

Synthesis, crystal structure and catecholase activity of a Ni(II) complex derived from a tetradentate Schiff base ligand

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Abstract. A new nickel(II) complex [Ni(L)] (**1**) [$H_2L = 1,1'-(1E,1'E)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol$] was synthesized and X-ray crystallographically characterized. **1** crystallizes in orthorhombic crystal system with Cmc21 space group. The unit cell dimensions of the crystal are $a = 30.6345(4) \text{ \AA}$, $b = 8.45340(10) \text{ \AA}$, $c = 7.75180(10) \text{ \AA}$. Structural analysis reveals a tetradentate chelation behaviour of the dianionic ligand H_2L having a distorted square planar geometry around Ni(II) with NiN_2O_2 chromophore in **1**. The title complex **1** behaves as an effective catalyst towards oxidation of 3,5-ditertiarybutyl catechol (3,5-DTBC) in acetonitrile to its corresponding quinone derivative in air. The reaction follows first-order reaction kinetics with rate constant $4.28 \times 10^{-5} \text{ min}^{-1}$. The reaction follows Michaelis-Menten enzymatic kinetics with a turnover number of (K_{cat}) 140.72 h^{-1} in acetonitrile.

Keywords. Nickel(II); Schiff base; X-ray structure; Catecholase activity.

1. Introduction

Oxidation of a range of *o*-diphenols (catechols) in presence of the enzyme catecholase to corresponding quinone is known as catecholase activity^{1–5} which is a very important process in bacteria, fungi and plants. Crystal structure determination of the met-form of catecholase in 1988 revealed that the active site of the enzyme consists of a hydroxo bridged dicopper(II) centre in which each copper(II) centre is coordinated to three histidine nitrogens and adopts a trigonal pyramidal environment with one nitrogen in the apical site.⁶ As soon as this discovery was made, a huge number of dicopper(II) molecules with several nitrogen containing ligands and bridging moieties designed to model catecholase.^{1–5} Some monocopper(II) compounds⁷ and compounds with Mn(II/III),^{7c,8} Fe(III),⁹ Co(II/III),¹⁰ Zn(II)¹¹ have also been reported in literature that mimic catecholase activity. Recent investigations have shown that a few nickel(II) complexes with Schiff base ligands can also mediate such catalytic oxidation.¹² All these findings reveal that the metal ion oxidation state, ligand environment, nuclearity of the complexes, etc. play important role(s) in catalyzing catechols and its

derivatives to their corresponding quinones. Moreover, the straightforward structure-property relationship in catecholase activity is yet to be explored appropriately. Therefore designing new molecules with catecholase activity is attractive even today.

Herein, we report the synthesis and crystallographic characterization of a mononuclear Ni(II) complex with a dianionic (N,O) donor Schiff base ligand which catalyses a 3,5-ditertiarybutyl catechol to the corresponding quinone derivative in acetonitrile in air. An investigation of Michaelis-Menten enzyme kinetics along with the calculation of turnover number of the catalytic reaction is also reported.

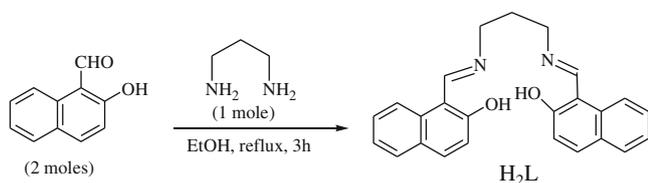
2. Experimental

2.1 Materials

Nickel dichloride ($NiCl_2 \cdot 6H_2O$), 1,3-diaminopropane, 3,5-di-*tert*-butylcatechol (Aldrich, UK) and all other solvents were purchased from the respective concerns and used as received. Solvents were dried according to standard procedure and distilled prior to use.

The starting material, 2-hydroxy-1-naphthaldehyde was prepared according to the published procedure in

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Scheme 1. Synthesis of the Schiff base ligand: 1,1'-(1E, 1'E)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol.

literature.¹³ The ligand H₂L was synthesised (scheme 1) by refluxing 2-hydroxy-1-naphthaldehyde (1.0 g, 5.8 mmol) with 1,3-diaminopropane (0.215 g, 2.9 mmol) in 30 mL dehydrated ethanol. After 3 h, the reaction solution was evaporated under reduced pressure to yield a yellow coloured solid, which was dried under vacuum and stored over CaCl₂ for subsequent use.

