

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Instrument and Equipment

Gas chromatography (GC) was carried out on a Shimadzu Gas Chromatograph GC-14A Flame Ionization Detector with N<sub>2</sub> 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. Melting points were determined on a Fisher-Johns melting point apparatus or electrothermal digital melting points apparatus model IA 9100 and are uncorrected. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgel 60 PF<sub>254</sub>). 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 while liquid samples were incorporated to sodium chloride cells. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained in deuterated chloroform (CDCl<sub>3</sub>) or deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) with tetramethylsilane (TMS) as an internal reference on a Bruker model ACF 200 spectrometer. Atomic absorption spectrometer (AAS) was carried out on a Shimadzu AA-670/G U-5 and acetylene gas was used as flammable inducer.

#### 2.2 Chemicals

All solvents used in this research were purified prior to use by standard methodology. The reagents for synthesizing Schiff base ligands, 1,3-dicarbonyl ligands, the iron complexes including supported iron complexes were purchased from Fluka and Merck company and they were used without further purification. Silica gel used for synthesis of catalyst on support by impregnation method was purchased from Merck company. Solid small bead with 230-400 mesh ASTM. Celite 545 or clay was purchased from Merck company, off white powder which particle size 0.02-0.1 mm.

For synthesis of doped silica gel was prepared follow:<sup>21</sup>  
Cetyltrimethylammonium bromide (CTAB) was dissolved in an aqueous solution of

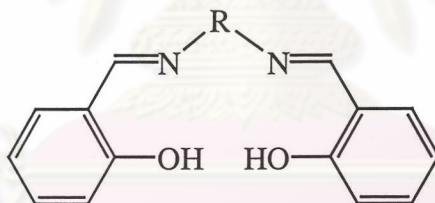
NaOH 0.1 M under vigorous stirring and maintained at 60°C. Methanol was then added. The ligand (salen or sal-*o*-phen) was next introduced into the mixture, still under stirring. After its dissolution, tetraethoxysilane (TEOS 98 %) was added. Silica precipitation was observed. The stirring was maintained at ambient temperature during 24 hours then the yellowish precipitate was filtered, washed with water until neutral pH and dried in an oven at 60°C overnight.

## 2.3 Syntheses

### 2.3.1 Syntheses of Schiff base ligands

#### General Procedure<sup>22</sup>

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. Eight synthesized Schiff base ligands namely salen (1), sal-*o*-phen (2), saltn (3), 4-nitro(sal-*o*-phen) (4), sal-*o*-phen(pyridine)<sub>4</sub> (5), salen(pyridine)<sub>4</sub> (6), sal-4-nitro-*o*-phen(pyridine)<sub>4</sub> (7), (salen)<sub>2</sub>O (8) are shown below.



salen (1): R = (CH<sub>2</sub>)<sub>2</sub>

saltn (2): R = (CH<sub>2</sub>)<sub>3</sub>

sal-*o*-phen (3): R = Ph

sal-(4-nitro)-*o*-phen (4): R = 4-NO<sub>2</sub>Ph

*Bis(salicylaldehyde)-N,N'-ethylenediimine (1) (salen)*<sup>23</sup>: Bright yellow plate crystal (97%), m.p. 125-126°C (recrystallized from 95 % ethanol), R<sub>f</sub> 0.40 (dichloromethane), IR (KBr, cm<sup>-1</sup>) 3500, 3050-3010, 2950-2870, 1640, 1600, 1450, 1280 and 1170; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 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);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 59.5 (2C), 116.8 (2C), 118.5 (2x2C), 131.4 (2C), 132.2 (2C), 160.9 (2C) and 166.3 (2C).

*Bis(salicylaldehyde)-N,N'-trimethylenediimine (2) (saltn)*<sup>24</sup>: Yellow plate crystal (93%), m.p. 51-52°C (recrystallized from n-hexane),  $R_f$  0.71 (ethyl acetate), IR (KBr,  $\text{cm}^{-1}$ ) 3500, 3080-3020, 2950-2860, 1640, 1600, 1450, 1290, and 1160;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 2.05-2.10 (2H, q,  $J = 6.71$  Hz), 3.66-3.69 (4H, dt,  $J = 6.72$ , 0.92 Hz), 6.85 (8H, m), 8.33 (2H, s) and 13.42 (2H, s);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 31.6 (1C), 56.7 (2C), 116.8 (2 x 2C), 118.7 (2C), 131.2 (2C), 132.2 (2C), 118.5 (2C), 161.0 (2C) and 165.8 (2C).

