, 1,2-diaminobenzene and 1,2aminobenzylamine were first synthesized and characterized. The reaction of these amines with Ni(OAc)₂ · $4H_2O$ and NiCl₂ · $6H_2O$ in methanol or tetrahydrofuran resulted in the production of four novel nickel complexes I, II, III, and IV. The structure of each complex was determined by X-ray diffraction analysis. Each complex was also characterized using elemental analysis, ¹H NMR and IR. The complexes were then used to catalyze the Henry reaction, and good catalytic results (65–99%) were achieved. The catalytic activity of the complexes was determined by ¹H NMR.

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INTRODUCTION

Nickel complexes have widely been used as the catalysts in organic reactions and polymerization [1-6]. In the metal complex catalysis, nickel has low price and toxicity and good coordination ability. Therefore, it is more desirable to be placed at the center of the metal elements, and many nickel-based metal complex catalysts have been designed and synthesized. For example, chiral Ni(II) complex of glycine with (N-trans-enovl)oxazolidines was used as the catalyst in asymmetric Michael addition reactions [7]. The Henry reaction is a classical C-C bond reaction. It is widely used in pharmaceutical intermediates and natural product synthesis [8]. β-Nitro alcohol addition product is an important intermediate in the subsequent reaction by the formation of a variety of groups, such as through oxidation of the corresponding aldehydes, ketones, or carboxylic acid and amino compounds by the reduction reaction. Recently, it has been reported that the zinc and copper complexes can also catalyze the Henry reaction [9-11]. Inspired by their work, our efforts have been focused on devising new late transition metal complexes bearing simple ancillary ligands for catalytic co-addition of aldehyde to other monomers. In this paper, we first describe the synthesis of novel complexes with a simple one-pot method, and our complexes were used to catalyze the Henry reaction.

EXPERIMENTAL

1,2-Aminobenzylamine, 1,2-diaminobenzene and 1,3-xylylenediamine were purchased from Acros, Ald-

rich and Fluka. Elemental analysis was carried out with a Perkin–Elmer 2400-CHN instrument. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer.

Synthesis of complex I. 2.6 mL of 1,3-xylylenediamine (0.02 mol) was added to 30 mL of a THF solution of 1.2450 g (0.005 mol) Ni(OAc)₂ · 4H₂O in a dry 100 mL Schlenk flask. The reaction mixture were refluxed for 24 h. The solvent was reduced under vacuum. Blue solids were obtained after rotary evaporation, and then recrystallized with hexane and ethanol. The blue crystals were obtained. The yield was 45%.

For C ₂₀ H ₃₀ N ₄ O	₄ Ni		
anal. calcd., %:	C, 53.48;	Н, 6.73;	N, 12.47.
Found, %:	C, 52.88;	Н, 6.62;	N, 12.14.

IR (KBr; v, cm⁻¹): 3248, 3166, 2962, 1599, 1347, 1025, 715, 599.

Synthesis of complex II. 1.0814 g (0.01mol) of 1,2diaminobenzene was added to 30 mL of THF, and 1.1884 g (0.005 mol) of NiCl₂ \cdot 6H₂O in a dry 100 mL Schlenk flask. The reaction mixture was refluxed for 72 h. After hot filtration, the residue was washed with THF first, and then dissolved in DMF. The solvents reduced under vacuum, and the light blue crystals were obtained. The yield was 41.3%.

¹ The article is published in the original.

¹H NMR (300 MHz; CDCl₃; 27°C; δ, ppm): 6.93 (t., 1H), 6.11–6.12 (d., *J* = 6.5 Hz, 2H), 6.04(s., 1H), 3.82 (s., 4H), 2.11(s., 6H).

IR (KBr; v, cm⁻¹): 3292, 3196, 3164, 3108, 1608, 1572, 1495, 1249, 1219, 1099, 1027, 942, 751, 622, 500.

Synthesis of complex III. 0.6109 g (0.005 mol) of 1,2-aminobenzylamine was added to 30 mL of THF, (0.6221 g, 0.0025 mol) Ni(OAc)₂ \cdot 4H₂O in a dry 100 mL Schlenk flask. The reaction mixture was refluxed for 72 h. After hot filtration, the residue was recrystallized with CH₂Cl₂ and hexane, and the blue crystals were obtained. The yield was 35.8%.

For C₁₈H₃₄N₄O₈Ni

anal. calcd., %:	C, 43.83;	Н, 6.94;	N, 11.36.
Found, %:	C, 43.77;	Н, 6.82;	N, 11.09.

IR (KBr; v, cm⁻¹): 3341, 3238, 3040, 2887, 2326, 1554, 1498, 1409, 1333, 1271, 1056, 942, 864, 753, 653, 511.