For catecholase activity study, 1×10^{-4} mol dm⁻³ solution of **1** (0.0009 g) was treated with 1×10^{-2} mol dm⁻³ (100 equivalents) of 3,5-DTBC (0.0222 g) under aerobic conditions.

2.2 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. UV-Vis and IR spectra (KBr discs, 4000–300 cm⁻¹) were recorded using a Shimadzu UV-Vis 2450 spectrophotometer and Perkin-Elmer FT-IR model RX1 spectrometer, respectively. The ¹H NMR spectral data were collected in CDCl₃ on a Bruker 400 MHz spectrometer.

2.3 Preparation of **1**

Compound **1** was prepared by dropwise addition of H₂L (0.1 g, 0.262 mmol) solution in acetonitrile (15 mL) into a stirring solution of nickel dichloride (0.062 g, 0.262 mmol) in methanol-acetonitrile mixture (15 mL). The resulting red-brown coloured solution was kept in open air for slow evaporation. After 2–3 days, the deep brown crystals of **1** was collected, washed with hexane and dried in vacuo over silica gel indicator.

Yield: 88.5%, Anal. calc. for C₂₅H₂₀N₂O₂Ni (**1**): C, 68.38; H, 4.59; N, 6.38; Found: C, 68.24; H, 4.50; N, 6.32. Selected IR bands (KBr pellet, cm⁻¹): 1593(s). UV-Vis (λ, nm, MeOH): 416, 334, 313, 266, 217.

2.4 X-ray diffraction study

Single crystal data of **1** were collected on a Bruker AXS KAPPA APEX II diffractometer using Mo-K_α

radiation (λ = 0.71073 Å) at 293(2) K. Systematically absent reflections led to the identification of space groups Cmc21 for **1**. Of the 9247 total reflections for the complex, 2510 with [I > 2r(I)] were used for structure solutions. The structures were solved by direct methods, and the structure solution and refinement were based on |F²|. All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions when possible and given isotropic U values 1.2 times that of the atom to which they are bonded. The final differences Fourier map showed the maximum and minimum peak heights at 0.7897 and -0.8656 e⁻³ Å⁻³ for **1** with no chemical significance. All calculations were carried out using SHELXL-97¹⁴ and ORTEP-32.¹⁵ The crystal data and data collection parameters are listed in table 1.

3. Results and Discussion

3.1 Synthesis and formulation

Reaction at room temperature with required molar ratio among nickel(II) salt and H₂L in acetonitrile produces the complex **1** in good yield. The complex was characterized by microanalytical (C, H and N), spectroscopic and other physicochemical results. The microanalytical data are in good conformity with the formulations of **1**. The moisture insensitive complexes are stable over long periods of time in powdery and crystalline states, and are soluble in methanol, acetonitrile, etc. In the IR spectra, relatively intense peaks around 1593 cm⁻¹ due to the C=N stretching frequency, and weak bands in the range 2980–2900 cm⁻¹ due to the aliphatic C-H stretching frequency, appear in both the complexes.

3.2 X-ray structure

1 crystallizes in the orthorhombic space group Cmc21. The thermal ellipsoid plot of **1** is given in figure 1. Ni(II) in **1** adopts a square planar geometry with NiN₂O₂ chromophore as is evident from the bond angle-bond distance table (table 2). The imine nitrogens (N1 and N1*) and phenoxo oxygens (O1 and O1*) coordinate to the metal centre. The N1 and N1*, and O1 and O1* are in mutually *cis* orientation. Each of the metal-nitrogen and metal-oxygen bond distances are 1.873(2) and 1.845(19) Å, respectively. In the complex there is no deviation of the metal centre from the N₂O₂ square plane. The bond angle and bond distances of the complex are comparable with the other reported square planar nickel(II) complexes.¹⁶