*Bis(salicylaldehyde)-N,N'-o-phenylenediimine (3) (salophen)*<sup>25</sup>: Orange needle crystal (82%), m.p. 191-192°C (recrystallized from acetone),  $R_f$  0.53 (dichloromethane), IR (KBr,  $\text{cm}^{-1}$ ) 3500, 3050, 2950-2870, 1630, 1560-1485, 1275 and 1190;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (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);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 117.5 (2C), 118.9 (2C), 119.1 (2C), 119.6 (2C), 127.7 (2C), 132.3 (2C), 133.3 (2C), 142.4 (2C), 161.3 (2C) and 163.6 (2C).

*Bis(salicylaldehyde)-N,N'-4-nitro-1,2-phenylenediimine (4) (sal-4-nitro-o-phen)*<sup>26</sup>: yellow orange prism (24%), m.p. 210°C (recrystallized from acetone),  $R_f$  0.94 (dichloromethane), IR (KBr,  $\text{cm}^{-1}$ ) 3700-3300, 3100-3050, 1620, 1570, 1520, 1480, 1350 and 1285;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 6.93-7.69 (10H, m), 8.24-8.36 (2H, m), 8.98-9.08 (1H, d,  $J = 5.5$ ) and 12.53-12.64 (2H, s);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 123.3 (2C), 122.0 (2C), 120.2 (2C), 117.9 (2C), 177.8 (2C), 116.0 (2C), 134.9 (2C), 167.9 (2C) and 168.2 (2C).

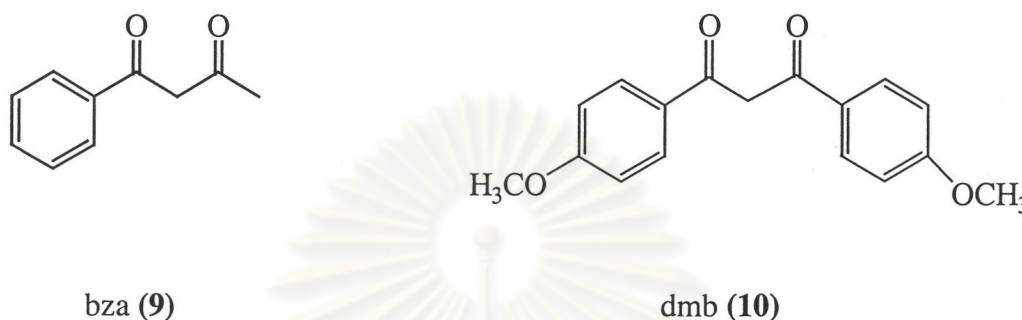
### 2.3.2 Syntheses of 1,3-dicarbonyl ligands

#### General Procedure<sup>27</sup>

Substituted acetophenone (1 mol-equiv) in dry benzene 50 mL and ethyl benzoate or ethyl benzoate derivatives (1 mol-equiv) in dry benzene 50 mL were added dropwise to a suspension at 60 % NaH. The mixture was refluxed and monitored the progress of the reaction by thin layer chromatography using 30% EtOAc/hexane as an eluent. The reaction mixture was cooled down to room temperature, quenched with 10% HCl solution, extracted with EtOAc, washed with brine and dried over  $\text{MgSO}_4$ . After removal of the solvent, the residue was

recrystallized from an appropriate solvent or purified by silica gel column chromatography using 10% EtOAc/hexane.

1,3-Dicarbonyl ligands namely, benzoylacetone: **bza** (**9**) and 4,4'-dimethoxydibenzoylmethane: **dmb** (**10**) are depicted as shown below.



