Nickel(II)-salen Schiff Base Complex as Anion Receptor

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ABSTRACT

The Schiff base salen was incorporated to nickel(II) ion to afford nickel(II) diethylamino-substituted salen complex. The diethylamino-substituted salen l salen complex were characterized by Fourier Transform Infrared Spectroscopy (FTIR), diffuse reflectance ultravisible spectroscopy (DR UV-Vis) and ^{1}H (^{1}H-NMR). The binding affinity of the nickel(II) diethylamino-substituted salen complex towards specific anion in dichloromethane was investigated by us

| nickel(II) diethylamino-substituted salen complex | binding affinity | specific anion | UV-Vis Spectroscopy |

1. INTRODUCTION

Schiff base salen ligand is multidendate N-N and N-O donors and act as stabilizer ligands for dinuclear metal complexes [1]. The Schiff base salen was synthesised by condensation reaction between salicyaldehyde and derivative of diamine [2]. The Schiff base salen has attracted attention of researcher as salen is cheap and easy to synthesis. The Schiff base salen ligand able to form stable complex with most of the transition metal. [3]

Various salen complexes has been synthesised to serve as functional mimic enzyme because salen complex shows excellent catalytic activity in high temperature reaction. As example, manganese(II) (R,R)-1,2-diphenylethylenediamine substituted salen complex showed catalytic activity in enantioselective epoxidation onunfunctionalized alkene [13]. Diagram 1 illustarated the structural formula of manganese(II) (R,R)-1,2-diphenylethylenediamine substituted salen complex

The Schiff base complex which is an organometallic that can form self-assembly complex which mean when suitable ligand coordinate transition metal will result in the formation of cavity capable of anion binding [4]. As example, Alizera Asghari and co-worker have reported bis(2-hydroxyanil)acetylacetone lead(II) as neutral carrier for nitrate ion.

Anionic species recognition by supramolecular receptor has attracted considerable attention as the highly salvation of anion in aqueous environment and anion played important roles in most biological process [5,6]. As example, the bromide ion will interfere metabolism of iodine in thyroid gland [7].

Therefore, the monitoring of anion is crucial. The determination of chloride and bromide ion in water sample by using solid-phase extraction gas chromatography required extensive treatment on water sample [8]. Therefore, this technique is not suitable and economical for daily anion level monitoring.
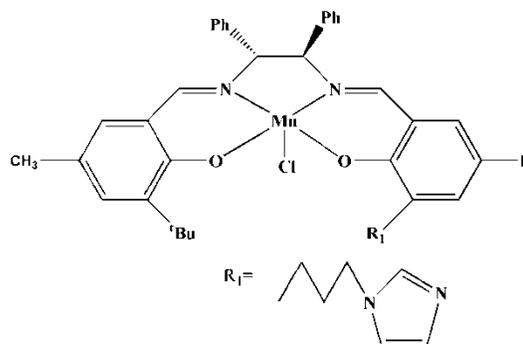

Diagram 1 manganese(II) (R,R)-1,2-diphenylethylenediamine substituted salen complex showed catalytic activity in epoxidation of olefin.
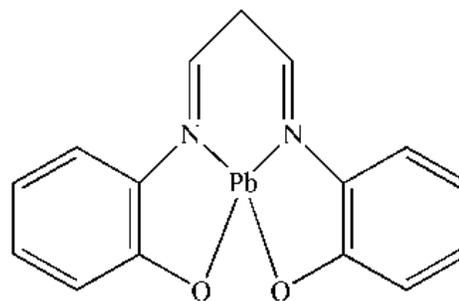

Diagram 2 bis(2-hydroxyanil)acetylacetone lead(II) as neutral carrier for nitrate ion.

