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A New Schiff base Ni(II)Complex Based on 2-hydroxy-1-naphthaldehyde and Glycine: Synthesis and Highly Effective Construction of C=C Bonds

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Abstract　A novel 2-hydroxy-1-naphthaldehydeglycine Schiff base nickel(II)complex $[Ni(Py)_3(2\text{-}O\text{-}C_{10}H_5CH{=}NCH_2CO_2)]_2 \cdot 3H_2O$ was synthesized and characterized by single crystal X-ray diffraction (SCXRD), power X-ray diffraction (PXRD), and elemental analyses. Complex exhibits a binuclear nickel(II)structure and it crystallizes in the Triclinic system, space group P-1 with $Z=2$, $a=11.023(19)$ Å, $b=13.30(2)$ Å, $c=18.33(3)$ Å, $V=2629(8)$ Å^3, $F(000)=1130$, $Dc=1.369$ g/cm^3, $\mu=0.778$ mm^{-1}, $R=0.1102$ and $wR=0.2892$. Remarkably, the Schiff base nickel complex was further investigated as catalyst in the Knoevenagel condensation, and found that complex show effective heterogeneous catalytic activities (yield up to 99%)for constructing C=C bonds and the catalyst can be recycled without losing activities after four runs catalytic cycle.

Key words　Schiff base; 2-hydroxy-1-naphthaldehydeglycine; construction; carbon-carbon double bonds

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0　Introduction

Schiff base and their transition metal complexes are a key class of inorganic and organic hybrids and have been widely investigated in the field of catalysis, magnetism, medicine, material science, biology, optics and nanotechnology because of their important structural versatility[1-4]. Up to now, lots of Schiff bases derivatives and their transition metal complexes have been extensively studied in different areas of science[5-7]. However, the investigation of Schiff bases and their complexes based on amino acid, especially glycine, are relatively few due to their solubility and purification difficulty[8]. Thus, the development of Schiff bases complexes based on the amino acid is still a topic of great interest and the studies of catalytic properties of Schiff bases complexes based on the amino acid are rather rare.

In the case of construction for carbon-carbon double bonds, Knoevenagel condensation of aromatic aldehydes with malononitrile compounds, is one of the most major reactions and has been extensively applied in the preparation of many fine chemical organic intermediates, such as numerous biological heterocyclic

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compounds[9-11]. Consequently, lots of metal catalysts have been applied to this conversion, such as, Ni-induced fabrication of hollow ZIF-8 nanoframes [12], $Ni_3(bdda)_2(OAc)_2 \cdot 6H_2O$ ($H_2bdda = 4,4'$-[benzene-1,4-diylbis(methylylidenenitrilo)]dibenzoic acid)[13] and Ni-SiO_2 supported heterogeneous catalysts [14], etc. Thus, the designed synthesis of suitable catalysts for Knoevenagel condensation is still a topic of great interest.

Owing to permanent porosities, effortless tunability and multiple functionality, Schiff bases complexes might be ideal catalysts for Knoevenagel condensation. Importantly, few Schiff bases complexes derived from the 2-hydroxy-1-naphthaldehyde with glycine as effective catalysts for Knoevenagel condensation are rather rare, and thus developing synthetic methods of 2-hydroxy-1-naphthaldehydeglycine Schiff bases transition metal hybrids with the application of mild and green methodologies for Knoevenagel conversion is highly desirable.

In the present study, we synthesized one 2-hydroxy-1-naphthaldehydeglycine Schiff bases nickel hybrids $[Ni(Py)_3(2\text{-}O\text{-}C_{10}H_5CH{=}NCH_2CO_2)]_2 \cdot 3H_2O$ via the reaction of 2-hydroxy-1-naphthaldehyde with glycine and nickel chloride, and develop our investigation in the catalytical Knoevenagel condensation field of Schiff bases hybrids. Complex was fully characterized by SXRD, PXRD, IR and element analyses. The new organic-inorganic 2-hydroxy-1-naphthaldehydeglycine Schiff base nickel hybrid was further used as highly efficient heterogeneous catalyst in the Knoevenagel condensation of malononitrile with various aldehydes under mild conditions.