Synthesis of complex IV. 0.6108 g (0.005 mol) of 1,2-aminobenzylamine was added to 30 mL of anhydrous methanol and (0.5942 g, 0.0025 mol) of NiCl₂· $6H_2O$ in a dry 100 mL Schlenk flask. The reaction mixture was refluxed for 72 h. After hot filtration, the residue was recrystallized with DMF and anhydrous ethyl ether, and the light blue crystals were obtained. The yield was 38.6%.

For $C_{12}H_{16}Cl_2N_4Ni$ anal. calcd., %: C, 41.66; H, 4.66; N, 16.19. Found, %: C, 41.46; H, 4.52; N, 16.09.

¹H NMR (300 MHz; CDCl₃; 27°C; δ, ppm): 6.93 (t., 1H), 6.11–6.12 (d., *J* = 6.5 Hz, 2H), 6.04 (s., 1H), 3.82 (s., 4H), 2.11(s., 6H), IR (KBr; ν, cm⁻¹): 3292, 3196, 3164, 3108, 1608, 1572, 1495, 1249, 1219, 1099, 1027, 942, 751, 622, 500.

Synthesis of 2-nitro-1-phenylethanol (V). Catalysts I, II, III, and IV (0.148 mmol), benzaldehyde (0.10 mL,

0.986 mmol), and nitromethane (0.50 mL, 9.255 mmol) were successively added together at room temperature. After 72 h, the reaction was quenched. Purification was performed using silica gel chromatography (petroleum ether-dichloromethane (v/v = 7 : 3). The title compound was obtained as a colorless liquid in a 50% yield of compound V. ¹H NMR (300 MHz; CDCl₃) 7.187.23 (m., 2H, Ar–H), 7.29–7.43 (m., 3H, Ar–H), 4.73–4.78 (m., 3H), 4.26–4.30 (m., 1H).

Synthesis of (E)- β -nitrostyrene radical anion (VI). Following the procedure describing the synthesis of V. ¹H NMR (300 MHz; CDCl₃) 8.00 (d., J = 23Hz, 1H), 7.47–7.63 (m., 6H). The yield was 40%.

X-ray structure determination. Crystal of complexes I, II, III, and IV were chosen and mounted on a SMART 1000 CCD diffractometer. The data were collected with graphite-monochromated MoK_{α} radiation $(\lambda = 071073 \text{ Å})$ using an $\omega - 2\theta$ scan technique. The structures were solved using direct methods and refined by a full-matrix least-squares technique. All non-hydrogen atoms were assigned to anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structures were refined on F^2 using SHELXTL-97 [12–14]. The crystal used for the diffraction study showed no decomposition during data collection. The crystal data and refinement data for compound I are listed in Table 1. Selected bond lengths and bond angles are given in the figure captions.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 818121-818124); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISSCUSSION

The synthetic routes of the title four complexes can be summarized as follows:





Table 1. Crystallographic data and refinement details for I-IV

Parameter	Value			
	Ι	II	III	IV
Formula weight	493.20	345.90	465.06	619.44
Temperature, K	291(2)	291(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P\overline{1}$	C2/c
<i>a</i> , Å	8.3507(4)	11.404(3)	8.2321(5)	39.447(2)
b, Å	10.9610(6)	5.9200(14)	11.2475(6)	9.8541(4)
<i>c</i> , Å	13.7503(10)	12.168(3)	13.5369(7)	18.4277(8)
α, deg	90.00	90.00	65.589(4)	90.00
β, deg	106.342(6)	115.31(3)	74.636(4)	96.583(5)
γ, deg	90.00	90.00	86.903(5)	90.00
Volume, Å ³	1207.74(12)	742.7(3)	1098.35(11)	7115.9(6)
Ζ	2	2	2	8
$\rho_{calcd,}$ mg/mm ³	1.356	1.547	1.406	1.156
<i>F</i> (000)	524	356	488	2672
Crystal size, mm	$0.34 \times 0.31 \times 0.30$	$0.36 \times 0.33 \times 0.30$	$0.30 \times 0.20 \times 0.20$	$0.40 \times 0.40 \times 0.30$
θ Range for data collection, deg	5.25-62.61	4.29-62.68	3.72-67.08	2.87-26.02
Parameter	159	88	264	403
Goodness-of-fit on F^2	1.070	1.006	1.092	1.046
Final <i>R</i> indexes $(I > 2\sigma(I))$	$R_1 = 0.0334,$ $wR_2 = 0.0946$	$R_1 = 0.0518,$ $wR_2 = 0.1246$	$R_1 = 0.0540,$ $wR_2 = 0.1400$	$ R_1 = 0.0581, \\ wR_2 = 0.1533 $
Final <i>R</i> indexes (all data)	$R_1 = 0.0386,$ $wR_2 = 0.0995$	$R_1 = 0.0611,$ $wR_2 = 0.1291$	$R_1 = 0.0575,$ $wR_2 = 0.1433$	$R_1 = 0.1098,$ $wR_2 = 0.1623$
Largest diff. peak/hole, $e \text{ Å}^{-3}$	0.354/-0.326	0.591/-0.363	0.884/-1.532	0.890/-0.510

