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SYNTHESIS, CHARACTERIZATION AND CATECHOLASE ACTIVITY OF COBALT (II) COMPLEXES WITH PHENOL BASED N_2O_2 CHELATING LIGAND

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ABSTRACT

Two mononuclear octahedral Co(II) complexes [$Co(H_2L)(PhCOO)_2$] and [$Co(H_2L)(C_8H_4O_4Na)_2$] using H_2L (N,N'-dimethyl-N,N'-bi(2-hydroxy-3,5-dichlorobenzyl)-ethylenediamine) as a facially coordinating sterically constrained N_2O_2 ligand have been synthesized and characterized. [$Co(H_2L)(PhCOO)_2$] shows catecholase activity in methanol at room temperature.

Keywords: Co (II) Complex, Synthesis, Characterization, Properties, Catecholase Activity

INTRODUCTION

The presence of metal ion-phenoxo linkage in a large number of metalloenzymes is believed to have an enormous influence on the reactivity of these enzyme active sites[1]. Transition metal complexes with N, O donor chelating agent have been the subject of intensive research due to their versatile applications[2-4]. Metal complex with phenol-based chelating ligand with pre-orga nized donor set can mimic the structural model as well as a functional model of metalloenzyme[5-7].

A large number of cobalt(II) complexes of phenol-based ligands are known to bind dioxygen more or less reversibly and are therefore are frequently studied as model compounds for natural oxygen carriers and for O_2 storage[8]. In the present time, significant attention has been focused on these synthetic oxygen transport systems. The aim is that these carriers mimic the biological systems in fixation, release, storage and activation of dioxygen[9].

Keeping in view, in this present work, we synthesize sterically constrained tetradentate ligand *N,N'*-dimethyl-*N,N'*-bis(2-hydroxy-3,5-dichlorobenzyl)-ethylenediamine (H_2L).Using this ligand we have synthesized two octahedral mononuclear mixed ligand cobalt(II) complexes [$Co(H_2L)(PhCOO)_2$] **1**. and [$Co(H_2L)(C_8H_4O_4Na)_2$] **(2)**. All these complexes and ligand have been characterized by various spectroscopic techniques. Complex **(1)** shows catecholase activity in methanol solvent under the aerobic condition at room temperature.

EXPERIMENTAL

Materials

N,N′ -di-methylethylenediamine was procured from Aldrich. Solvents were collected from the local market and purified using appropriate drying agents[10]. All other chemicals were also received from the local market.

Synthesis of Ligand

N,N′-dimethyl-*N,N′* -bis(2-hydroxy-3,5dichlorobenzyl)-ethylenediamine (H_2L)

10 mmol N,N'-Dimethylethylenediamine (0.88 g) was taken in a methanol. About 20 mmol (0.60 g) paraformaldehyde was added to it. The solution was boiled for 2h. To this 20 mmol (3.26 g) 2,4-dichlorophenol was added slowly, with constant stirring. The mixture was refluxed for 12h. A white crystalline compound was obtained and it is filtered off. The compound was washed with methanol and

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diethyl ether and recrystallized from acetone-pet ether (60-80^{0}C) mixture. Yield: 3.1 g (87%); ^{1}HNMR (300 MHz, $CDCl_3$, 25^{0}C), δ/ppm: 2.25 (s, 6H, N-CH_3), 2.64(s, 4H, CH_2-CH_2), 3.62(s, 4H, benzylic), 6.85 (s, 2H, aryl).IR (KBr disk, cm^{-1}): 3082, 2823, 1452, 1272, 1155, 1014, 862, 729. ESI-MS in CH_2Cl_2: m/z ($M+H^+$): 439.

Preparation of Complex

[Co(H_2L)($PhCOO$)$_2$] (1)

$Co(ClO_4)_2.6H_2O$ (0.18 g, 0.5 mmol) and the ligand H_2L (0.19 g ,0.5 mmol) was mixed in MeOH (25mL) and refluxed for 30 minute. A pinch of sodium benzoate was added to this solution and refluxed for another hour. Then the solution was cooled and filtered. The filtrate was kept in the open air for crystallization. A pink color crystalline compound was collected. IR (KBr disk, cm^{-1}): 3417, 2886, 1653, 1451, 1352, 1255, 751, 716. UV-Vis [λ_{max}/nm (ε/M^{-1}cm^{-1})]: 310 (1086).