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Therefore, an inexpensive, simple, sensitive determination of anion in aqueous environment is required and become popular. In order to satisfy this need, enormous studies have been conducted to find a suitable anion receptor as detecting material [14], [15], [16], [17]. For example, Diane L. Stone and David K. Smith have reported encapsulate ferrocene within a dendritic shell as the binding site of halide ions [18]. The following diagram shows the ferrocene as core of dendrimer for binding of halide ion:
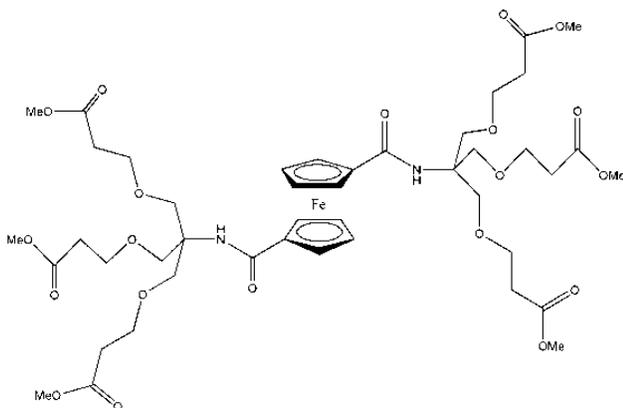

Diagram 3 Ferrocene encapsulated in dendrimer for halide ion binding site

2. EXPERIMENTAL

2.1 Materials, method and instruments

Melting point was measured on a Leica Galen III Kofler micro melting point apparatus and was uncorrected. Infrared (IR) spectra were Perkin-Elmer series 1600 spectrometers as thin film for KBr pellet for solid samples. ^{1}H NMR spectra (300 and 75 MHz, respectively) were recorded on a Bruker Avance 300 Spectrometer using CDCl$_3$ as solvent. Perkin-Elmer Lambda 900 DR UV-Vis was used for characterized complexation of nickel(II) diethylamino-substituted salen complex. The anion complexation between bromide or chloride ions with nickel(II) diethylamino-substituted salen complex was monitored with Perkin-Elmer Lambda 900 U V-Vis spectrometer.

2.2 Synthesis diethylamino-substituted salen ligand

The synthesis method was according to literature [20]. The diethylamino-substituted salen ligand was synthesized according molar ratio 1 ethylenediamine : 2 4-(N,N-diethylamino)salicyladehyde. Ethylenediamine (15 mmol) was dissolved in ethanol (40 mL). The mixture was slowly added to 4-(N,N-diethylamino)salicyladehyde (30 mmol) in ethanol (60 mL). The resulting mixture was refluxed at 95˚C for 2 hour. After that, the solvent was

disilled out to approximately 50 mL. The mixture was leave it cools to ambient temperature. The mixture was cooled in ice bath to yeild solid. The solid was filtered with vacuum pump. The solid was recrystalized from methanol and recovered by filtration. The melting point of yellow crystal was measured. (Percentage yield: 80.64 %, melting point: 137.2-138.5 ˚C). The following diagram shows the synthesis route of diethylamino-substituted salen ligand:

2.3 Synthesis nickel diethylamino-substituted salen complex

The nickel(II) diethyamino-substituted salen complex was synthesized according to the molar ratio of 1 nickel(II) acetate monohydrate : 1 salen ligand. The salen ligand (4mmol) and nickel(II) acetate monohydrate were dissolved in acetonenitrile (60mL) and stirred at room temperature for 2 hours. The resulting solution was leaved in fume hood for the formation of precipitate. The resulting precipitate was filtered with vacuum pump. The solid was recrystalized from 1 hexane : 1 a cetone solvent to obtain red-brown crystal. The resulting complex was measured with DR UV-Vis to further verified the complexation of salen ligand with nickel metal.

2.4 UV-Vis spectrum for anion receptor interaction with chloride and bromide

The anion binding properties with nickel(II) Schiff Base Salen complex was investigated by UV-VIS spectrometer as mentioned in literature. [9].

Stoichiometric amounts of tetrabutylamonium salts : chloride or bromide was added to diluted salen complex in dichloromethane solvent. The UV-Vis spectrum of salen complex was compared with UV-Vis spectra of complex salen after adding bromide or chloride ions.