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C ₂₅ H ₂₀ N ₂ O ₂ Ni	
Formula weight	439.14	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c 21	
Unit cell dimensions	a = 30.6345(4) Å	$\alpha = 90^\circ$
	b = 8.45340(10) Å	$\beta = 90^\circ$
	c = 7.75180(10) Å	$\gamma = 90^\circ$
Volume	2007.45(4) Å ³	
Z	4	
Density (calculated)	1.453 Mg/m ³	
Absorption coefficient	0.991 mm ⁻¹	
F(000)	912	
Crystal size	0.25 × 0.15 × 0.15 mm ³	
Theta range for data collection	1.33 to 28.28°	
Index ranges	-33 ≤ h ≤ 40, -11 ≤ k ≤ 9, -10 ≤ l ≤ 10	
Reflections collected	9247	
Independent reflections	2510 [R(int) = 0.0285]	
Completeness to theta = 28.28°	100.0 %	
Absorption correction	multi scan	
Max. and min. transmission	0.8656 and 0.7897	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2510/ 1/140	
Goodness-of-fit on F ²	1.011	
Final R indices [I > 2sigma(I)]	R1 = 0.0352, wR2 = 0.0778	
R indices (all data)	R1 = 0.0562, wR2 = 0.0866	
Absolute structure parameter	0.027(17)	
Largest diff. peak and hole	0.530 and -0.170 e.Å ⁻³	

3.3 Catecholase activity: Spectrophotometric study

In order to study the catecholase activity of the complex **1**, 3,5-DTBC with two bulky *t*-butyl substituents on the ring and low quinone-catechol reduction potential has been chosen as substrate. This makes it easily oxidized to the corresponding *o*-quinone, 3,5-DTBQ

which is highly stable and shows a maximum absorption at 401 nm in methanol.^{7e} Solution of **1** was treated with 100 equivalents of 3,5-DTBC under aerobic conditions. The repetitive UV-Vis spectral scan was recorded in pure acetonitrile (figure 2). Spectral bands at 416, 334, 313, 266 and 217 nm appear in the electronic spectrum of complex **1**, whereas 3,5-DTBC shows a single

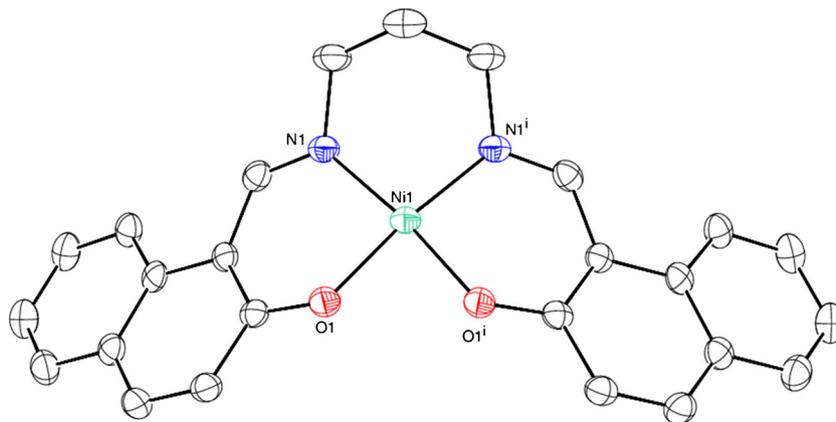
**Figure 1.** ORTEP of **1** with 30% thermal ellipsoid plot.

Table 2. Bond lengths [\AA] and angles [$^\circ$] for **1**.

Bond distances			
Ni(1)-O(1)	1.8458(19)	Ni(1)-O(1*)	1.8458(19)
Ni(1)-N(1)	1.873(2)	Ni(1)-N(1*)	1.873(2)
Bond angles			
O(1)-Ni(1)-O(1*)	82.53(12)	O(1)-Ni(1)-N(1)	91.18(9)
O(1)-Ni(1)-N(1*)	173.62(9)	O(1*)-Ni(1)-N(1*)	91.18(9)
N(1)-Ni(1)-N(1*)	95.08(14)		

