

CHAPTER II

EXPERIMENTAL

2.1 General procedure

Melting points were determined on a Fisher-Johns melting point apparatus or Electrothermal digital melting point apparatus model IA9100 and are uncorrected. Column chromatography was carried out on silica gel (Merck Kieselgel 60, 70-230 mesh). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60 PF₂₅₄).

2.2 Instruments

The FT-IR spectra were recorded on a Fourier Transform Infrared Spectrophotometer on Nicolet model Impact 410: solid samples were mixed with potassium bromide to form pellets and liquid samples were incorporated to sodium chloride cells. The ¹H- and ¹³C-NMR spectra were obtained in deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide (DMSO-d₆) with tetramethylsilane (TMS) as an internal reference on a Bruker model ACF 200 Spectrometer. The UV-Visible spectra were recorded on Diode Array Spectrophotometer on Hewlett Packard 8452A. Gas chromatography analysis was carried out on a Shimadzu Gas Chromatograph GC-9A and GC-14A instrument equipped with flame ionization detector (FID) with N₂ as a carrier gas. The column used for chromatography was a capillary column type of DB-wax (30 m x 0.250 mm) from J&W Scientific.

2.3 Chemicals

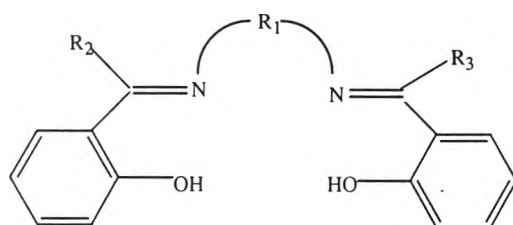
The reagents for synthesizing Schiff base ligands and metal Schiff base complexes were purchased from Fluka and Merck chemical companies. All solvents used in this research were purified prior to use by standard methodology except for those, which were reagent grades.

2.4 Syntheses

2.4.1 Syntheses of Schiff base ligands

General procedure²³

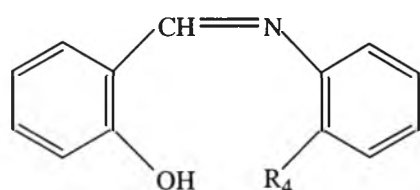
An interested aldehyde or ketone (1 or 2 mol-equiv) was slowly added to a solution of aromatic amine (1 mol-equiv) in methanol. The solution was stirred at room temperature until precipitate occurred. The precipitate was filtered off and recrystallized by an appropriate solvent. Five synthesized Schiff base ligands namely salophen (**1**), salen (**2**), hean (**3**), sap (**4**) and sac (**5**) are depicted as shown below



(1): $R_1 = C_6H_6$, $R_2 = H$, $R_3 = H$

(2) : $R_1 = C_2H_4$, $R_2 = H$, $R_3 = H$

(3) : $R_1 = C_2H_4$, $R_2 = CH_3$, $R_3 = CH_3$



(4) : $R_4 = OH$

(5) : $R_4 = COOH$

*Bis(salicylaldehyde)-N,N'-o-phenylenediimine (salophen)*²⁴ (**1**): Orange needle crystal (81%), m.p. 191-192 °C (actone), R_f 0.53 (dichloromethane). IR (KBr, cm^{-1}) 3500, 3050, 2950-2870, 1630, 1560-1483, 1275 and 1190; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 6.85 (2H, t, $J = 7.32$ Hz), 7.02 (2H, d, $J = 13.24$ Hz), 7.20 (4H, m), 7.31 (2H, m) 7.35 (2H, m) and 8.60 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 117.5 (2C), 118.9 (2C), 119.1 (2C), 127.7 (2C), 132.3 (2C), 133.3 (2C), 142.4 (2C), 161.3 (2C) and 163.6 (2C).

*Bis(salicylaldehyde)-N,N'-ethylenediimine (salen)*²⁵ (**2**): Bright yellow plate crystal (96%), m.p. 125-126 °C (95% ethanol), R_f 0.40 (dichloromethane). IR (KBr, cm^{-1}) 3500, 3050-3010, 2950-2870, 1640, 1600, 1450, 1280 and 1170; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.84 (4H,s), 6.83 (2H, dt, $J = 7.48, 1.22$ Hz), 6.93 (2H, d, $J = 8.24$ Hz), 7.18 (2H, dd, $J = 7.63, 1.83$ Hz), 7.26 (2H, dt, $J = 7.78, 1.53$ Hz), 8.29 (2H, s) and 13.20 (2H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 59.5 (2C), 116.8 (2 x 2C), 131.4 (2C), 132.2 (2C), 160.9 (2C), and 166.3 (2C).