3. RESULTS & DISCUSSION

3.1 FTIR Spectrum of diethyamino-substituted salen ligand

In Figure 1 shows the IR spectrum of diethyamino-substituted salen ligand. The medium intensity broad absorption band from 2400-3200 cm^{-1} assigned to the phenolic group. The broad hydroxyl absorption band is due to the intramolecular hydrogen bonding of phenolic group with lone pair electron of nitrogen atom [10]. The absorption band at 3051 cm-1 showed the =C-H of aromatic ring for salicyaldehyde. The absorption at band 1633 cm^{-1} assigned to C=N imine. The C-N and C-O absorption bands were assigned to 1372 cm^{-1} and 1283 cm^{-1} respectively. These results showed that the condensation of ethylenediamine and 4-(N,N-diethylamino)salicyaldehyde was successfully synthesis diethylamino-substituted salen ligand.

3.2   ¹H-NMR of diethylamino-substituted salen ligand

Based on proton NMR of salen ligand, a singlet at $\delta 8.57$ indicated the presence of CH=N. The multiplet at $\delta 7.23$ assigned to the H-C of aromatic ring. The low field singlet at $\delta 13.22$ is assigned to the phenolic group of salen ligand. The proton is highly deshielded is due to the intramolecular hydrogen bonding between nitrogen and and oxygen atoms and their position is located between two aromatic rings.
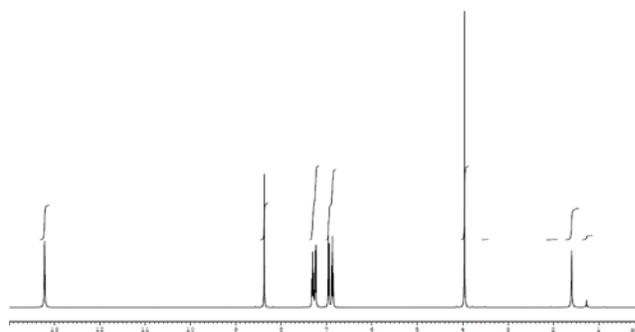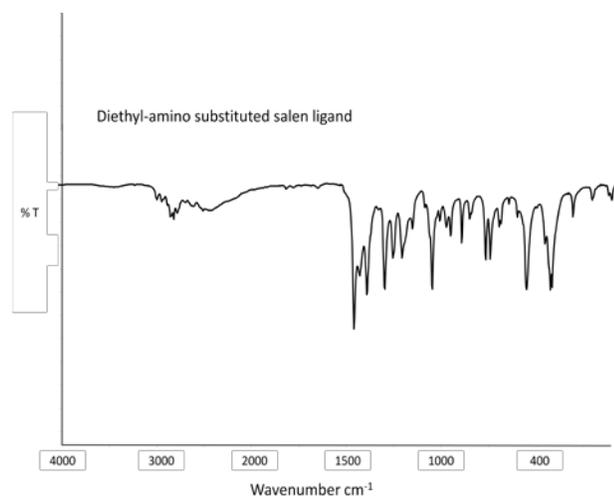

Fig. 2 ¹H-NMR of diethylamino-substituted salen ligand

3.3   FTIR Spectrum of nickel(II) diethylamino-substituted salen complex

The complexation of salen ligand with metal yield red brown crystal. It is obviously found that dissapearance the broad stretching band at 3200-2400 cm^{-1} as the diethylamino-substituted salen ligand successfully coordinate the nickel to form complex cause the lost of intramolecular hydrogen bonding [11]. The bonding of nickel with nitrogen of imine group cause C=N absorption band shifts to lower frequency at 1593 c m^{-1} which is overlap with absorption band of C=C aromatic. Figure 2 shows the FTIR spectrum of nickel(II) diethylamino-substituted salen complex.

