# CHAPTER III
# MATERIALS AND METHODS

## 3.1 Experimental

### 3.1.1 Chemicals

All solvents used were of analytical reagent (AR) grade, and all reactions were carried out under ambient atmospheric conditions. The chemicals were purchased from Sigma-Aldrich or TCI Chemicals and were used without further purification.

### 3.1.2 Physical measurements

Infrared spectra were recorded using ATR on a Bruker Tensor 27 FT-IR spectrometer with OPUS software, covering the range of 400–4000 cm$^{-1}$. Electronic spectra were recorded in solution for all complexes in $CHCl_3$ (0.25 mM) at room temperature on PG Instruments T80+ UV/Vis Spectrometer in the range of 250-900 nm. Elemental analyses were performed using a Eurovector EA3000 analyzer, while electrospray ionization mass spectrometry (ESI-MS) was conducted on a Bruker AmaZon X LCMS mass spectrometer.

### 3.1.3 X-ray Crystallography

Crystallographic data for complexes **1**, **4** and **5** were carried out with Cu$K\alpha$ radiation using a Rigaku SuperNova (HyPix3000 detector) diffractometer. The data were scaled, integrated, and subjected to absorption correction using CrysAlisPro. The structures were determined using SHELXT and refined through full-matrix least-squares minimization on $F^2$using SHELXL. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atom positions were determined geometrically and refined using the riding model. All structural illustrations were created with OLEX2. Complexes **2** and **3** were collected using a Bruker D8 VENTURE diffractometer with MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å). Unit cell parameters were determined, and data collection was performed using APEX4. The structures were solved by intrinsic phasing with SHELXT and refine.

Powder X-ray diffraction data for the precipitates were obtained using a PANalytical X'Pert PRO MPD diffractometer equipped with Bragg-Brentano geometry, Cu-K$\alpha$1,2 radiation ($\lambda$ = 1.54184 Å), and a graphite backscattering monochromator. Standard Si sample holders were used, and the samples were finely ground before data collection over a 2$\theta$ = 0-50°. Le Bail and Rietveld refinements were conducted using JANA2020 (Petříček et al., 2023).

### 3.1.4 Hirshfeld surface analysis

The Hirshfeld surface properties of complexes **1-5** were analyzed using Crystal Explorer 17. The crystal structures were imported from CIF files, and high-resolution Hirshfeld surfaces were generated, mapped with the $d_{norm}$ and shape index functions. Additionally, 2D fingerprint plots were created using the same software (Spackman et al., 2021).

### 3.1.5 Magnetic susceptibility

Magnetic susceptibility measurements were performed using a Quantum Design MPMS 5 SQUID magnetometer under an applied field of 1–2 T over a temperature range of 10–300 K for samples **1**, **2**, and **5**, and 10–380 K for samples **3** and **4**. Powdered or polycrystalline samples were placed in gel capsules, ensuring sufficient thermal equilibration at each temperature. Samples **6**–**10** were analyzed using a Quantum Design MPMS 3 SQUID magnetometer, with measurements conducted between 1.8–300 K or 1.8–400 K under an applied field of 1000 Oe. These samples were loaded into plastic caps for measurement.