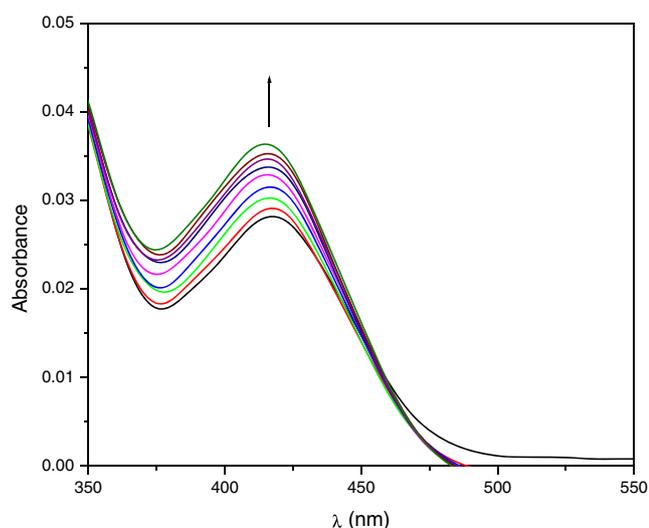
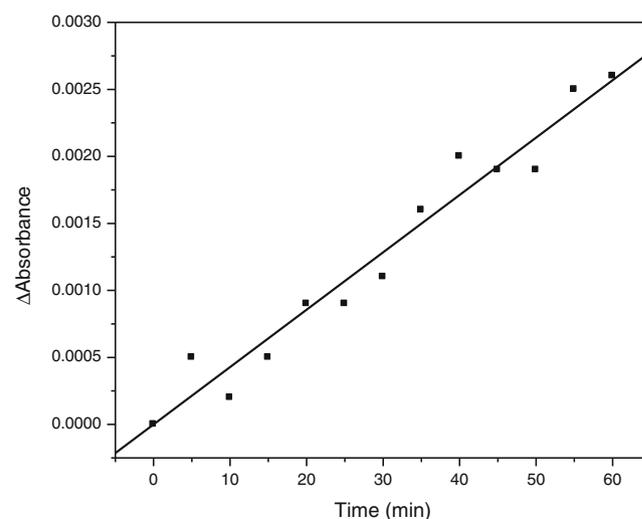
band at 282 nm. As the reaction proceeds, there is a gradual decrease in intensity of the band at 282 nm due to the catechol and a new band is formed at 415 nm which indicates the formation of the respective quinone derivative. The product 3,5-DTBQ was purified by column chromatography, isolated in high yield (89.70%) by slow evaporation of the eluant and was identified by ^1H NMR spectroscopy (figure S1). ^1H NMR (CDCl_3 , 400 MHz): $\delta_{\text{H}} = 1.16$ (s, 9H), 1.20 (s, 9H), 6.15 (d, $J = 2.4$ Hz, 1H), 6.86 (d, $J = 2.4$ Hz, 1H).

In order to find out the reaction rate between 3,5-DTBC and **1**, the reaction kinetics between them was studied by observing the time dependent change in absorbance at a wavelength of 415 nm. The colour of the solution was gradually turned into deep brown indicative of gradual conversion of 3,5-DTBC to 3,5-DTBQ. The difference in absorbance ΔA at 415 nm, was plotted against time to obtain the velocity (r_0) for that particular catalyst to substrate concentration ratio (figure 3). A first-order catalytic reaction was observed, with velocity $4.28 \times 10^{-5} \text{ min}^{-1}$ for **1**.

3.4 Enzyme kinetics study

Kinetic experiments were performed spectrophotometrically with complex **1** and the substrate 3,5-DTBC in acetonitrile, thermostated at 20°C . 0.04 mL of the complex solution, with a constant concentration of 1×10^{-4} M, was added to 2 mL of 3,5-DTBC of a particular concentration (varying its concentration from 1×10^{-3} M to 1×10^{-2} M) to achieve the ultimate concentration of the complex as 1×10^{-4} M. The conversion of 3,5-DTBC to 3,5-DTBQ was monitored with time at a wavelength of 415 nm for solutions in MeCN. The rate for each concentration of the substrate was determined by the initial rate method.

The rate versus concentration of substrate data were analyzed on the basis of Michaelis-Menten approach of enzymatic kinetics to get the Lineweaver-Burk (double reciprocal) plot as well as the values of the various kinetic parameters V_{max} , K_{M} and K_{cat} . The observed rate vs. [substrate] plot in acetonitrile solution as well as Lineweaver-Burk plot is given in figure 4. The kinetic

**Figure 2.** Change in spectral pattern of complex **1** after addition of 3,5-DTBC during 6 h of reaction in acetonitrile.**Figure 3.** A plot of the difference in absorbance (ΔA) vs. time.