1 EXPERIMENTAL

1.1 Reagents

2-Hydroxy-1-naphthaldehyde, glycine, nickel chloride hexahydrate and other reagents and solvents were purchased from commercial sources and used without further purification.

1.2 Instruments

PXRD patterns of the samples were analyzed with monochromatized Cu-Kα ($\lambda = 1.54178$ Å) incident radiation by a Shimadzu XRD-6000 instrument operating at 40 kV voltage and 50 mA current, and PXRD patterns were recorded from 4° to 50° (2θ) at 298 K. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. The C, H and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-1701 Sil capillary column.

1.3 Synthesis of complex

2-Hydroxy-1-naphthaldehyde (0.172 g, 1 mmol), glycine (0.075 g, 1 mmol) and NaOH (0.04 g, 1 mmol) were successively dissolved in MeOH (20 mL) and reacted for 6 h at 80 ℃. After the reaction was completed, this mixture was allowed to cool to room temperature and nickel chloride hexahydrate (0.24 g, 1 mmol) was then added, the reaction mixture was stirred for another 4 h at room temperature. Finally, a green solid was filtrated and washed with methanol (2×5 mL), and then dried in air. The solid was dissolved with pyridine, and stirred for 30 min, filtered and left at room temperature. The green crystals were formed after a few days and collected by filtration. Yield: 37%. IR (KBr, cm^{-1}): 3490 (s), 3418 (s), 1639 (m), 1613 (s), 1468 (w), 1387 (m), 1295 (w), 618 (s), 475 (w) cm^{-1}. Anal. Calcd. (found) for $C_{56}H_{54}Ni_2N_8O_9$: C, 61.12 (61.16); H, 4.95 (4.25); N, 10.18 (10.09).

1.4 Procedure for catalytic Knoevenagel condensation of aromatic aldehydes and malononitrile

Knoevenagel condensation of aromatic aldehydes and malononitrile catalyzed by different catalysts were carried out in a 25 mL round-bottomed flask using aromatic aldehyde (1 mmol) and malononitrile (1.5 mmol) as starting materials. The reaction mixture was subsequently heated at 50 ℃ in the reactor for 1 h with stirring. After the reaction was completed, catalyst was retrieved by filtration and washed with methanol (ca. 3×5 mL), and air-dried prior to being used for the reuse experiment. The obtained reaction mixture was analyzed using an Shimadzu 2014C GC equipped with a flame ionization detector. All the products were analyzed over an Agilent 7890B-7000D MSD GC-MS.

1.5 Reuse Experiments

The reuse experiments were performed for Knoevenagel condensation under the optimum conditions as listed in Table 3. After the reaction was completed, the catalyst was easily reclaimed by filtration, washed with methanol (ca. 3 × 5 mL), and air-dried prior to being used for the recycle experiment. The experiment of the four runs was prepared in the similar way as that for the second run, and finally the 95.7% yield of product was determined by GC.

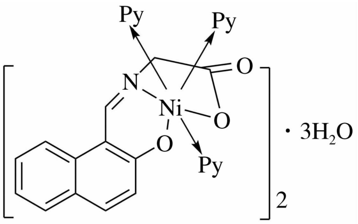
1.6 Structure determination

Single-crystal X-ray diffraction data for complex was determined with MoKα radiation ($\lambda = 0.71073$ Å) on a Bruker-AXS CCD diffractometer equipped with multi-scan technique at 296 K. The structures were solved by direct methods and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package[15,16]. The final refinements included anisotropic displacement parameters for all atoms. The crystal data of complex was shown in Table 1 and the selected bond lengths and bond angles of complex was shown in Table 2, respectively.

