# Nickel(II) catalyzed oxidation of aldehyde derivatives to their carboxylic acid or ester analogs

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**Abstract** Diverse aromatic, aliphatic and conjugated aldehydes were converted to the corresponding carboxylic acid or methyl ester derivatives with 30 %  $H_2O_2$  as the oxidant in the presence of a catalytic amount of nickel(II) complex as precursor. Ni(II) complex was prepared from the reaction of methyl 2-{3-[(E)-4-oxopent-2-en-2-ylamino]propylamino}cyclopent-1-enecarbodithioate as a tetra-dentate ligand with Ni(II) acetate in 60 % yield and was tested for its catalytic activity in the oxidation reaction. The prepared complex was characterized on the basis of <sup>1</sup>H NMR, FT–IR, MASS, and CHN analysis. Aldehydes were oxidized to their corresponding carboxylic acid in acetonitrile as solvent and were converted to methyl esters in methanol as solvent. For all substrates, a considerable rate enhancement was observed. The present methodology offers several advantages such as applicability to a wide range of aldehydes, convenient work-up, mild reaction conditions, and good yields and reasonable time of the reactions.

Keywords Oxidation  $\cdot$  Aldehyde  $\cdot$  Acid  $\cdot$  Methyl ester  $\cdot$  H<sub>2</sub>O<sub>2</sub>  $\cdot$  Ni(II) complex

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#### Introduction

An acceptable demand of organic chemists is to use cheap, non-toxic, and environmentally friendly reactants, including reducing agents, oxidants, etc., in organic transformations. In this context, oxidation reactions and especially oxidation of aldehydes to carboxylic acids is a fundamental chemical transformation in organic chemistry [1–3]. The oxidation of aldehydes to carboxylic acid with various oxidants has been intensively studied during recent years [3–11]. One of the best of these oxidants is aqueous hydrogen peroxide that has some advantages, such as cheapness, ease of handling, and having a high percentage of available oxygen. Unluckily, hydrogen peroxide has a high activation barrier for its reaction with organic substrates [12]. To overcome this, a number of catalytic procedures for  $H_2O_2$  oxidation have been developed [13–25].

To expand this number, the present paper deals with the use of methyl-2-{N-[4-(pent-2-enolato)methylidynenitrilo]ethyl}aminato(-1)-1-cyclopentenedithiocarbox-ylate Ni(II) (**A**) as catalyst in the oxidation of aldehydes to corresponding carboxylic acids in acetonitrile as solvent (Scheme 1).

## **Results and discussion**

Methyl  $2-\{3-[(E)-4-\text{oxopent-2-en-2-ylamino}]$ propylamino $\}$ cyclopent-1-enecarbodithioate as a ligand for Ni(II) and their corresponding complex (**A**) was synthesized with high yields according to previously published literature procedures [25–28]. The prepared complex was characterized on the basis of <sup>1</sup>H NMR, FT–IR, MASS, and CHN analysis.

The distinctive peaks in the <sup>1</sup>H NMR spectra of the ligand and the Ni(II) complex are presented in Table 1. In the <sup>1</sup>H NMR spectra of the free ligand, the OH signal was seen at 12.41 ppm and SH signal at 10.93 ppm, and these disappear in the Ni(II) complex, indicating that the OH and SH groups have been bonded to the Ni(II) ions





after de-protonation (Table 1). The methyl protons connected to the sulfur atom of the ligand (2.58 ppm) are shifted to higher fields in the Ni(II) complex (2.64 ppm). The CH<sub>2</sub> protons connected to nitrogen atom ( $-CH_2-N=C$ ) appeared at 3.48–3.55 ppm in the free ligand, shifting to a higher field (3.57–3.74 ppm), confirming the coordination of the Ni(II) to nitrogen atoms (Table 1).

The appearance of the strong vibration in the region 440–550 cm<sup>-1</sup> in the FT–IR spectrum confirms the presence of Ni–N, Ni–O, and Ni–S bonds [29, 30].

The catalytic activity of A has been studied in the mild oxidation of various aromatic and aliphatic aldehydes (Scheme 1).

In an initial screening, the oxidation of 4-chlorobenzaldehyde in acetonitrile as solvent at 60 °C has been investigated (Table 2) in the presence of various kind of Ni(II) salts. Reaction with NiSO<sub>4</sub>, NiO, Ni(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub> and Ni(en)<sub>2</sub>Cl<sub>2</sub> yielded less than **A** (Table 2), indicating that **A** is the specific catalyst for the oxidation of aldehydes. We therefore proceeded with the oxidation of 4-chlorobenzaldehyde to the corresponding carboxylic acids using **A** as catalyst (Table 2). At room temperature, the conversion of 4-chlorobenzaldehyde to the product was found to be low (60 %). The results revealed that the presence of H<sub>2</sub>O<sub>2</sub> as co-catalyst is required for the oxidation reaction.