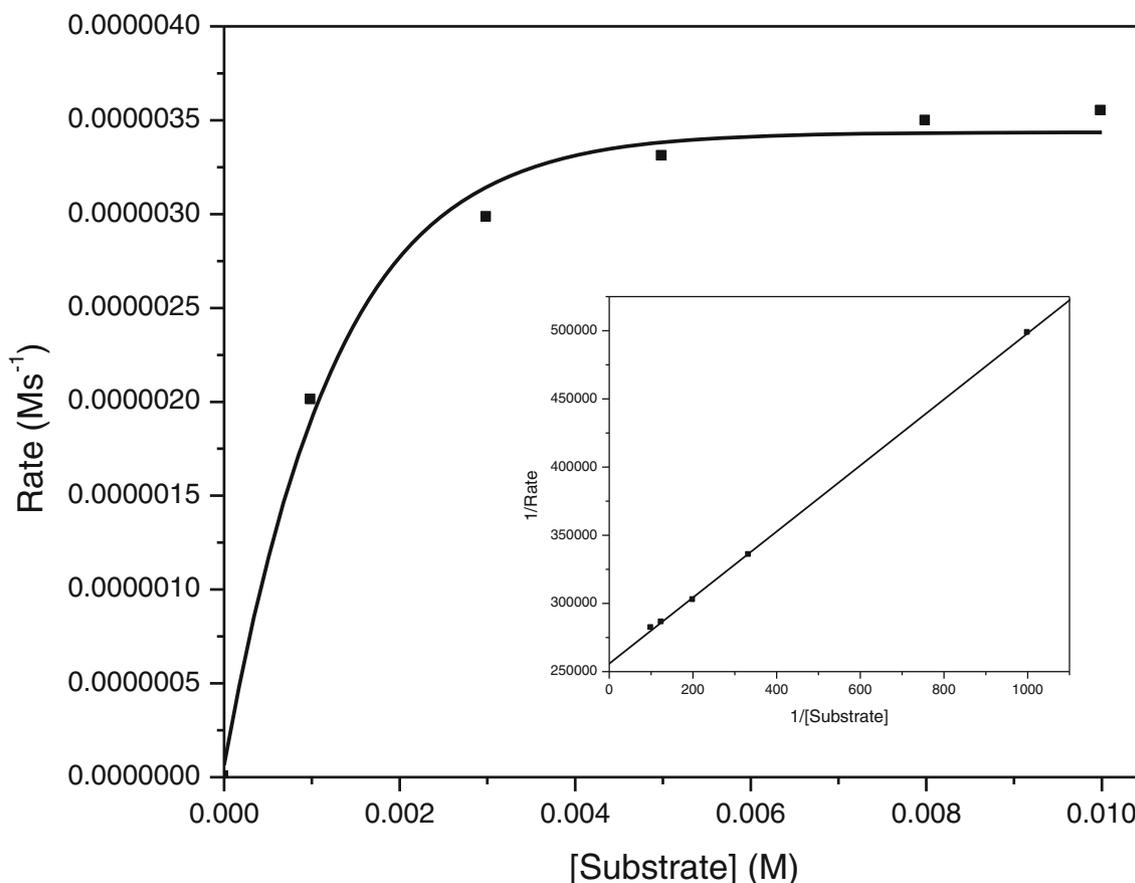


Figure 4. Plot of rate vs. [substrate] in presence of **1** in MeCN; inset: Lineweaver-Burk plot.

Table 3. Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by **1**.

Solvent	V _{max} (Ms ⁻¹)	Std. error	K _M (M)	Std. error	K _{cat} (h ⁻¹)
MeCN	3.91 × 10 ⁻⁶	4.74 × 10 ⁻⁷	9.47 × 10 ⁻⁴	7.30 × 10 ⁻⁵	140.72

parameters are listed in table 3. The turnover number (K_{cat}) found is 140.72 h⁻¹ in MeCN.

4. Conclusion

We have designed and synthesized a new nickel(II) compound **1** which has been characterized by X-ray crystallography. The newly synthesized compound catalyses the oxidation of 3,5-ditertiarybutyl catechol to its corresponding quinone form in acetonitrile solution. Kinetic investigation revealed that the reaction followed the first order path with rate constant 4.28 × 10⁻⁵ min⁻¹. The turnover number reported for this very catalytic reaction is 140.72 h⁻¹ which is quite high in comparison to a recently reported work.^{12a}

Supplementary Information

CCDC No. 1009492 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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