2 Results and discussion

2.1 Structure description

The novel nickel(II)Schiff base complex was prepared via the reaction of 2-hydroxy-1-naphthaldehyde with glycine, and the molecular structures of the nickel (II)complex was determined by single crystal X-ray analyses. The complex crystallize in the Triclinic system with space group P-1. As depicted in Scheme 1 and Fig. 1, the crystal structure of complex consists of two discrete Ni(II)Schiff base units and three free water molecules with formula $[Ni(Py)_3(2\text{-}O\text{-}C_{10}H_5CH{=}NCH_2CO_2)]_2 \cdot 3H_2O$. As Ni(1)and Ni(2)units have similar structure motif, only the structure of Ni(1)unit is described in detail here. In the crystal structure of Ni(1)unit, the nickel atom is six-coordinated in the form of a slightly distorted octahedral geometry. The Ni(II)ion is coordinated to one 2-hydroxy-1-naphthaldehydeglycine Schiff base anions acting as tridentate ligand through their adjacent carbonyl group, imine group and phenol oxygen atom group [the bond distances of Ni-O1, Ni-O3 and Ni-N1 are 2.045(11)Å, 2.019(11)Å and 1.943(15)Å, respectively]. The other positions around the Ni cation are occupied by three pyridine molecules [the bond distances of Ni(1)-N(2), Ni(1)-N(3)and Ni(1)-N(4)are 2.201(16)Å, 2.148(14)Å and 2.059(15)Å, respectively]. The O-Ni-O, N-Ni-N angles in the NiN4O2 core are in the range from 88.9(6)to 177.0(5)°, which is in agreement with those of the previously reported nickel complex with formula catena-[(μ_3-N-(2-Oxynaphthylmethylene)glycinato-N,O,O,O′,O″)-methanol-nickel(ii)] [17]. It is noted that the Nickel(II)moiety, the phenolic oxygen atom and carboxyl oxygen atom is nearly linear, and shows bent coordination with the metal atom (the bond angles of O(1)-Ni(1)-O(3), N(1)-Ni(1)-O(3)and O(1)-Ni(1)-N(1)are 171.6(5) 90.0(5)and 81.8(6), respectively).



Scheme 1 The molecular structure of the complex

In the catalytical reaction, the higher catalytic activity of complex is probably attributed to the coordination pyridine molecules of nickel ions, which may leave enough space for the organic substrates as potential active sites in Knoevenagel condensation.

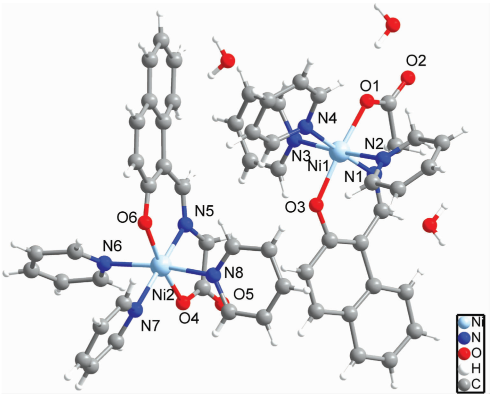


Fig. 1 **The crystal structure of the complex**

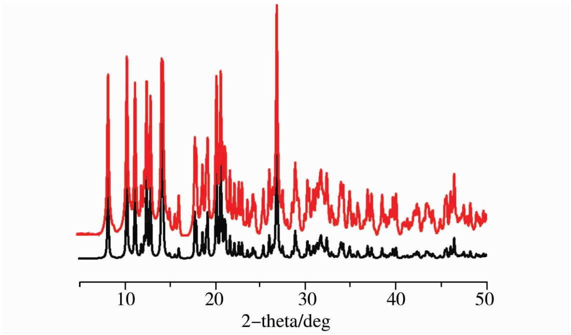


Fig. 2 **Powder X-ray diffraction patterns of complex**

2.2 PXRD analysis

The experimental and simulated PXRD patterns of complex was shown in Fig. 2. As shown in Fi. 2, these peak positions were in good agreement with each other, indicating that the phase purity of complex.

