DOI: 10.1002/zaac.201100040

Synthesis, Characterization, and Catalytic Performance in Oxidation of Styrene and α-Methyl Styrene of a Nickel(II) Complex Derived from a Schiff Base Ligand

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Keywords: Catalyst; Crystal structure; Nickel; Oxidation; Schiff bases

Abstract. A tetrahedrally-distorted square-planar nickel(II) complex of tetradentate Schiff base ligand derived from 2-hydroxypropiophenone and 2,2'-dimethylpropandiamine [bis(2-hydroxypropiophenone)2,2'-dimethylpropylenediimine] (**H_2L**) was prepared and used as catalyst for oxidation of styrene and α-methyl styrene with *tert*-butylhydroperoxide (TBHP). Oxidation of styrene with TBHP gave benzaldehyde and styrene oxide, but in the case of α-methylstyrene a mixture of α-methylstyrene oxide and acetophenone was obtained. The structure of nickel(II) complex (**NiL**) was determined by X-ray crystallography. Crystal data for **NiL** at –173 °C: orthorhombic, space group $P2_12_12_1$, $a = 907.7(1)$, $b = 1289.4(1)$, $c = 1752.4(1)$ pm, $Z = 4$, $R_1 = 0.0454$.

1. Introduction

Schiff base ligands and their metal complexes are easily synthesized. Therefore, transition metal complexes with Schiff base ligands have been extensively used as catalyst in various reactions such as oxidation,[1–3] ring opening reaction of epoxides,[4,5] aldol condensation[6–8] and epoxidation.[9–19] A wide variety of transition metals such as chromium(III),[20] manganese(II),[21,22] oxovanadyl(IV),[23,24] cobalt(II),[25,26] nickel(II),[27] and copper(II)[28] were used in preparation of Schiff base complexes and tested for their activity in the oxidation reactions.

The study of nickel compounds attracts considerable attention in different aspects of chemistry, because these compounds are present in active sites of urease and are widely used in the design and construction of novel magnetic materials.[29–31] Also a large number of Ni^{II} complexes are applied as models in biological process for understanding the structure of biomolecules.[32,33]

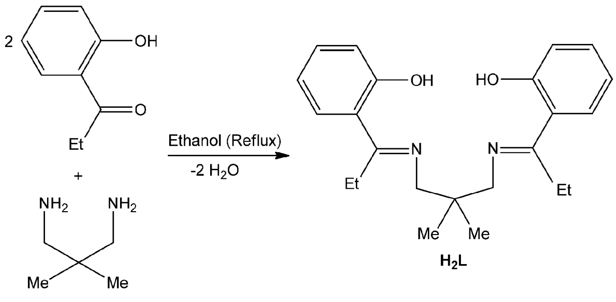
Great attention has recently been paid to 2-hydroxy Schiff base ligands owing to their different crystallographic, structural, and magnetic characteristics.[34–38] Their enduring appeal and increasing popularity can be explained by the ease with which they are synthesized, the outstanding versatility they have, and a great deal of complexing ability they show[39]. Moreover, Schiff base ligands may be tuned both sterically and electronically by the variation of respective amine and aldehyde or ketone ligand precursors.[40]

In this paper, the synthesis, characterization, and molecular structure of a Ni^{II} complex of a Schiff base ligand derived from 2,2'-dimethylpropylenediamine and 2-hydroxypropiophenone are reported and also catalytic performance of the complex for oxidation of styrene and α-methyl styrene with *tert*-butylhydroperoxide (TBHP) are investigated.

2. Results and Discussion

2.1. Synthesis and Spectroscopic Characterization

The tetradentate Schiff base ligand (**H_2L**) was synthesized by 1:2 condensation reaction of 2,2'-dimethylpropylenediamine and 2-hydroxypropiophenone in ethanol under reflux in good yield according to Scheme 1. The analytical data of **H_2L** is in agreement with the formulation of this compound.



(1)

Scheme 1. Preparation of the Schiff base ligand.