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Fig. 1. The molecular structure of complex **I**: selected bond lengths and angles, Ni(1)–O(1) 2.105(3), Ni(1)–O(3) 2.111(3), Ni(1)–N(3) 2.116(4), Ni(1)–N(2) 2.129(4), Ni(1)–N(4) 2.140(3), Ni(1)–N(1) 2.148(4), O(3)–C(19) 1.263(5), O(1)–C(17) 1.246(5), N(2)–C(9) 1.482(5), N(1)–C(1) 1.464(5) Å; O(1)Ni(1)O(3) 87.37(11)°, O(1)Ni(1)N(3) 87.71(13)°, O(3)Ni(1)N(3) 89.31(12)°, O(1)Ni(1)N(2) 89.33(13)°, O(3)Ni(1)N(2) 88.60(13)°, N(3)Ni(1)N(2) 176.45(14)°, O(1)Ni(1)(4) 90.73(14)°, O(3)Ni(1)N(4) 178.09(14)°, N(3)Ni(1)N(4) 90.78(14)°, N(2)Ni(1)N(4) 91.21(15)°, O(1)Ni(1)N(1) 175.35(13)°, O(3)Ni(1)N(1) 88.00(13)°, N(3)Ni(1)N(1) 92.67(15)°, N(2)Ni(1)N(1) 90.12(15)°, N(4)Ni(1)N(1) 93.90(15)°.



Fig. 2. The molecular structure of complex **II**: selected bond lengths and angles, Ni(1)–N(2) 2.081(3), Ni(1)–N(1) 2.094(3), Ni(1)–Cl(1) 2.4551(10), N(1)–C(6) 1.435(5), N(2)–C(1) 1.444(5), N(2)Ni(1)N(1) 81.44(13)°, N(2)Ni(1)Cl(1) 87.99(10)°, N(1)Ni(1)Cl(1) 89.33(9)°, C(6)N(1)Ni(1) 108.4(2)°, C(1)N(2)Ni(1) 108.6(2)°.

The synthesis of complex I was carried out in tetrahydrofuran at a ratio of 4:1 of the ligand to nickel acetate. After refluxing for 24 h, a large amount of blue solids was obtained. The blue crystals were precipitated after recrystallization from ethanol and hexane.

The synthesis of complex **II** was carried out in tetrahydrofuran using a ratio of 2 : 1 of the ligand to nickel chloride. After refluxing for 72 h, complex **II** was recrystallized with N-dimethylformamide, and brown crystals were obtained at 90°C.

The synthesis of complex **III** was carried out in tetrahydrofuran using a ratio of 2 : 1 of the ligand to nickel acetate. After refluxing for 72 h, complex **III** was recrystallized with dichloromethane and *n*-hexane (v/v = 1 : 1), and brown crystals were obtained. Complex **III** also contains two molecules of ethanol and two molecules of water with a freed root.

The synthesis of complex IV was carried out in anhydrous methanol, using a ratio of 2 : 1 of ligand to nickel acetate. After refluxing for 72 h, complex IV was recrystallized with N-dimethylformamide and anhydrous ethyl ether (v/v = 1 : 1), and brown crystals were obtained.

The four complexes were all easily dissolved in dichloromethane, chloroform, ethanol, and methanol and were difficult to dissolve in hexane, petroleum ether, and ether. The coordination number was 6 for the nickel complexes.

Complex I contained a $Ni(OAc)_2$ molecule and two 1,3-xylylenediamine molecules. The Ni^{2+} ion was co-



Fig. 3. The molecular structure of complex III: selected bond lengths and angles, Ni(1)-O(1) 2.0691(14), Ni(1)-N(2) 2.1158(17), Ni(1)-N(1) 2.1275(17), N(1)-C(1)1.433(3), O(3)-C(8) 1.246(3), O(2)-C(8) 1.245(3), N(2)-C(7) 1.478(3), C(8)-C(9) 1.502(3) Å; O(1)Ni(1)N(2) 91.33(7)°, O(1)Ni(1)N(1) 85.87(7)°, N(2)Ni(1)N(1) 88.34(7)°, C(1)N(1)Ni(1) 116.55(12)°, C(7)N(2)Ni(1) 115.44(13)°.

ordinated with two oxygen atoms, O(1) and O(3), and with nitrogen atoms N(1), N(2), N(3), and N(4) from two 1,2-aminobenzylamine molecules (Fig. 1). Thus, the complex was six-coordinate, and three molecules of ethanol and one molecule of methanol were rooted out.