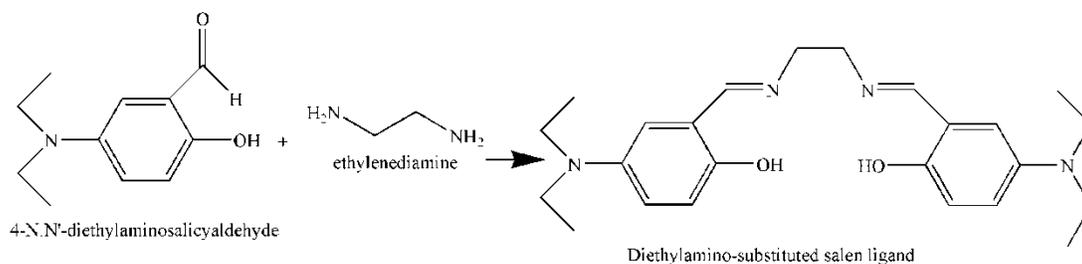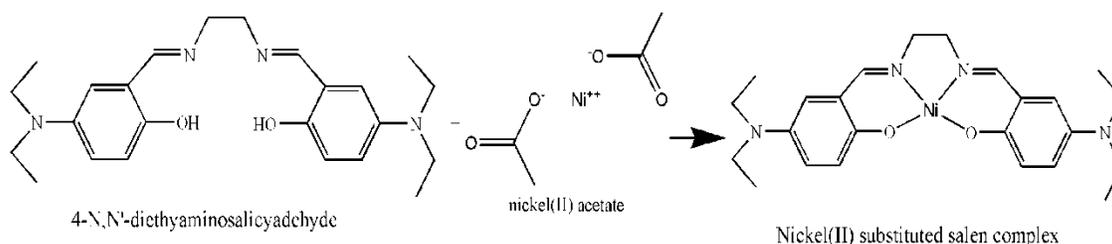Fig. 1 FTIR spectrum of diethylamino-substituted salen ligand

Diagram 1 Synthesis route of diethylamino-substituted salen

Diagram 2 Synthesis nickel(II) salen complex

Fig. 3 FTIR of nickel(II) diethylamino-substituted salen complex

substituted salen complex. The electron from donor is transfer to an acceptor orbital. The electrons are shared between the donor and acceptor. This showed that nickel (II) salen complex act as electron acceptor from the chloride and bromide ions.
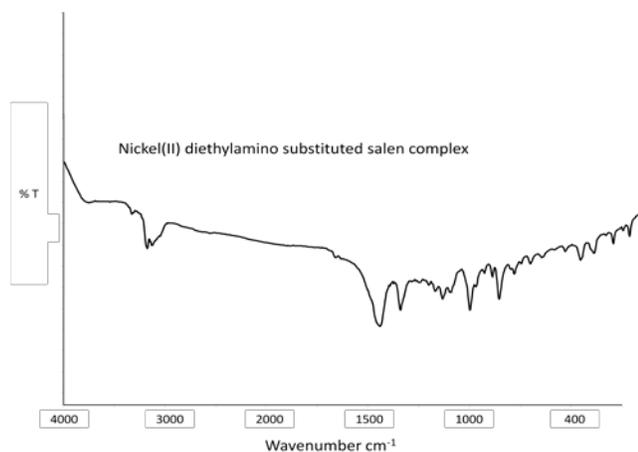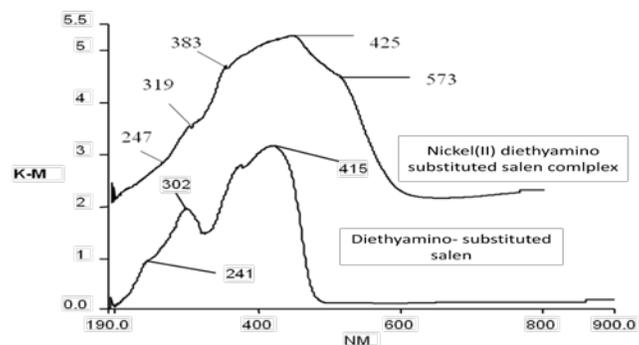

Fig. 4 DR UV-Vis of diethyamino-substituted salen and nickel(II) diethylamino-substituted salen complex

3.4   DR UV-Vis comparison of salen ligand and nickel(II) salen complex

The DR UV-Vis spectra of diethylamino-substituted salen ligand and diethylamino-substituted salen complex were compared to verified the coordination of salen ligand to nickel. From the nickel(II) diethylamino-substituted salen complex spectrum a new broad band at 573 nm is observed and indicated the d-d transition of nickel was occurred in nickel(II) diethyamino-substituted salen complex. The band at 425 nm indicated the ligand-to-metal charge transfer transition [12]. This further verified that the salen ligand successfully coordinates the nickel metal centre.