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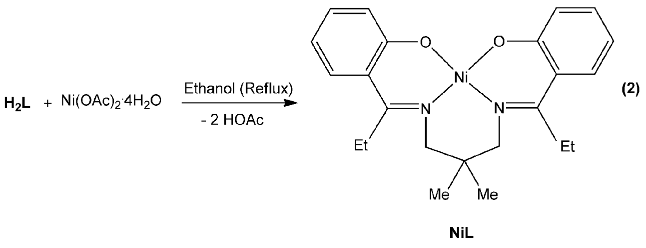
The nickel(II) complex with this ligand was prepared by treatment of $\mathbf{H_2L}$ with $Ni(OAc)_2{\cdot}4H_2O$ in molar ratio 1:1 in ethanol according to Scheme 2.



Scheme 2. Preparation of the nickel(II) complex.

The complex, which was identified by IR, UV/Vis, and ^{1}H NMR spectroscopy and elemental analysis, are remarkably stable to air, water, and heat.

The infrared spectra for the ligand ($\mathbf{H_2L}$) and its complex (**NiL**) exhibit the characteristic vibrational frequencies. The band corresponding to the azomethine group of the free ligand is observed at 1617 cm^{-1}. Another broad band around 1570 cm^{-1} in $\mathbf{H_2L}$ is related to aromatic (C=C) vibration. The lowering of the positions of the bands indicates their coordination to the metal atom.[41] The IR spectra of complex has a very strong and broad band corresponding to ν(C=N) centered at 1606 cm^{-1}. The bands are broad probably due to their overlapping with the aromatic ring-carbon stretching. The C–O stretching vibration in free ligand is observed at 1220 cm^{-1}. This frequency shifts in the complex towards lower or higher values as a result of coordination of the oxygen to the metal ion.[42] The ν(C–O) band of $\mathbf{H_2L}$ at 1220 cm^{-1} shifts to 1206 cm^{-1} in **NiL**.

The electronic spectrum of the Schiff base ligand recorded in $CHCl_3$ exhibits two bands, a relative intense band at 250 nm (ε = 18780 $\mathrm{M}^{-1}{\cdot}\mathrm{cm}^{-1}$) and a band of low intensity at 330 nm (ε = 7740 $\mathrm{m}^{-1}{\cdot}\mathrm{cm}^{-1}$). Based on their extinction coefficients these are assigned as due to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively.[43,44]

The formation of $\mathbf{H_2L}$ was followed by NMR spectroscopy until the complete disappearance of the amine proton signals at 1.10 ppm in the ^{1}H NMR spectrum, and the ketone C=O signal at 207.11 ppm in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum of the tetradentate Schiff base ligand of N_2O_2 donor sets shows the signals of two phenol groups at 12.34 ppm. The spectrum also shows signals of the aromatic protons in the range 6.73–7.50 ppm. The signals of the methylene protons appear at 2.74–2.81 ppm and those of the methyl protons at 1.15–1.23 ppm.

The comparison of the ^{1}H NMR spectrum of the free ligand with its nickel complex shows disappearance of the OH protons present in the free ligand, which is in agreement with the bis-deprotonation of the ligand. The signals of the methylene and methyl protons of **NiL** appear at 3.56–2.07 ppm and 1.23–0.66 ppm, respectively. The signals of the aromatic protons in **NiL** lie in the range of 7.76–6.52 ppm.

2.2. Crystal Structure Analysis of NiL

Deep green crystals of **NiL**, suitable for X-ray diffraction studies, were obtained. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. An ORTEP view of **NiL** is shown in Figure 1. L^{2-} acts as a tetradentate ligand. The most interesting phenomenon observed is the fact that both of the phenol groups of the ligand are coordinated as phenolate, which neutralizes the 2+ charge of Ni^{II}. Selected bond lengths and bond angles for the complex are summarized in Table 1.

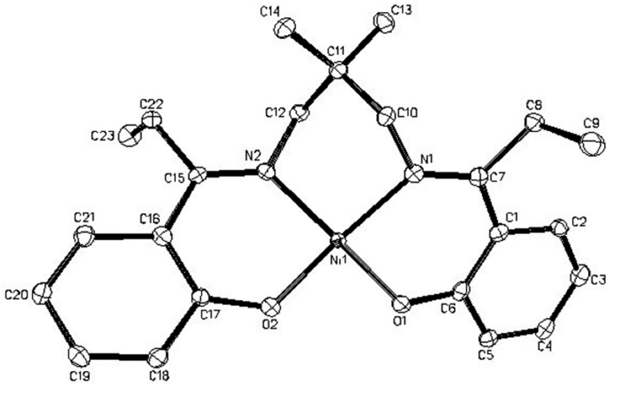


Figure 1. Molecular structure of **NiL** (thermal ellipsoids are at the 40 % probability level).