[Co(H_2L)($C_8H_4O_4Na$)$_2$](2)

$Co(ClO_4)_2.6H_2O$ (0.18 g, 0.5 mmol) and the ligand H_2L(0.19 g ,0.5 mmol) were kept in MeOH solution (25mL) and the mixture was boiled for 30 minutes. Then sodium terephthalate (0.1 g, 0.5mmol) was added to this solution and heated again for another 1 hour. The resulting solution was kept in the open air for slow evaporation. A sky blue crystalline compound was obtained and was collected by filtration. IR (KBr disk, cm^{-1}): 3476, 3415, 2921, 1673, 1453, 1307, 1283, 754. UV-Vis [λ_{max}/nm (ε/M^{-1}cm^{-1})]: 309 (2140).

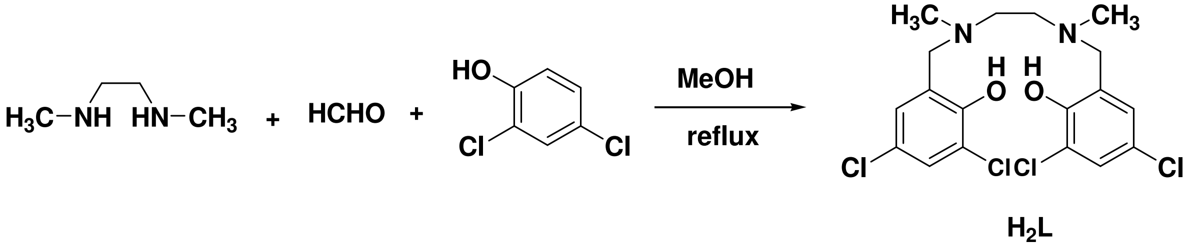
Physical Measurements

UV-visible spectra in solution were employed on a Perkin-Elmer 950 UV/vis/NIR spectrophotometer. Infrared spectra of these compounds were taken by Perkin-Elmer FT-IR spectrometers, with samples prepared as KBr pellets. Proton NMR spectra were carried out with a Bruker AC 300 apparatus while Mass spectra (ESI-MS in positive ion mode) were recorded on a QTOF Model YA263 Micro Mass Spectrometer.

RESULTS AND DISCUSSION

Synthesis

The ligand H_2L (*N,N′*-dimethyl-*N,N′* -bis(2-hydroxy-3,5dichlorobenzyl)-ethylenediamine) has been synthesized by the knowledge of Mannich reaction. The reaction occurred in methanol. The reaction pathway of ligand synthesis is depicted in scheme1. The structure of the ligand is well established by ^{1}H NMR spectra and Mass spectra. The details data of ^{1}H NMR spectra and Mass spectra are summarized in the experimental section.



Scheme-1

Two mononuclear octahedral Co(II) complexes have been prepared using sterically constrained tetra dentate N_2O_2 ligand (H_2L). The geometry of these mononuclear mixed ligand compounds [Co(H_2L)($PhCOO$)$_2$] and [Co(H_2L)($C_8H_4O_4Na$)$_2$] are nearly octahedral. All the compounds were characterized by taking various spectroscopic techniques. Spectroscopic data are described in the experimental section.

Both the two complexes give characteristic bands of the coordinated ligand (H_2L). Complex **1** shows a prominent band at 1255 due to $\bar{\upsilon}_{\text{C-O / phenolate}}$ present in the ligand[11]. Another strong bands arise at 1653 cm^{-1} and at 1352 cm^{-1} due to the symmetric and asymmetric stretching modes of vibration of carboxylate group[12]. The difference between those two modes of vibration is greater than 260 cm^{-1} which indicates the presence of coordinating mono dentate carboxylate group[13].