### 3.1.6 Electrochemical measurements

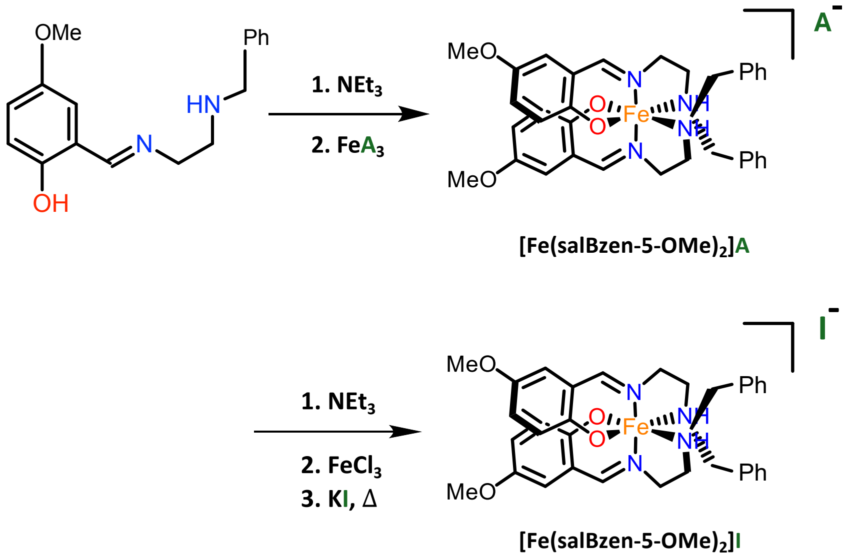
Electrochemical studies were carried out using a PalmSens4 in conjunction with a three-electrode cell consisting of a working electrode (2.0 mm diameter platinum disc), a counter electrode (platinum wire), and a reference electrode ([Ag/AgCl of LiCl 0.01 M in EtOH]). Solutions of the test compound (5 x $10^{-4}$ moldm$^{-3}$) were prepared in $CH_2Cl_2$, which had been dried over $CaH_2$. A supporting electrolyte, [N-*n*Bu$_4$][PF$_6$] (0.1 mol dm$^{-3}$), was used. Under these conditions, the $E^{o'}$

value for the one-electron oxidation and reduction of [Fe(η-$C_5H_5$)$_2$], which was added to the test solution for internal calibration, was measured at 0.52 V.

## 3.2 Synthesis of Fe(III) complexes

### 3.2.1 Synthesis of [Fe(salBzen-5-OMe)$_2$]A complexes

The synthesis of **1-5** is shown in Scheme 3.1.



**Scheme 3.1** Synthesis of [Fe(salBzen-5-OMe)$_2$]A complexes.

#### 3.2.1.1 Synthesis of [Fe(salBzen-5-OMe)$_2$]Cl 1

Firstly, HsalBzen-5-OMe was prepared by dissolving 2-hydroxy-5-methoxybenzaldehyde (0.8 mmol, 0.122 g) in ethanol (5 mL) in the round bottom flask then N-benzylethylenediamine (0.8 mmol, 120.2 μL) was added causing the solution to become a pale yellow. Then triethylamine 111 μL was added for deprotonation. In a separate vial, $FeCl_3$ (0.0648 g, 0.4 mmol) was dissolved in EtOH (3 mL). The bright orange solution was added dropwise into the HsalBzen-5-OMe ligand solution. The deep blue mixture was stirred for 3 hours. The crude was then reduced to approximately 2 mL *in vacuo* and precipitated with water (30 mL). The residue was filtered, washed with water, and dried in air. **1** was collected as black crystals after recrystallization by layering hexane on top of a $CH_2Cl_2$ solution of the complex (4:1

ratio of $CH_2Cl_2$:hexane) (0.124 g, 47%). Elemental analysis: cald (found) for $C_{34}H_{38}FeClN_4O_4$: C, 62.06 (61.92); H, 5.82 (5.80); N, 8.51 (8.54).

#### 3.2.1.2 Synthesis of [Fe(salBzen-5-OMe)$_2$]Br 2

**2** was synthesized in a similar method to **1** using $FeBr_3$ (0.120 g, 0.4 mmol) instead of $FeCl_3$. Recrystallization by layering hexane on top of a $CH_2Cl_2$ solution of the complex (4:1 ratio of $CH_2Cl_2$:hexane) yields black crystals of **2** (0.182 g, 64%). Elemental analysis: cald (found) for $C_{34}H_{38}FeBrN_4O_4$: C, 58.14 (57.66); H, 5.45 (5.39); N, 7.98 (7.97).