Table 1. Selected bond lengths /pm and bond angles /° for **NiL**.

Ni(1)–O(1)	189.2(2)	N(1)–Ni(1)–N(2)	92.8(1)
Ni(1)–N(1)	195.7(3)	O(1)–Ni(1)–N(1)	92.6(1)
O(1)–C(6)	130.9(4)	C(6)–O(1)–Ni(1)	125.3(2)
N(1)–C(7)	130.5(4)	C(7)–N(1)–Ni(1)	128.9(2)
N(1)–C(10)	146.6(4)	C(6)–C(1)–C(7)	123.1(3)
C(1)–C(6)	143.2(5)	N(1)–C(7)–C(1)	120.1(3)
C(1)–C(7)	147.2(5)	C(7)–N(1)–C(10)	123.8(3)
C(7)–C(8)	151.3(5)	O(2)–Ni(1)–N(2)	93.6(1)
Ni(1)–O(2)	188.5(2)	O(2)–Ni(1)–O(1)	92.7(1)
Ni(1)–N(2)	196.7(3)	C(17)–O(2)–Ni(1)	126.4(2)
O(2)–C(17)	130.7(4)	C(15)–N(2)–Ni(1)	128.4(2)
N(2)–C(15)	129.8(4)	C(17)–C(16)–C(15)	123.6(3)
N(2)–C(12)	147.8(4)	N(2)–C(15)–C(16)	121.2(3)
C(16)–C(17)	142.4(5)	C(15)–N(2)–C(12)	121.8(3)
C(15)–C(16)	147.2(5)	O(1)–Ni(1)–N(2)	154.1(1)
C(15)–C(22)	151.5(5)	O(2)–Ni(1)–N(1)	153.7(1)

The coordination sphere around Ni^{II} is a tetrahedrally distorted square-planar arrangement because of the *twist* conformation of the N1–C10–C11–C12–N2 sequence. In contrast, both Ni–N–C–C–C–O rings are almost planar. X-ray structure analysis of **NiL** shows that the nickel atom is coordinated by all four atoms of the N_2O_2 donor set. The distortion of the central NiN_2O_2 unit can be described by the angle of 36° between the two planes Ni1/N1/O1 and Ni1/O2/N2. The bond lengths and angles are in agreement with the values for tetracoordinate low-spin divalent nickel complexes.

The Ni–O(1) (189.2(2) pm), Ni–O(2) (188.5(2) pm), Ni–N(1) (195.7(3) pm), and Ni–N(2) (196.7(3) pm) distances are similar to the corresponding Ni–O (182 pm) and Ni–N(imine)

(189 pm) distances in [Ni(Me-sal)dpt]Cl,[45] and Ni–O (184 pm) and Ni–N (187 pm) in NiDAO.[46] As a result of the molecular packing in the crystal structure of **NiL** the complex molecules are packed in columns along [010].

2.3. Catalytic Activity Studies

Since studies of the non-enzymatic oxygenation reactions help us to the understanding of the oxygenase-catalyzed reactions, and on the other hand oxidation of organic substrates in the presence of metal complexes have immense importance from synthetic point of view, we have investigated the catalytic potential of the **NiL** for the oxidation of styrene and α-methyl styrene.

The oxidation of styrene and α-methyl styrene, catalyzed by **NiL** was carried out using *tert*-butylhydroperoxide as an oxidant and the results of oxidation reactions are shown in Table 2. Styrene catalyzed by *tert*-butylhydroperoxide in the presence of catalytic amounts of **NiL** gives two reaction products, styrene oxide and benzaldehyde. Styrene oxide was obtained only in poor yield, whereas the yield of benzaldehyde is higher. In the case of α-methyl styrene, epoxide and acetophenone were obtained as products, whereas acetophenone is the major product. The higher reactivity observed in the case of α-methyl styrene in comparison with styrene seems to be due to the electron donation effect of the methyl group to the double bond. The double bond may be considered as a nucleophile in the oxidation reaction. According to the results shown in Table 2, the obtained benzaldehyde and acetophenone products are due to the over oxidation of styrene oxide and α-methyl styrene respectively.[47] Additionally, higher conversion and turnover numbers were achieved in this catalytic system in comparison with other reported Ni^{II} Schiff base complexes.[48–50]

Table 2. Oxidation of styrene and α-methyl styrene with TBHP catalyzed by nickel complex in CH_3CN.