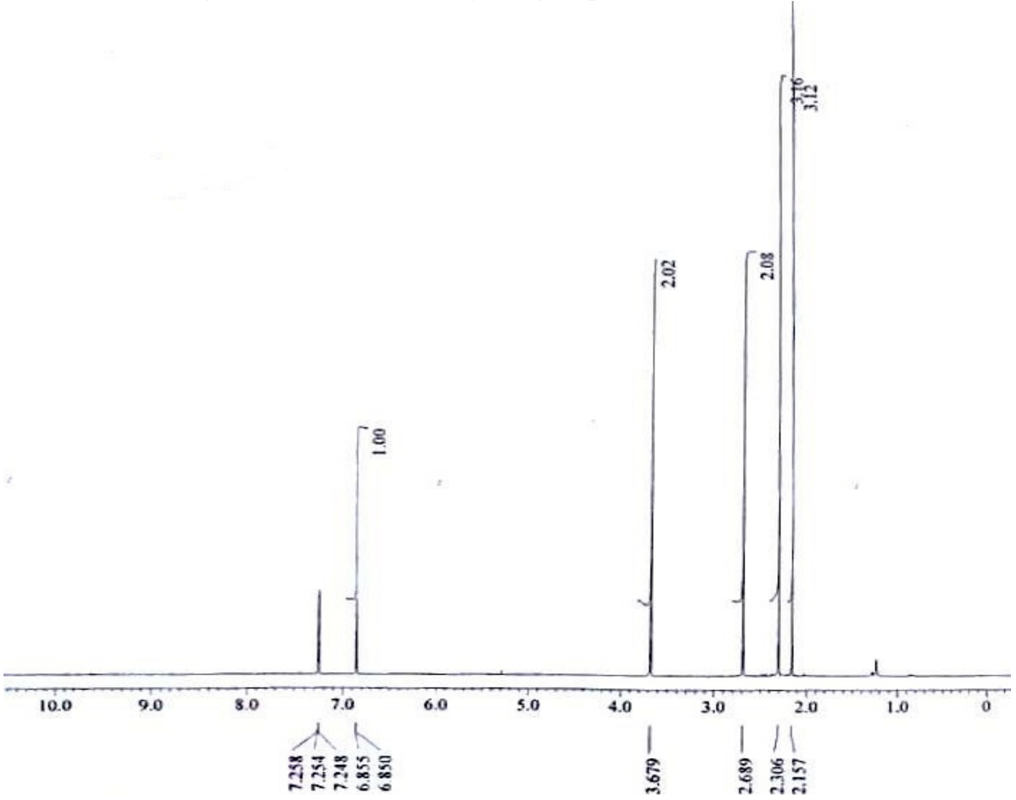


Fig.-1: ^{1}H NMR Spectrum of Ligand H_2L in $CDCl_3$.

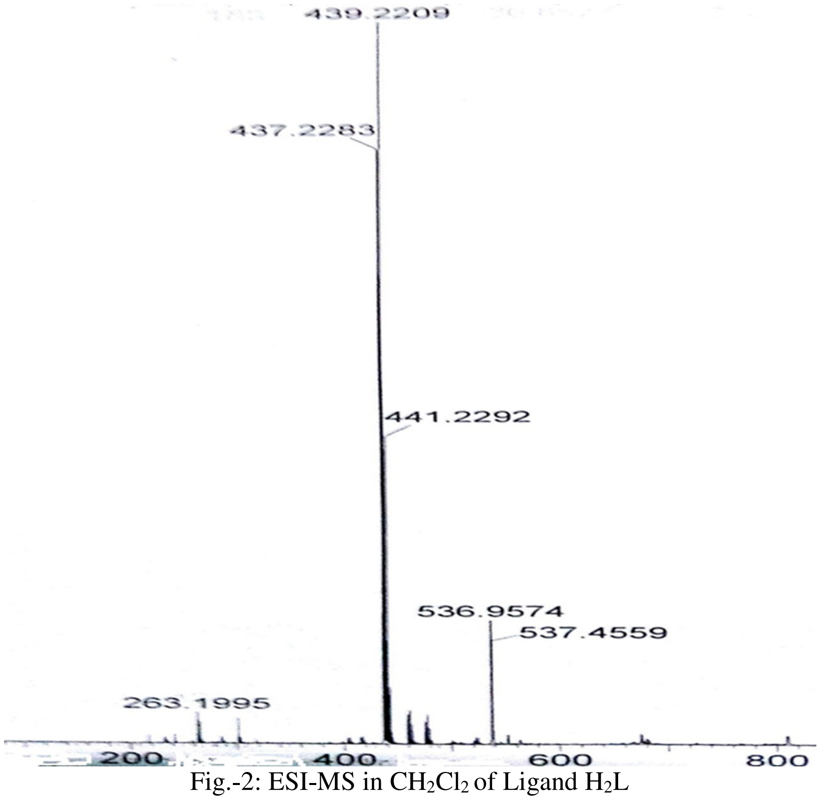
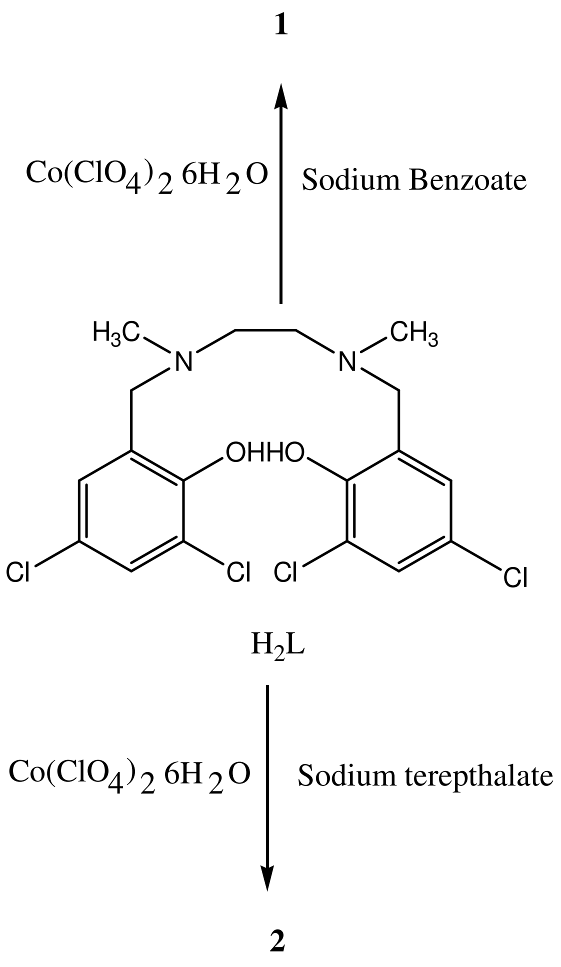