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	OH	SH	SCH <sub>3</sub>	CH(sp <sup>2</sup> )	(-CH2-N=C
Free ligand	12.41	10.93	2.58	7.67	3.48-3.55
Ni(II) complex	-	-	2.64	7.26	3.57-3.74

Table 1 <sup>1</sup>H NMR data (250 MHz; ppm; CDCl<sub>3</sub> as solvent) of the ligand and Ni(II) complex

Entry	Catalyst (mmol)	T (°C)	Solvent (5 mL)	Yield (%) <sup>a</sup>
1	NiSO <sub>4</sub> (0.13)	60	CH <sub>3</sub> CN	70
2	NiO (0.13)	60	CH <sub>3</sub> CN	50
3	Ni(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>2</sub> (0.13)	60	CH <sub>3</sub> CN	68
4	Ni(en) <sub>2</sub> Cl <sub>2</sub> (0.13)	60	CH <sub>3</sub> CN	30
5	A (0.13)	60	CH <sub>3</sub> CN	87
6	A (0.13)	60	CH <sub>3</sub> CN	10 (without H <sub>2</sub> O <sub>2</sub> )
7	A (0.13)	25	CH <sub>3</sub> CN	50
8	A (0.13)	60	<i>n</i> -Hexane	64
9	A (0.13)	35	$CH_2Cl_2$	65
10	A (0.13)	40	Et <sub>2</sub> O	71
11	A (0.13)	60	EtOAc	85
12	A (0.26)	60	CH <sub>3</sub> CN	85
13	A (0.07)	60	CH <sub>3</sub> CN	89
14	A (0.03)	60	CH <sub>3</sub> CN	58
15	A (0.01)	60	CH <sub>3</sub> CN	56

Table 2 Optimization of the reaction conditions in the synthesis of 4-Chlorobenzoic acid

<sup>a</sup> Isolated yields, reaction time: 3 h

In order to find the optimal reaction medium, the effect of various common organic solvents was investigated, from which it was deduced that acetonitrile appears to be the most favorable (Table 2, entry 5). Next, the oxidation reaction was carried out in the presence of 0.26, 0.13, 0.07, 0.03, and 0.01 mmol of **A** with the other parameters kept constant. Among the various amounts of the catalyst tested, the oxidation reaction was best catalyzed by 0.07 mmol (Table 2, entry 13).

Entry	Aldehyde	Time (h)	Yield (%) <sup>a</sup>
1	Benzaldehyde	2	90
2	4-Chlorobenzaldehyde	3	89
3	2-Chlorobenzaldehyde	4	80
4	2,4-Dichlorobenzaldehyde	4	84
5	2,4-Dimethoxybenzaldehyde	3	86
6	4-Methoxybenzaldehyde	2	85
7	2-Methoxybenzaldehyde	3	79
8	4-Methylbenzaldehyde	2	86
9	2-Methylbenzaldehyde	3	77
10	4-Bromobenzaldehyde	3	88
11	3-Bromobenzaldehyde	3	89
12	4-Nitrobenzaldehyde	4	89
13	3-Nitrobenzaldehyde	4	87
14	2-Nitrobenzaldehyde	5	84
15	Furfural	3	76
16	Butyraldehyde	5	70
17	Cyclohexanecarbaldehyde	5	85

Table 3 Synthesis of carboxylic acid derivatives using A as catalyst (Scheme 1)

<sup>a</sup> Isolated yields

Entry	Aldehyde	Time (h)	Yield (%) <sup>a</sup>
1	Benzaldehyde	4	92
2	4-Chlorobenzaldehyde	4.5	91
3	4-Methoxybenzaldehyde	2.5	88
4	2-Methoxybenzaldehyde	3	87
5	4-Methylbenzaldehyde	2.5	89
6	4-Bromobenzaldehyde	3.5	81
7	3-Bromobenzaldehyde	4.5	86
8	4-Nitrobenzaldehyde	6	90
9	Furfural	3.5	72

Table 4 Oxidative esterification of aldehydes to corresponding methyl esters using A as catalyst (Scheme 1)

<sup>a</sup> Isolated yields

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for the oxidation of various aromatic and aliphatic aldehydes. Generally, all the oxidation reactions proceeded well and afforded the desired products (Table 3, entries 1–17) in good to excellent yields. As shown in Table 3, the reaction was successfully compatible with a variety of aryl aldehydes having electron-donating and electron-withdrawing substituents. Aromatic aldehydes substituted with electron-withdrawing groups react slowly (Table 3, entries 12–14). The results show that aliphatic aldehydes can be successfully oxidized in good yields (Table 3, entries 16–17).

Under the same optimized reaction conditions (Table 2) and using methanol as solvent, the aldehydes can all be oxidized to the corresponding methyl esters in excellent yields (Scheme 1). The results are summarized in Table 4.