*Bis(2-hydroxyacetophenone)-N,N'-ethylenediimine (hean)*²⁶ (**3**): Yellow needle crystal (82%), m.p. 199-200 °C (95% ethanol), R_f 0.60 (dichloromethane). IR (KBr, cm^{-1}) 3590-3270, 3070, 2950-2870, 1620, 1600, 1450, 1250 and 1180; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 2.37 (6H, s), 3.97 (4H, s), 6.78 (2H, dt, $J = 7.70, 1.28$ Hz), 6.91 (2H, dd, $J = 8.55, 1.28$ Hz), 7.27 (2H, dt, $J = 7.91, 1.28$ Hz), and 7.52 (2H, dd, $J = 7.91, 1.50$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 14.7 (2C), 50.2 (2C), 117.4 (2C), 118.5 (2C), 119.4 (2C), 128.1 (2C), 132.4 (2C), 163.1 (2C) and 172.7 (2C).

*N'-salicylalidene-2-aminophenol (sap)*²⁷ (**4**): Bright red needle crystal (89%), m.p. 186-188 °C (acetone), R_f 0.44 (ethanol). IR (KBr, cm^{-1}) 3500, 3050, 1640, 1600-

1460, 1280 and 1150; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 5.79 (1H, s), 6.95-7.09 (4H, m), 7.15 (1H, dd, $J = 7.79, 1.53$ Hz), 7.22 (1H, dt, $J = 7.94, 1.53$ Hz), 7.40-7.45 (2H, m), 8.69 (1H, s) and 12.25 (1H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 115.9 (1C), 117.3 (1C), 118.3 (1C), 119.3 (1C), 119.6 (1C), 121.0 (1C), 128.8 (1C), 132.7 (1C), 133.7 (1C), 135.8 (1C), 149.9 (1C), 160.6 and 164.0 (1C).

N'-salicylalidene-anthranilic acid (*sac*)²⁷ (**5**): Orange solid (67%), mp.182-184 °C (ethanol), R_f 0.70 (ethanol). IR (KBr, cm^{-1}) 3500, 3100-3050, 1620, 1600, 1450, 1580-1460, and 1120; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.50 (1H, s), 6.66 (1H, dd, $J = 8.54, 0.91$ Hz), 6.67 (1H, d d, $J = 8.53, 1.22$ Hz), 6.99 (1H, d, $J = 8.85$ Hz), 7.03 (1H, dd, $J = 7.33, 0.92$ Hz), 7.30 (1H, dt, $J = 7.78, 1.52$ Hz), 7.52 (1H, dt, $J = 7.64, 1.83$ Hz), 7.56 (1H, dd, $J = 7.78, 1.53$ Hz), 7.90 (1H, dd, $J = 8.29, 1.83$ Hz), 9.90 (1H, s) and 11.0 (1H, s) cm^{-1} ; $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 114.5 (1C), 116.3 (1C), 117.2 (2C), 119.0 (2C), 119.4 (1C), 131.1 (1C), 136.4 (1C), 130.4 (1C), 151.5 (1C), 160.7 (1C), 169.6 and 191.8 (1C).

2.4.2 Syntheses of metal Schiff base complexes

General procedure²⁸

To an aqueous ethanolic solution of Schiff base (1 mol-equiv) and transition metal (1 mol-equiv), a solution of $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ (16.9 mmol) was added. A crystalline solid formed immediately. The mixture was further refluxed for approximately 3 h and then cooled overnight. The solid was washed with H_2O , EtOH and Et_2O and dried *in vacuo*.

Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Cobalt(II) (**6**): Dark-brown solid (87%), m.p. 276 °C, R_f 0.73 (acetone). IR (KBr, cm⁻¹): 3500, 3080, 1620, 1600-1450, 1287 and 1195.

Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Chromium(III) (**7**): Bright-brown solid (30%), m.p. 295 °C, R_f 0.79 (acetone). IR (KBr, cm⁻¹): 3500, 1616, 1600-1450, 1250 and 1190.

Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Copper(II) (**8**): Black-brown solid (30%), dec. about 300 °C, R_f 0.65 (acetone). IR (KBr, cm⁻¹): 3500, 1620, 1600-1461, 1205 and 1151.

Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Iron(II) (**9**): Yellow-brown solid (24%) dec. about 300 °C, R_f 0.78 (acetone). IR (KBr, cm⁻¹): 3500, 1616, 1600-1461 and 1190.

Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Manganese(II) (**10**): Green-yellow solid (21%), m.p. 229 °C, R_f 0.65 (30% dichloromethane in ethanol). IR (KBr, cm⁻¹): 3500, 1616, 1600-1471, 1200 and 1151.

Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Nickel(II) (**11**): Dark red solid (50%), dec. about 300 °C, R_f 0.71 (acetone). IR (KBr, cm⁻¹): 3500, 1611, 1600-1461, 1205 and 1151.

*Bis(salicylaldehyde)-N,N'-o-phenylenediimine-Oxovanadium(IV)*²⁸ (**12**): Greenish solid (83%), dec about 169 °C, R_f 0.78 (30% dichloromethane in ethanol). IR (KBr, cm⁻¹): 3500, 3010, 2890, 1620 and 988.