Alkene	Con.a) /%	Yield b) /%		TON c)
Styrene	58	9 (epoxy)	49 (benzaldehyde)	181
α-Methyl styrene	97	13 (epoxy)	84 (acetophenone)	303

a) GC yields are based on starting alkenes. b) All the reactions were run at least in triplicate, and the data represent an average of these reactions. c) Turnover number (TON) is the ratio of the number of moles of products to number of moles of catalyst.

3. Conclusions

N_2O_2 tetradentate Schiff base ligand (**H_2L**) and its Ni^{II} complex were prepared and characterized. Crystal structure of the complex (**NiL**) was determined. In the crystal structure, the nickel atom has a tetrahedrally distorted square-planar arrangement. This complex has potential activity for oxidation of styrene and α-methyl styrene. The conversion of styrene is 58 % and for α-methyl styrene 97 %.

4. Experimental Section

4.1. General Information

Solvents (ethanol and acetonitrile) were dried and distilled by standard methods before use.[51] 2,2'-Dimethylpropylenediamine (Merck, 98 %), 2-hydroxypropiophenone (Across, 97 %) were used as received.

4.2. Instrumentation

Infrared spectra were recorded as KBr pellets with a Unicam Mattson 1000 FT-IR. Elemental analysis (C, H, N) were performed with a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analyze System KBr pellets, GmbH, Germany). ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions with a Bruker FT-NMR 250 (250 MHz) spectrometer. The residual $CHCl_3$ in conventional 99.8 at.-%. $CDCl_3$ gives a signal at 7.26 ppm, which was used for calibration of the chemical shift scale, and $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). A digital melting point measuring device (Electrotermal 9100) was used. A double beam spectrophotometer (Shimadzu, UV-240) was used for the UV-Vis absorption determination.

4.3 Preparations

H_2L: A solution of 2,2'-dimethylpropylenediamine (0.102 g, 1 mmol) in ethanol (30 mL) was treated with 2-hydroxypropiophenone (0.300 g, 2 mmol). The bright yellow solution was stirred and heated to reflux for 1 h. A yellow precipitate was obtained that was filtered off, washed with diethyl ether (2 × 5 mL). The crude was dissolved in dichloromethane (10 mL) and kept at room temperature to give bright yellow crystals of **H_2L** after a few days. Yield 0.326 g, 89 %. **^{1}H NMR** ($CDCl_3$): δ = 12.34 (s, 2 H, OH), 7.50–6.73 (m, 8 H, Ar–H), 3.56 (s, 4 H, NCH_2), 2.81–2.74 [q, ^3J(H,H) = 7.7 Hz, 4 H, N = CCH_2], 1.23 (s, 6 H, CH_3), 1.20–1.15 [t, ^3J(H,H) = 7.7 Hz, 6 H, N = CCH_2CH_3]. **IR** (KBr): $\tilde{\nu}$ = ν(O–H) 3419 m, ν(C=N) 1617 s, ν(C=C) 1570 m, ν(C–O) 1220 m cm^{-1}. $C_{23}H_{30}N_2O_2$ (366.49): calcd. C 73.37, H 8.25, N 7.67 %; found C 73.45, H 8.31, N 7.56 %. **$^{13}C\{^1H\}$ NMR**: δ = 55.66 (C=NCH_2), 35.72 [C=$NCH_2C(CH_3)_2$], 24.61 [C=$NCH_2C(CH_3)_2$], 21.00 (N=CCH_2CH_3), 11.61 (N=CCH_2CH_3), 116.92–165.09 (aromatic C), 177.29 (C=N).