Table 1 **Crystallographic Data for Complex**

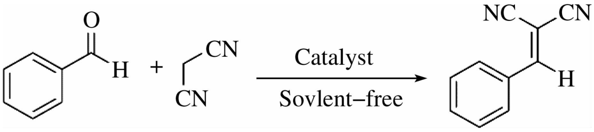
Complex	Value
Formula	$C_{56}H_{54}Ni_2N_8O_9$
M_r	1100.48
Crystal system	Triclinic
Space group	P-1
Temperature	298(2)K
a (Å)	11.023(19)
b (Å)	13.30(2)
c (Å)	18.33(3)
α (deg)	78.32(2)
β (deg)	88.83(3)
γ (deg)	88.41(3)
V (Å^3)	2629(8)
Z	2
D(Mg/m^3)	1.369
F(000)	1130
Reflections collected/unique	12689 / 8659
R(int)	0.1177
$R_1[I>2\sigma(I)]$	0.1102
$wR_2[I>2\sigma(I)]$	0.2892
GOOF	0.901

Table 2 **Selected bond distances (nm) and bond angles (°) for the complex**

Complex	Value	Complex	Value
Ni(1)-N(1)	1.943(15)	Ni(2)-N(5)	2.026(13)
Ni(1)-O(3)	2.019(11)	Ni(2)-O(6)	2.033(12)
Ni(1)-O(1)	2.045(11)	Ni(2)-N(7)	2.062(14)
Ni(1)-N(4)	2.059(15)	Ni(2)-O(4)	2.080(13)
Ni(1)-N(3)	2.148(14)	Ni(2)-N(8)	2.142(13)
Ni(1)-N(2)	2.201(16)	Ni(2)-N(6)	2.211(15)
N(1)-Ni(1)-O(3)	90.0(5)	N(5)-Ni(2)-O(6)	89.4(5)
N(1)-Ni(1)-O(1)	81.8(6)	N(5)-Ni(2)-N(7)	175.8(5)
O(3)-Ni(1)-O(1)	171.6(5)	O(6)-Ni(2)-N(7)	94.1(6)
N(1)-Ni(1)-N(4)	177.0(5)	N(5)-Ni(2)-O(4)	81.5(5)
O(3)-Ni(1)-N(4)	91.4(5)	O(6)-Ni(2)-O(4)	170.7(5)
O(1)-Ni(1)-N(4)	96.8(6)	N(7)-Ni(2)-O(4)	95.1(6)
N(1)-Ni(1)-N(3)	93.7(6)	N(5)-Ni(2)-N(8)	94.2(5)
O(3)-Ni(1)-N(3)	89.6(5)	O(6)-Ni(2)-N(8)	90.0(5)
O(1)-Ni(1)-N(3)	89.1(5)	N(7)-Ni(2)-N(8)	88.2(5)
N(4)-Ni(1)-N(3)	88.9(6)	O(4)-Ni(2)-N(8)	88.7(5)
N(1)-Ni(1)-N(2)	91.9(6)	N(5)-Ni(2)-N(6)	93.2(5)
O(3)-Ni(1)-N(2)	92.7(5)	O(6)-Ni(2)-N(6)	92.1(6)
O(1)-Ni(1)-N(2)	89.4(5)	N(7)-Ni(2)-N(6)	84.3(5)

2.3 Knoevenagel condensation reaction

At the outset of our investigations, different catalysts were applied to evaluate the catalytic activities of the Schiff bases nickel catalyst (Scheme 2). In a typical experiment benzaldedyde (1 mmol) and malononitrile (1.5 mmol) along with the catalyst proceeded at 50 ℃ for 1 h under solvent-free conditions. The blank experiment indicates that only trace conversion was achieved in the absence of catalyst (Fig. 3a). To assess the influence of cation and anion of Schiff base complex on the Knoevenagel condensation, a series of control experiments were performed. Besides, poor yields of 2-benzylidenemalononitrile were achieved with $NiCl_2 \cdot 6H_2O$ (Fig. 3b); Although pyridine as homogeneous catalyst can produce 2-benzylidenemalononitrile (Fig. 3d), the yield (34.6%) is obviously lower than those of complex. When the reactions were performed under the same conditions using $NiCl_2 \cdot 6H_2O$ and pyridine as catalysts, the yield was 47% (Fig. 3f). Further screening of different catalysts resulted in 85% yield of the desired product in the presence of complex (Fig. 3g). Increasing the complex amount from 3 mol% to 5 mol% finally raised the yield to 99% 2-benzylidenemalononitrile as the only product within 1 h (Fig. 3h). Those control experiments clearly reveal that complex played a crucial role in the Knoevenagel condensation reaction. And indeed, yield of complex outperform many effective heterogeneous catalysts reported to date, i. e. Ni-induced fabrication of ZIF-8 nanoframes(yield: 68.8%)[12], interface-active metal organic frameworks(yield: 85%)[18] etc.