Fig.-2: ESI-MS in CH_2Cl_2 of Ligand H_2L



Scheme-2

At the same time, Complex **2** displays band at 1283 cm^{-1} due to $\bar{\upsilon}_{\text{C-O / phenolate}}$ stretch. In addition, two strong bands for symmetric and asymmetric stretching modes of vibration of carboxylate groups arise at 1673 cm^{-1} and 1307 cm^{-1}. Here also the difference is greater than 260 cm^{-1} as expected for the presence of coordinated mono dentate carboxyl ate group.

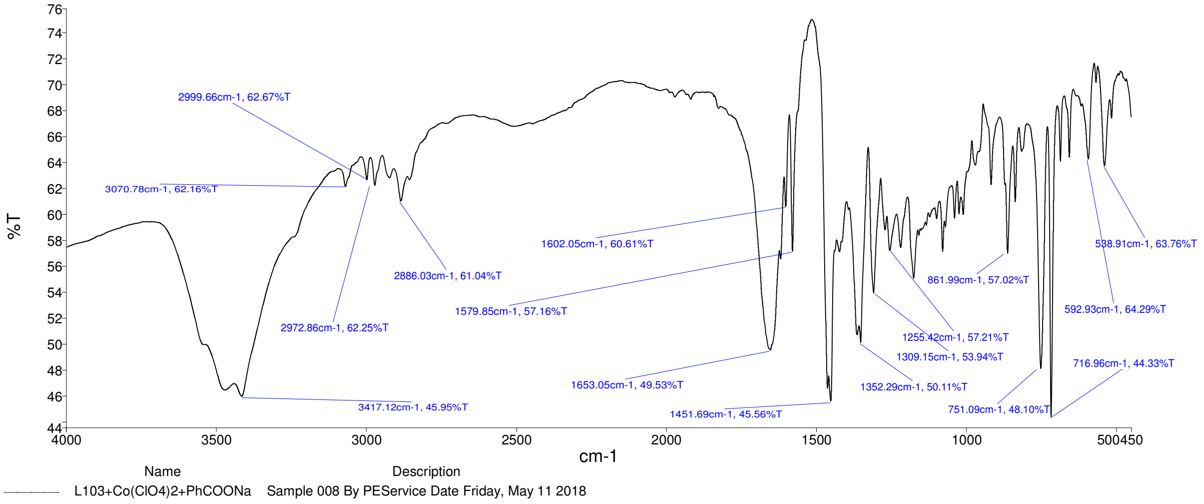


Fig.-3: IR Spectrum (in KBr Disk) of Complex **1**

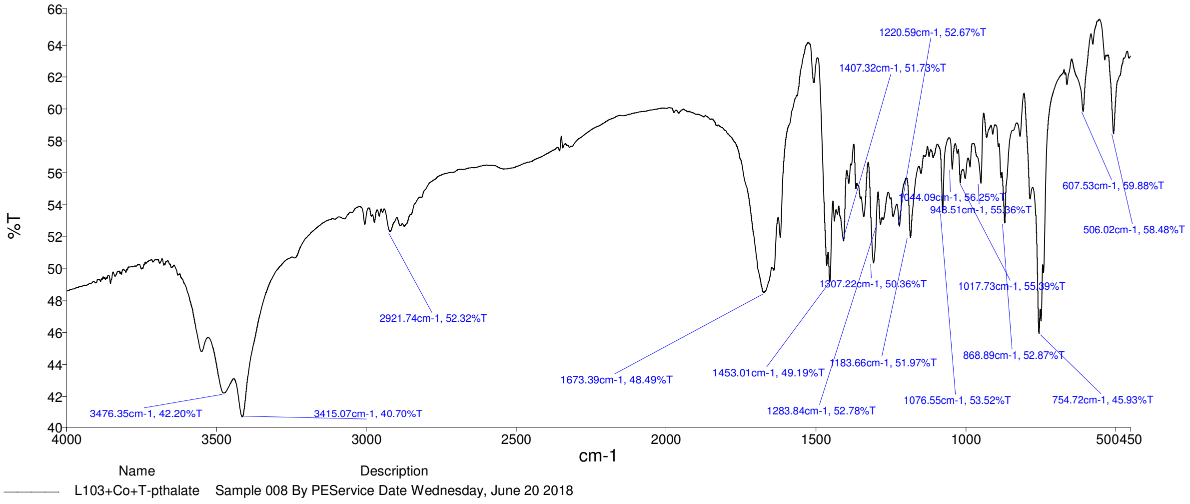


Fig.-4: IR Spectrum (in KBr Disk) of Complex **2**