*4,4'*-Dimethoxydibenzoylmethane (**10**) (*dmb*)<sup>28</sup>: Yellowish solid (42%), m.p.113-114°C (recrystallized from ether/hexane) (lit. m.p. 114-116°C),  $R_f$  0.35 (EtOAc: hexane; 3: 7), IR (KBr,  $\text{cm}^{-1}$ ) 2980, 2840, 1690, 1610, 1520, 1430, 1270, 1230 and 1180;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm); 3.85 (6H, s), 6.73 (1H, s), 6.91 (4H, d,  $J = 8.81$  Hz), 8.04 (4H, d,  $J = 8.93$  Hz);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 55.5 (2C), 91.5 (1C), 113.4 (4C), 129.1 (4C), 131.3 (2C), 163.0 (2C) and 184.6 (1C).

### 2.3.3 Syntheses of Schiff base iron complexes

#### General Procedure<sup>29</sup>

##### Method I

Dissolve Schiff base **1**, **2** and **3** (5 mmol) in hot ethanol 50 mL and stirred until ligand was completely soluble. Dissolve ferrous sulfate 1.39 g (5 mmol) in hot water, add to the former solution dropwise. The precipitate of iron complex occurred, filtered and washed the precipitate with cold ethanol. Recrystallize the precipitate with an appropriate solvent.

##### Method II

Dissolve ferrous sulfate 2.78 g (0.01 mol) in boiling water 25 mL, add pyridine 3.23 mL (0.04 mol) and ethylenediamine 0.67 mL (0.01 mol) dropwise and stir the solution homogeneously. Then salicylaldehyde 2.50 mL (0.02 mol) was added

to the former solution. The precipitation of iron-pyridine complex was gained, filtered and washed the precipitate with water, dried in dessicator.

By using method II, *o*-phenylenediamine (0.01 mol) and 4-nitro-1, 2-phenylenediamine (0.01 mol) was employed instead of ethylenediamine for synthesizing of Fe sal-*o*-phen (**13**) and Fe sal-(4-nitro)sal-*o*-phen (**14**), respectively.

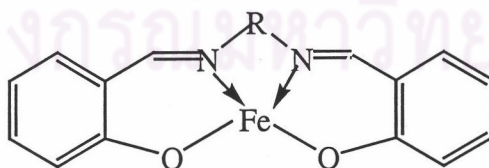
### Synthesis of (Fe salen)<sub>2</sub>O (**15**)<sup>30</sup>

Dissolve salen (**1**) 2.68 g (0.01 mol) in hot methanol 50 mL and stirred until ligand was completely dissolved. Ferric chloride 2.70 g (0.01 mol) was dissolved in methanol containing potassium hydroxide 0.56 g (0.01 mol) and add dropwise to the ligand solution. The precipitate was occurred, filtered and recrystallized with chloroform 2-3 times.

### Synthesis of Fe salen(pyridine)<sub>4</sub><sup>31</sup>

Dissolve ferrous sulfate 2.78 g (0.01 mol) in boiling water 25 mL. Then pyridine 3.23 mL (0.04 mol) and ethylenediamine 0.67 mL (0.01 mol) were added, stir the solution until homogeneously. Drop salicylaldehyde 2.50 mL (0.07 mol) into the former solution. Precipitate of iron salen(pyridine)<sub>4</sub> (**16**) occurred. After cooling the crystals were filtered, washed with water and then dried in a vacuum desiccator.

By the same procedure, *o*-phenylenediamine 1.00 g (0.01 mol) and 4-nitro-1,2-phenylenediamne 1.50 g (0.01 mol) were employed instead of ethylenediamine for synthesizing of Fe sal-*o*-phen(pyridine)<sub>4</sub> (**17**) and Fe sal-(4-nitro)-*o*-phen(pyridine)<sub>4</sub> (**18**), respectively.



Fe salen (**11**): R = (CH<sub>2</sub>)<sub>2</sub>

Fe saltn (**12**): R = (CH<sub>2</sub>)<sub>3</sub>

Fe sal-*o*-phen (**13**): R = Ph

Fe 4-nitro sal-*o*-phen (**14**): R = 4-NO<sub>2</sub>Ph



Bis(salicylaldehyde-*N,N'*-ethylenediimine-Iron(II)) (11) Fe(salen): Red brown fine powder (18 %), m.p. 198-200°C,  $R_f$  0.43 (30% dichloromethane in ethanol), IR (KBr,  $\text{cm}^{-1}$ ): 3048, 2899, 1639, 1610, 1450, 1281, 1157, 753.