Scheme 2　Knoevenagel condensation of benzaldedyde and malononitrile

Further, the recyclability of complex was tested by utilizing benzaldehyde as a substrate. Complex was simply collected by filtration after the completeness of the condensation reaction and washed using methanol, which can be used for the successive three runs. Notably, the catalytic activities of complex in the Knoevenagel condensation was kept without any appreciable loss of its high catalytic performance even after three recycles [Yields of products: 99% (First run), 97% (Second run), 98 % (Third run), 97 % (Fourth run)] (Fig. 4). At the same time, the IR skeleton of complex remained unaltered after four run recycles (Fig. 5).

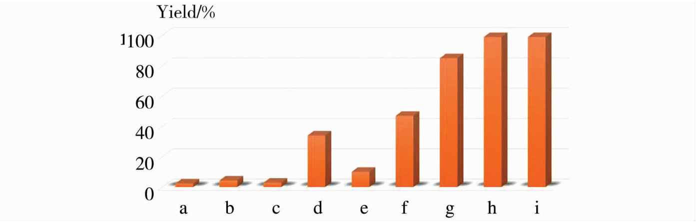


Fig. 3　Knoevenagel condensation of benzaldehyde with malononitrile with different catalysts. Reaction condtions: benzaldehyde (1 mmol), malononitrile (1.5 mmol), catalysts (5 mol%), 50 ℃, 1 h; (a)Blank; (b)NiCl$_2$ · 6H$_2$O; (c)Schiff base ligand; (d)Pyridine; (e)the mixture of NiCl$_2$ · 6H$_2$O and Schiff base ligand; (f)the mixture of NiCl$_2$ · 6H$_2$O, Schiff base ligand and Pyridine; (g)complex (3 mol%); (h)complex (5 mol%); (i)complex (8 mol%).

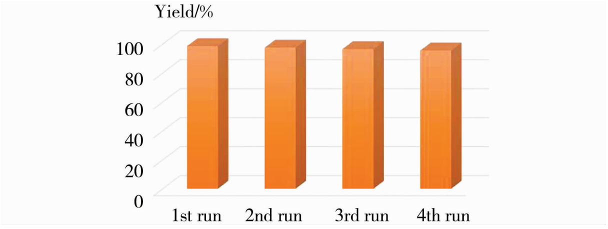


Fig. 4　The reaction results of Knoevenagel condensation catalysed by complex in four runs recycle experiments. Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.5 mmol), compound 1 (0.1 mol%), 50 ℃, 1 h.

With these optimized reaction conditions in hand, a series of benzaldehyde derivatives were expanded in the condensation reaction and the corresponding results were listed in Table 3. From the Table 3, various substituted benzaldehyde with electron-withdrawing groups and electron-donating groups (-Cl, -Br, -NO$_2$, -CH$_3$ and -OCH$_3$) on the para-position of the benzene ring were investigated. As anticipated, benzaldehyde derivatives with electron-withdrawing groups (-Cl, -Br, -O$_2$) reached nearly full conversion (>99%), However, electron-donating benzaldehyde derivatives (CH$_3$, OCH$_3$) obtained relatively lower yields (Table 3, entries 56) varying from 91 to 82% since OCH$_3$ and CH$_3$ are known to be of the strong electron-donating nature and it is no advantage to this reaction. Based on the above results, it was obviously that highly selective and efficient Knoevenagel condensation of various substituted aldehydes can be realized by applying [Ni(Py)$_3$(2-O-C$_{10}$H$_5$CH=NCH$_2$CO$_2$)]$_2$ · 3H$_2$O as catalysts.