*Bis(salicylaldehyde)-N,N'-ethylenediimine-Oxovanadium(IV)*²⁸ (**13**): Dark green solid (51%), m.p. 167 °C, R_f 0.42 (30% dichloromethane in ethanol). IR (KBr, cm⁻¹): 3500, 3020, 2920, 1630 and 994.

*Bis(2-hydroxyacetophenone)-N,N'-ethylenediimine-Oxovanadium(IV)*²⁹ (**14**): Black solid (77%), dec. about 289 °C, R_f 0.80 (30% dichloromethane in ethanol). IR (KBr, cm⁻¹): 3500, 3020, 2900, 1605, and 972.

N'-salicylalidene-2-aminophenol-Oxovanadium(IV) (**15**): Dark-brown solid (94%), dec. about 260 °C, R_f 0.52 (acetone). IR (KBr, cm⁻¹): 3500, 3010, 2930, 1615 and 994.

N'-salicylalidene-anthranilic acid-Oxovanadium(IV) (**16**): Black solid (19%), dec. about 297 °C, R_f 0.50 (ethanol). IR (KBr, cm⁻¹) 3500, 3030, 2940, 1605, and 984.

Bis(salicylaldehyde)-N,N'-ethylenediimine-Iron(II) (**17**): Brown solid (89%), dec. about 297 °C, R_f 0.75 (ethanol). IR (KBr, cm⁻¹) 3500, 3015, 2903, 1625, and 969.

Bis(2-hydroxyacetophenone)-N,N'-ethylenediimine-Iron(II) (**18**): Brown solid (87%), dec. about 289 °C, R_f 0.77 (acetone). IR (KBr, cm⁻¹): 3500, 3146, 2996, 1621 and 887.

N'-salicylalidene-2-aminophenol-Iron(II) (**19**): Bright-brown solid (91%), dec. about 260 °C, R_f 0.52 (acetone). IR (KBr, cm⁻¹): 3500, 3062, 2903, 1625, and 969.

N'-salicylalidene-anthranilic acid-Iron(II) (**20**): Brown solid (92%), dec. about 297 °C, R_f 0.74 (acetone). IR (KBr, cm⁻¹) 3500, 3128, 2992, 1588, and 866.

2.5 Oxidation of cyclohexane catalyzed by metal Schiff base complexes

The oxidation reaction of cyclohexane to cyclohexanone and cyclohexanol was examined utilizing Schiff base metal complexes as a catalyst.

General procedure for the oxidation of cyclohexane³⁰

Catalyst (0.25 mmol), cyclohexane (30 mmol), pyridine (14 mL), acetonitrile (14 mL) and H₂O₂ 30% (15 mmol) or TBHP 70% (15 mmol) was placed in an Erlenmeyer flask. The mixture was stirred continuously for 24 h at room temperature for H₂O₂ or at 50 °C for TBHP. After the reaction was proceeded for a designed period of time, 1 mL of the reaction mixture was taken and acidified with cold 25% H₂SO₄ and extracted with diethyl ether. The combined extracts were washed with saturated solution of NaHCO₃. The organic layer was dried over anhydrous Na₂SO₄ and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

2.6 Examination of the redox reaction of metal Schiff base complexes

The metal Schiff base complexes were explored for redox property by cyclic voltammetry technique.

General procedure for examination of redox reaction

The metal Schiff base complexes (0.01 mol) was dissolved in 0.05 M C₁₆H₃₆FNP solution. The sample solution was examined the redox reaction in electrochemical cell using glassy carbon or boron-doped diamond electrode as working electrode, silver wire as reference electrode and platinum wire as auxillary electrode.

2.7 Kinetic study on the reaction rate of cyclohexane oxidation

The general oxidation procedure of cyclohexane utilizing metal Schiff base complexes: bis(salicylaldehyde)-*N,N'*-*o*-phenylenediimine-Iron(II) (**9**), bis(salicylaldehyde)-*N,N'*-*o*-phenylenediimine-Manganese(II) (**10**) and bis(salicylaldehyde)-*N,N'*-*o*-phenylenediimine-Oxovanadium(IV) (**12**) as catalysts was carried out. At different reaction time proceeded (60, 120, 240, 360 and 480 min), an aliquot from the reaction time mixture was taken and analyzed by GC or examined by cyclic voltammetry.

2.8 Analysis of oxidizing power in cyclohexane oxidation

An aliquot from the oxidation reaction of cyclohexane at different reaction proceeded (60, 120, 240, 360 and 480 min) was pipetted and transferred into 150 mL flask. Fifty milliliter of distilled water and about two grams of KI were added. The sample solution was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.05 M until the intense yellow solution was changed to yellow solution then the starch solution was added. After that, the sample solution was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.05 M until the solution changed to clear solution.

2.9 Oxidation reaction of other organic compounds

Employing the same oxidation manner as previously described, cyclohexanol and cyclohexene were used as substrate instead of cyclohexane.