## Conclusion

In conclusion, a Ni(II) complex catalyzed one-pot reaction sequence for the oxidation of aldehydes to the corresponding carboxylic acid or methyl ester has been developed. The prepared catalyst was characterized using <sup>1</sup>H NMR, FT–IR, MASS, and CHN analysis. Various kinds of aromatic and aliphatic aldehydes were investigated and the desired products were obtained in high yields.  $H_2O_2$  was used as oxidant. The present method represents a simple and highly efficient method for the oxidation of aldehydes to their carboxylic acid or methyl ester analogs under mild conditions.

## Experimental

## Material and instrumentation

All reagents were purchased from Merck and Aldrich and were used as received. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in  $CDCl_3$  relative to TMS (0.00 ppm). IR spectra were recorded on a Perkine Elmer 781 spectrophotometer. TLC was performed on silica gel polygram SIL G/UV 254 plates.

## Preparation of A

Methyl 2-{3-[(E)-4-oxopent-2-en-2-ylamino]propylamino}cyclopent-1-enecarbodithioate was prepared by the known reported procedures [29–31]. Complex preparation: using a solution of the appropriate ligand (0.1 mmol) in 10 mL of chloroform/methanol 2:1 (V:V) was added Ni(II) acetate (0.1 mmol) dissolved in 10 mL of methanol, and the solution was stirred for 15 min. After that time, the reaction mixture was allowed to stand at room temperature for 24 h. Finally, the crude product was filtered and recrystallized from acetonitrile/methanol 1:1 (V:V) to afford the pure product. Spectroscopic data for **A** are as follows: Yield: 63 %, m.p.: 233 °C; <sup>1</sup>H NMR ( $\delta$ , ppm, 250 MHz, CDCl<sub>3</sub>): 1.77 (3H, s, CH<sub>3</sub>), 1.25–2.03 (5H,m), 2.44–2.61 (4H, m), 2.64 (3H, s, SCH<sub>3</sub>), 3.57–3.74 (4H, m), 7.26 (1H (sp<sup>2</sup>), s); IR (KBr, cm<sup>-1</sup>): 440–550 ( $\nu_{Ni-S+}\nu_{Ni-N+}\nu_{Ni-O}$ ), 750 ( $\nu_{C-S}$ ), 1,010 ( $\nu_{C-S+}\nu_{C-N}$ ), 1,284 ( $\nu_{C-O}$ ), 1,463 ( $\nu_{C=C}$ ), 1,558, 1,595 ( $\nu_{C=N}$ ), 2,900 ( $\nu_{C-H}$ ); MS Spectra: m/z (%) = 356[M + 1]<sup>+</sup>, 355[M]<sup>+</sup>, 309, 294, 279, 189, 111, 97, 57; Elemental Anal.: % Found (% Calc): C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>OS<sub>2</sub>Ni, C: 47.47 (47.35); H: 5.77 (5.68); N: 7.95 (7.89); S: 18.14 (18.06).

#### Typical procedure for the preparation of carboxylic acids

A solution of 4-chlorobenzaldehyde (1 mmol) and **A** (0.07 mmol) in 5 mL of CH<sub>3</sub>CN was added to aqueous H<sub>2</sub>O<sub>2</sub> (0.5 mL, 30 % in water). The resulting reaction mixture was stirred at 60 °C for the appropriate time (Table 3). After completion of the reaction, as indicated by TLC, the solvent was evaporated and, to obtain the crude reaction mixture, NaHCO<sub>3</sub> (10 %) was added and then the reaction mixture was extracted with ethyl acetate. The aqueous layer was acidified to pH 2.0 using 2 N HCl and extracted with ethyl acetate. The organic layer was concentrated and purified by plate chromatography (*n*-hexane/ethyl acetate 95/5) to give the pure product (Table 3).

#### Typical procedure for the preparation of methyl esters

To a solution of 4-chlorobenzaldehyde (1 mmol) and **A** (0.07 mmol) in 5 mL of CH<sub>3</sub>OH was added aqueous H<sub>2</sub>O<sub>2</sub> (0.5 mL, 30 % in water). The resulting reaction mixture was stirred at 60 °C for the appropriate time (Table 4). After completion of the reaction, as indicated by TLC, the solvent was evaporated and the resulting crude reaction mixture was purified by plate chromatography (*n*-hexane/ethyl acetate 95/5) to give the pure product (Table 4).

#### Selected data

*Methyl benzoate* (Table 4, entry 1): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.05$  (d, 2H, J = 7.4 Hz), 7.46–7.58 (m, 3H) 3.91 (s, 3H).

*Methyl* 4-chlorobenzoate (Table 4, entry 2): <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 7.95$  (d, 2H, J = 8.5 Hz), 7.41 (d, 2H, J = 8.5 Hz), 3.90 (s, 3H).

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