The electronic spectra of complexes (**1**- **2**) have been monitored in methanolic solution and the data are depicted in the experimental section. Complex **1** exhibits one intense shoulder near 300 nm and another one near 250 nm. On the basis of their high intensities, these bands are assigned as charge transfer in nature. Since in complex **1** cobalt(II) is in the low spin octahedral field ,it has $t_{2g}^6e_g^1$ electronic configuration and the band near 300 nm may be due to the ligand to metal charge transfer transition as reported earlier[14-15]. Complex **2** gives a similar type of UV- visible spectra in methanol solvent.

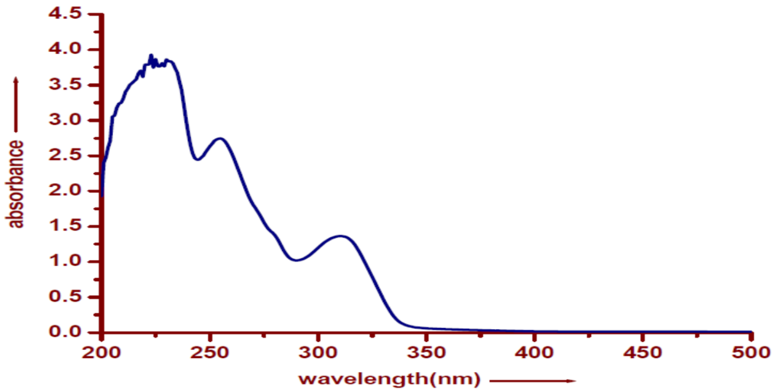
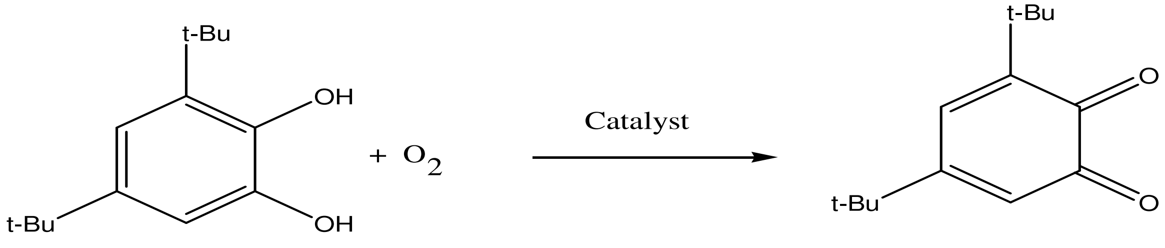