Bis(salicylaldehyde)*N,N'*-trimethylenediimine-iron(II) (12) Fe saltn: Brown powder (72%), m.p. 90°C,  $R_f$  0.40 (30% dichloromethane in ethanol) IR (KBr,  $\text{cm}^{-1}$ ): 3050, 2925, 1614, 1600, 1439, 1306.

Bis(salicylaldehyde)*N,N'*-*o*-phenylenediimine-iron(II) (13) Fe sal-*o*-phen: Black brown powder (24%), m.p. about 300°C,  $R_f$  0.78 (acetone) IR (KBr,  $\text{cm}^{-1}$ ): 3032, 1613, 1600, 1465, 1372, 743.

Bis(salicylaldehyde)*N,N'*-(4-nitro)-1,2-phenylenediimine-iron(II) (14) Fe 4-nitro sal-*o*-phen: Brown powder (42%), m.p. 235°C,  $R_f$  0.86 (30% dichloromethane), IR (KBr,  $\text{cm}^{-1}$ ): 3042, 2914, 1613, 1460, 1337, 753.

$\mu$ -oxobis[Bis(salicylaldehyde)*N,N'*-ethylenediimine]iron(III) (Fe salen)<sub>2</sub>O (15) Black brown powder (49%), m.p. 120°C,  $R_f$  0.45 (30% dichloromethane in ethanol), IR (KBr,  $\text{cm}^{-1}$ ): 3040, 2930, 1629, 1600, 1450, 1311, 1127.

Bis(salicylaldehyde)*N,N'*-ethylenediimine-iron(II)(pyridine)<sub>4</sub> (16) Fe salen(pyridine)<sub>4</sub>: Red brown fine powder (41 %), m.p. 70°C,  $R_f$  0.90 (30% dichloromethane in ethanol), IR (KBr,  $\text{cm}^{-1}$ ): 3032, 2899, 1629, 1600, 1445, 1306, 1153, 758.

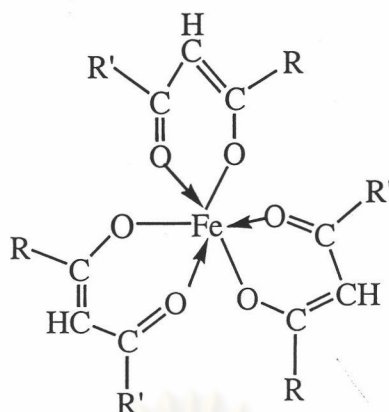
Bis(salicylaldehyde)*N,N'*-*o*-phenylenediimine-iron(II)(pyridine)<sub>4</sub> (17) Fe sal-*o*-phen(pyridine)<sub>4</sub>: Brown fine powder (42 %), m.p. 235°C,  $R_f$  0.86 (30% dichloromethane in ethanol), IR (KBr,  $\text{cm}^{-1}$ ): 3042, 1609, 1593, 1465, 1306.

Bis(salicylaldehyde)*N,N'*-(4-nitro)-1,2-phenylenediimine-iron(II)(pyridine)<sub>4</sub> (18) Fe sal-(4-nitro)-*o*-phen(pyridine)<sub>4</sub>: Red brown fine powder (47 %), m.p. 242°C,  $R_f$  0.89 (ethanol), IR (KBr,  $\text{cm}^{-1}$ ): 3050, 1660, 1603, 1531, 1460, 1383, 753.

### 2.3.4 Syntheses of 1,3-dicarbonyl iron complexes

#### Syntheses of Tris-(benzoylacetato)-Iron(III): Fe(BZA)<sub>3</sub> (19)<sup>32</sup>

Ferric chloride anhydrous 0.16 g (0.99 mmol) and benzoylacetone (BZA) 0.46 g (2.80 mmol) were dissolved in ethanol 50 mL. To this solution an aqueous solution (10 mL) of sodium acetate 0.15 g was added. The mixture was left to stand overnight at room temperature to give dark red solid. It was collected by filtration and recrystallized from hexane.