3.5   The UV-Vis spectrum of nickel(II) diethylamino-substituted salen complex after addition of bromide or chloride ion

The UV-Vis spectra of nickel (II) salen complex and after additional of bromide and chloride ions in dichloromethane solvent is showed in Figure 4.

The anion binding properties of receptor have been investigated by monitoring UV-Vis spectral change upon stoichiometric addition of chloride or bromide ion in a dichloromethane solvent. The dichloromethane is selected as solvent as the solvation energy of chloride ion and bromide ion in water will affect the binding of chloride ion and bromide ion with nickel(II) diethylamino-substituted salen complex.

Upon adding chloride ion to receptor in dichloromethane solution, the peak at 438 nm show increase in intensity (hyopchromic) while upon adding bromide ion to receptor in dichloromethane solution, the peak at 438 nm show decrease in intensity (hypochromic).

The hyperchromic and hypochromic effect on the spectrum of nickel(II) diethylamino-substituted salen complex a fter addition of bromide or chloride ion to the nickel(II) diethylamino-substituted salen complex is due to the charge - transfer-complex (CTC) is occur between bromide ion or chloride ion with nickel(II) diethylamino-
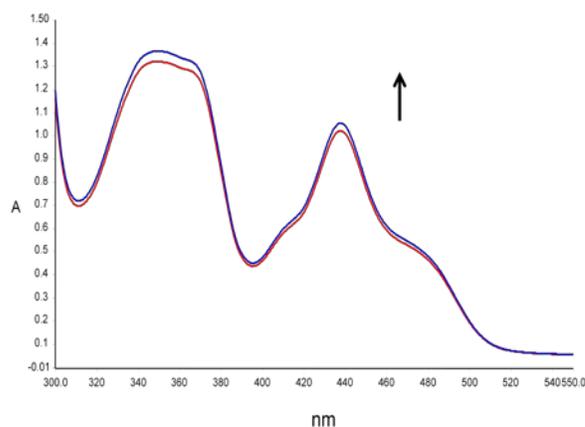

Fig. 4 The UV-Vis spectra of nickel(II) diethylamino-substituted salen complex and upon addition of chloride ion
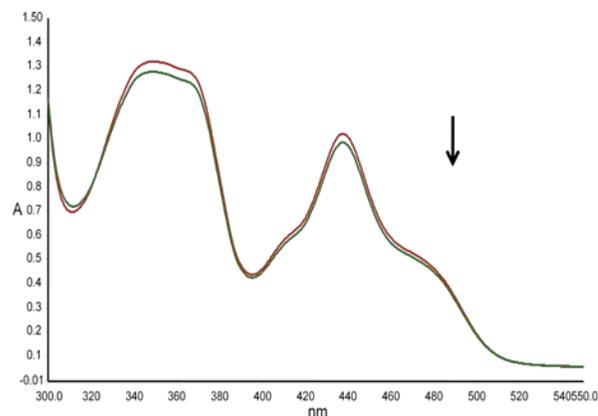

Fig. The UV-Vis specta of nickel(II) diethylamino-substituted salen complex and upon addition of bromide ion

From the perturbation of UV-Vis spectrum predict that certain interaction occur between receptor and anion. Refer to the literature proposed that the nickel(II) salen complex provide cavity for the binding of chloride and bromide ion due to the spherical shape of chloride and bromide ions [4].

Although the anion receptor proposed in this work showed is perturbation of UV-Vis spectrum, the reason of behaviour and type of interaction is not clear. Therefore, the further investigation binding constant, potentiometry and detection limit of the anion receptor is needed.

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