Complex II also consisted of one NiCl₂ molecule and two 1.2-aminobenzylamine molecules. The Ni²⁺ ion was coordinated with two atoms Cl(1) and $Cl(2)^{i}$ and with two 1,2-aminobenzylamine nitrogen atoms N(1), N(2), $N(1)^i$, and $N(2)^i$ (Fig. 2). Thus, the complex was six-coordinate.

Similarly complex III was a Ni–N complex that consisted of a Ni(OAc)₂ molecule and two 1,2-aminobenzylamine molecules. A Ni²⁺ ion was complexed with two oxygen atoms, O(1) and $O(1)^i$ of two water molecules, and with nitrogen atoms N(1), N(2), $N(1)^{i}$, and $N(2)^{i}$ from two 1.2-aminobenzylamine molecules (Fig. 3). Thus, the complex was six-coordinate.

Complex IV consisted of a NiCl₂ molecule and two 1,2-diaminobenzene molecules. The Ni²⁺ ion was coordinated with one molecule of DMF solvent. one water molecule, and the nitrogen atoms N(1), N(2), N(3), and N(4) of two 1,2-diaminobenzene (Fig. 4), forming a six-coordinate complex with two chloride ions rooted out.

Catalysis of the Henry reaction was achieved using 15 mol % of the four complexes without any additives. The catalytic activity of the four novel complexes in the Henry reaction is shown in Table 2.





Fig. 4. The molecular structure of complex IV: selected bond lengths and angles, Ni(1)-O(1) 2.061(3),Ni(1)-N(1) 2.141(3), Ni(1)-N(2) 2.092(3), Ni(1)-N(4)2.103(3), Ni(1)-N(3) 2.116(3), Ni(1)-O(2) 2.120(3), N(2)-C(7) 1.483(5), N(3)-C(8) 1.432(5), N(4)-C(14) 1.482(5), N(1)-C(1) 1.445(5), C(15)-N(5) 1.383(4), C(16) - N(5) 1.384(4) Å; O(1)Ni(1)N(2) 86.91(13)°. O(1)Ni(1)N(4) 86.06(14)°, N(2)Ni(1)N(4) 93.38(12)°, O(1)Ni(1)N(3) 173.28(13)°, N(2)Ni(1)N(3) 90.59(12)°, N(4)Ni(1)N(3) 87.86(12)°, O(1)Ni(1)O(2) 90.90(12)°, N(2)Ni(1)O(2) 176.17(12)°, N(4)Ni(1)O(2) 89.60(12)°, N(3)Ni(1)O(2) 91.92(12)°, O(1)Ni(1)N(1) 91.76(13)° N(2)Ni(1)N(1) 89.62(12)°, N(4)Ni(1)N(1) 176.19(13)° N(3)Ni(1)N(1) 94.46(12)°, O(2)Ni(1)N(1) 87.31(12)° C(7)N(2)Ni(1) 115.6(2)°, C(15)O(1)Ni(1) 139.2(4)°. C(8)N(3)Ni(1) 114.9(2)°, C(14)N(4)Ni(1) 118.6(2)°, C(1)N(1)Ni(1) 115.4(2)°.



Based on Table 2, the conversion effciency for each of these complexes was high than 80%; thus, they are all good catalysts for the Henry reaction. In this reaction, the overall conversion rate was high, but

Table 2. Catalytic activity of complexes I-IV for the Henry reaction

Complex	Conversion, % (V)	Yield, % (VI)
Ι	>99	32
II	82	24
III	>99	20
IV	86.4	64

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compound V was prone to dehydration to form VI. Products V and VI were characterized using ¹H NMR. The configuration of V was identified as the E-configuration by ¹H NMR experiments.

Among the four complexes, complex I showed the best catalytic activity. The following mechanism can be proposed: the complexes activate the C=O bond, and then there is a nucleophilic addition reaction of

$CH_2NO_2^-$ to the carbonyl group.

In conclusion, four complexes were first synthesized with a simple one-pot method, and their crystal structures were determined. The four complexes were first applied in the Henry reaction and achieved good effects. Additional research on the use of these complexes in other organic reactions, such as the Baylis— Hillman reaction and allylation, is ongoing.

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