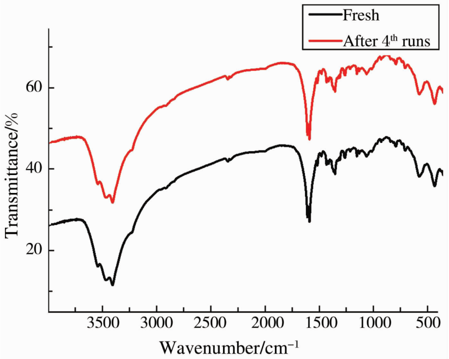
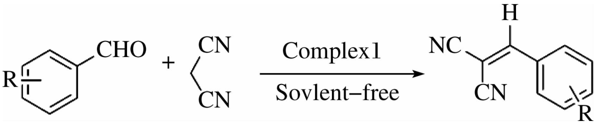
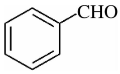
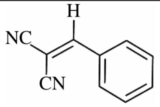
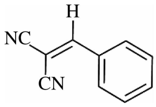
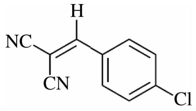
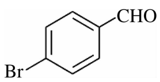
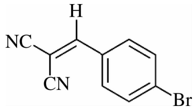
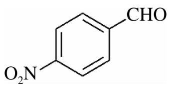
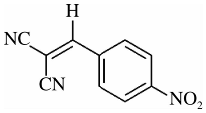
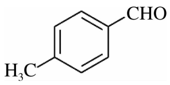
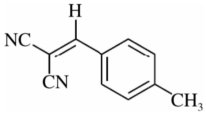
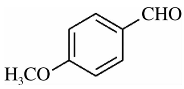
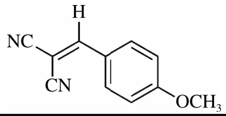


Fig. 5　The IR of compound 1 after three four runs recycles

Table 3 Compound 1-Catalyzed Knoevenagel Condensation of Aromatic Aldehydes[a]



Entry	Substrates	Products	Yield[b](%)
1			99
2			99
3			99
4			99
5			91
6			82

a Reaction performed at 50 ℃ under solvent-free conditions, 1 mmol aldehyde, 1.5 mmol malononitrile, 5 mol% complex, 1h; b Yield of products were determined by GC.

5 Conculsion

In summary, one 2-hydroxy-1-naphthaldehydeglycine Schiff base nickel complex has been successfully synthesized and found that the Schiff base complex can used as highly efficient heterogeneous catalysts of a Knoevenagel condensation with high activities (yield up to 99%). The synthesis and application of Schiff base complexes in catalytic other organic reactions is in process, which will be reported timely.

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基于2-羟基1-萘甲醛缩甘氨酸席夫碱镍配合物的合成及其高效构建C=C键

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摘　要　合成和表征了一个新颖的2-羟基1-萘甲醛缩甘氨酸席夫碱镍配合物$[Ni(Py)_3(2\text{-}O\text{-}C_{10}H_5CH{=}NCH_2CO_2)]_2\cdot 3H_2O$，并通过X-单晶衍射分析、粉末衍射及元素分析确定了其结构.配合物为二核的镍配合物结构，晶体为三斜晶系，P-1空间群，$Z=2$，$a=11.023(19)$ Å，$b=13.30(2)$ Å，$c=18.33(3)$ Å，$V=2629(8)$ Å^3，$F(000)=1130$，$Dc=1.369$ g/cm^3，$\mu=0.778$ mm^{-1}，$R=0.1102$，$wR=0.2892$.值得注意的是，配合物进一步应用于克脑文格缩合反应中，发现配合物在构建C=C双键的反应中具有有效的非均相催化活性（产率高达99%），并且催化剂可以循环四次后活性没有明显的损失.

关键词　席夫碱；2-羟基1-萘甲醛缩甘氨酸；构建；碳碳双键