NiL: A solution of **H_2L** (0.366 g, 1 mmol) in ethanol (20 mL) was added to a suspension of $Ni(OAc)_2{\cdot}4H_2O$ (0.248 g, 1 mmol). The reaction mixture was heated to reflux for 1 h. The colored solution was concentrated to yield colored powders. The product was washed with warm ethanol. The clear filtrate was kept at 25 °C to give the green crystals of the nickel complex. Yield 0.402 g, 95 %. **^{1}H NMR** ($CDCl_3$): δ = 7.76–6.52 (m, 8 H, Ar–H), 3.56 (s, NCH_2), 3.03–2.07 (q, 4 H, N=CCH_2), 1.23 (s, 6 H, CH_3), 1.02–0.66 (t, 6 H, $NCCH_2CH_3$).]. **IR** (KBr): $\tilde{\nu}$ = ν(C=N) 1606 s, ν(C=C) 1581 s, ν(C–O) 1206 m cm^{-1}. **UV/Vis** ($CHCl_3$): λ_{max} = 256 (ε = 9600 $\text{M}^{-1}{\cdot}\text{cm}^{-1}$), 337 ($\varepsilon$ = 2690 $\text{M}^{-1}{\cdot}\text{cm}^{-1}$) nm. $C_{23}H_{28}N_2NiO_2$ (423.18): calcd. C 65.27, H 6.66, N 6.61, Ni 13.87 %; found C 65.43, H 6.51, N 6.69, Ni 13.72 %. **$^{13}C\{^1H\}$ NMR** δ = 55.83 (C=NCH_2), 31.04 [C=$NCH_2C(CH_3)_2$], 24.10 [C=$NCH_2C(CH_3)_2$], 20.42 (N=CCH_2CH_3), 11.07 (N=CCH_2CH_3), 116.35–164.03 (aromatic C), 176.73 (C=N).

4.4. General Oxidation Procedure

The catalyst (**NiL**) (0.032 mmol) was dissolved in acetonitrile (10 mL) in a 50 mL round-bottomed flask equipped with a condenser. Afterwards, the alkene (styrene or α-methyl styrene) (10 mmol) and TBHP (30 mmol) were added, respectively. The mixture was heated to reflux for 6 h. Samples were taken at periodic time intervals and analyzed by gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

4.5. X-ray Crystallography

The selected crystals of **NiL** were covered with perfluorinated oil and mounted on the top of a glass capillary in a flow of cold gaseous nitrogen. The orientation matrix and the unit cell dimensions were determined from 4000 reflections [Stoe IPDS 2T graphite-monochromated Mo-K_α radiation ($\lambda = 71.073$ pm); see also Table 3]. The intensities were corrected for Lorentz and polarizations effects. In addition, absorption corrections were applied for **NiL** (numerical). The structure was solved by direct methods using SIR-92 and was refined against F^2 by full-matrix least-squares using the program SHELXL-97. The hydrogen atoms were calculated in ideal positions and were refined with a common displacement parameter. Programs used were SHELXL-97,[52] SIR-92,[53] SHELXTL-Plus,[54] and PLATON.[55]

Table 3. Crystal data and structure refinement for **NiL**.

	NiL
Empirical formula	$C_{23}H_{28}N_2NiO_2$
Formula mass	423.18
Crystal size /mm	0.18 × 0.12 × 0.04
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a /pm	907.7(1)
b/pm	1289.4(1)
c /pm	1752.4(1)
α /°	90
β /°	90
γ /°	90
Volume /pm^3 × 10^6	2051.0(3)
Z	4
$D_{calcd.}$ /g• cm^{-3}	1.37
Absorp. correction	numerical
μ /cm^{-1} (Mo-K_α)	9.67
T /K	100
2θ_{max} /°	56.74
Index range	$-12 \le h \le 10$
	$-14 \le k \le 17$
	$-23 \le l \le 19$
Reflections collected	8564
Uniq. reflect.	4931
R_{int}	0.0669
Reflect. with $F_o > 4\sigma(F_o)$	4088
Parameters	258
Flack parameter	–0.02(2)
R_1	0.0454
wR_2 (all data)	0.1049$^{a)}$
Max. residual electron density / e•pm^{-3} × 10^{-6}	0.385

a) $w = 1/[\sigma^2(F_o^2)+(0.0575P)^2]$; $P = [\max(F_o^2, 0)+2F_c^2]/2$.

The crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-806604 (**NiL**). Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-Mail: data_request@ccdc.cam.ac.uk or via the internet: http://www.ccdc.cam.ac.uk/products/csd/request.)

Acknowledgement

This work was supported by the K.N. Toosi University of Technology.

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Received: January 17, 2011