Fig.-5: Electronic Absorption Spectra of Complex 1 in MeOH

Catalytic Oxidation of 3,5-DTBC

The catecholl oxidase activity of mononuclear cobalt complex $[Co(H_2L)(PhCOO)_2]$ was monitored by taking 3,5-di-tert-butyl catechol (3,5-DTBC) as a substrate in methanol under the aerobic condition at room temperature. There was a gradual increase in absorbance at 400 nm when 3,5- di-tert-butyl catechol was added to the methanolic solution of the complex under the aerobic condition as described in Fig.-6 . Such a characteristic band was obtained due to the formation of 3,5-di-tert-butyl benzoquinone. 3,5-di-tert-butyl catechol (3,5 - DTBC) has been taken as the model substrate as it can readily be oxidised to 3,5-di-tert-butyl benzoquinone (3,5 - DTBQ). Two bulky substituents on the catechol ring make it easily oxidizable to the corresponding o-quinone 3,5-DTBQ and show maximum absorption at 400 nm in methanol[16]. Kinetic experiments were observed spectrophotometrically with complex **1** and the substrate 3,5-DTBC in methanol at 25°C. The conversion of 3,5–DTBC to 3,5-DTBQ (Quinone band maxima) was noticed with time at a wavelength of 400 nm for (**1**) in methanol. The rate constant for a particular complex–substrate concentration ratio was monitored by the change in absorbance versus time plot by choosing the initial rate method. Initial rate constant was found 74 ×10^{-4} h^{-1}.



3,5-DTBC

3,5-DTBQ

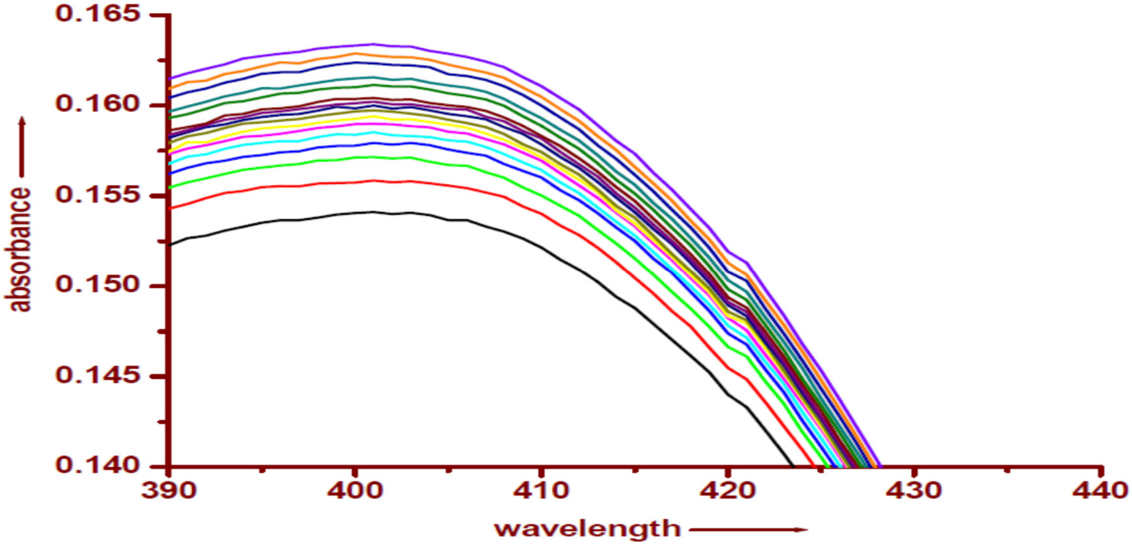


Fig.-6: Increase of Quinone Band at 400 nm after Addition of 100 Equivalents of 3,5-DTBC to a Solution Containing Complex 1 (10^{-4} M) in Methanol at 25 °C.

CONCLUSION

A sterically constrained tetra dentate phenol based ligand with N, O donor site has been taken here to synthesize mononuclear mixed ligand octahedral cobalt(II) complexes. IR, UV-Visible, mass and ^1H NMR spectroscopy have been used here to characterize the products. The tetradentate H_2L behaves as a capping ligand in **1-2** because of its enormous flexibility. IR spectra indicate that the carboxylate is coordinated to the metal center *via* monodentate fashion. Complex **1** shows catecholase activity.

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Financial support received from the Department of Science and Technology, Government of West Bengal, Kolkata (Project memo no. 1071(Sanc-4/2015 dated 23.02.2016) is gratefully acknowledged. We are grateful for the instrumental support from the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata.

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