Fe(bza)<sub>3</sub> (**19**): R = H, R' = Ph

Fe(dmb)<sub>3</sub> (**20**): R = 4-PhOCH<sub>3</sub>, R' = 4-PhOCH<sub>3</sub>

Fe(acac)<sub>3</sub> (**21**): R = CH<sub>3</sub>, R' = CH<sub>3</sub>

### 2.3.5 Syntheses of supported iron catalyst<sup>33</sup>

Iron(III)nitrate nonahydrate 2.25 g was added to acetone 37.5 mL in round bottom flask 50 mL, followed by the addition of silica gel (230-400 mesh ASTM) 2 g. The mixture was stirred vigorously for 5 min until completely dissolution of the crystals of hydrate iron(III)nitrate. After that the solvent was removed to yield dry solid by evaporation.

FeCl<sub>3</sub>·6H<sub>2</sub>O on silica gel and Fe(acac)<sub>3</sub> on silica gel were prepared employing the similar method to that described for Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O on silica gel.

### 2.3.6 Syntheses of iron supported on doped silica gel<sup>34</sup>

The method based on the principle that ligand was doped in silica gel. The catalysts were prepared as follows: Ferrous sulfate 200 ppm was dissolved in 10<sup>-3</sup> M HNO<sub>3</sub> to protect hydroxide ion from Fe(OH)<sub>2</sub>. The 25 mL solution was added into doped silica gel 0.2 g. Stirring for 24 hours at room temperature. Cloudy solution was centrifuged and separated by filtration. Dry the precipitate *in vacuo*. The concentration of iron absorbed in doped silica gel was detected about 70% by AAS. The amount of iron on doped silica gel was detected by calibration plot compared with iron standard solution.

## 2.4 The general procedure for the oxidation of alcohol<sup>35</sup>

A solution composing of pyridine 28 mL, alcohol 10 mmol, acetic acid 2.3 mL, metal salt or metal complex 0.25 mmol and oxidizing agent 10 mmol in an Erlenmeyer flask. The mixture was stirred for any time at any temperature designed. After the reaction was finished, 1 mL of the reaction mixture was taken and extracted with diethyl ether. The combined extract was washed with saturated solution of NaHCO<sub>3</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

By the same procedure, iron on doped silica gel 0.025 mmol was used as catalyst in oxidation reaction.

## 2.5 Optimum conditions study for cyclohexanol oxidation

### 2.5.1 Effect of catalysts

The oxidation reaction was carried out according to the general procedure using various catalysts: FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, FeSO<sub>4</sub>·7H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Fe salen, Fe sal-*o*-phen, Fe(4-nitro sal-*o*-phen), Fe sal-*o*-phen(pyridine)<sub>4</sub>, Fe saltn, Fe salen(pyridine)<sub>4</sub>, Fe sal-(4-nitro)-*o*-phen(pyridine)<sub>4</sub>, (Fe salen)<sub>2</sub>O, Fe(acac)<sub>3</sub>, Fe(DMB)<sub>3</sub>, and Fe(BZA)<sub>3</sub> 0.25 mmol.

### 2.5.2 Effect of oxidizing agent

The oxidation reaction was carried out as described in the general procedure but the amount of oxidizing agent was varied: 1, 3, 5, 10 and 20 mmol.

### 2.5.3 Effect of temperature

The temperature used in oxidation reaction was changed from 0-5°C, room temperature (28°C), 40°C, 60°C and 100°C.

### 2.5.4 Effect of the amount of substrate

The oxidation reaction was carried out according to the general procedure but the amount of cyclohexanol was changed to 2, 5, 10 and 20 mmol.



## 2.6 Comparative kinetic study of the oxidation of cyclohexanol catalysed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Fe salen

According to the general oxidation procedure employing  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and Fe salen as catalysts. The oxidation reaction was carried out. At different reaction times proceeded 2, 4, 6, 8, 24 and 48 hours, an aliquot from the reaction mixture was taken, worked up and analyzed by GC.



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