#### 3.2.1.3 Synthesis of [Fe(salBzen-5-OMe)$_2$]I 3

**3** was synthesized via post-complexation anionic exchange from $FeCl_3$ (0.4 mmol, 0.0646 g) and was dissolved in EtOH (3 mL) to give a bright yellow solution to which the ligand solution was added. The solution immediately turned black and THF (4 mL) was added to improve solubility and a solution of KI (1.2 mmol, 0.1996 mg) in EtOH:$H_2O$ (4 ml:1 ml) was added. The flask was heated at 60 °C overnight. After anionic exchange, the reaction mixture was allowed to cool to room temperature and reduced to approximately 2 mL *in vacuo*. Water (30 mL) was added to precipitate the product. The residue was filtered, washed with water, and dried in air. **3** was collected as black crystals after recrystallization by layering hexane on top of a $CH_2Cl_2$ solution of the complex (4:1 ratio of $CH_2Cl_2$:hexane) (0.177 g, 59%). Elemental analysis: cald (found) for $C_{34}H_{38}FeIN_4O_4$: C, 54.49 (54.49); H, 5.11 (5.08); N, 7.48 (7.59).

#### 3.2.1.4 Synthesis of [Fe(salBzen-5-OMe)$_2$]NO$_3$ 4

**4** was synthesized in a similar method to **1** using $Fe(NO_3)_3$ (0.162 g, 0.4 mmol) instead of $FeCl_3$. Recrystallization by layering hexane on top of a $CH_2Cl_2$ solution of the complex (4:1 ratio of $CH_2Cl_2$:hexane) yields black crystals of **4** (0.155 g, 57%). Elemental analysis: cald (found) for $C_{34}H_{38}FeN_5O_7$: C, 59.66 (59.08); H, 5.60 (5.52); N, 10.23 (10.23).

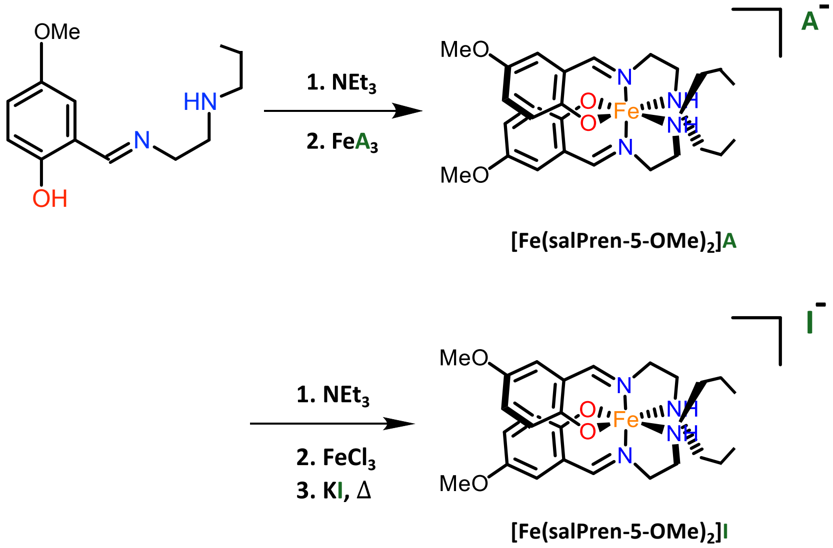
#### 3.2.1.5 Synthesis of [Fe(salBzen-5-OMe)$_2$]ClO$_4$ 5

**5** was synthesized in a similar method to **1** using $Fe(ClO_4)_3$ (0.143 g, 0.4 mmol) instead of $FeCl_3$. Recrystallization by layering hexane on top of a $CH_2Cl_2$ solution of the complex (4:1 ratio of $CH_2Cl_2$:hexane) yields black crystals of **5**

(0.119 g, 41%). Elemental analysis: cald (found) for $C_{34}H_{38}FeClN_4O_8$: C, 56.56 (56.48); H, 5.31 (5.26); N, 7.76 (7.81).

### 3.2.2 Synthesis of [Fe(salPren-5-OMe)$_2$]A complexes

The synthesis of **6-10** is shown in Scheme 3.2.



**Scheme 3.2** Synthesis of [Fe(salPren-5-OMe)$_2$]A complexes.

#### 3.2.2.1 Synthesis of [Fe(salPren-5-OMe)$_2$]Cl 6

Firstly, HsalPren-5-OMe was prepared by dissolving 2-hydroxy-5-methoxybenzaldehyde (0.8 mmol, 0.122 g) in ethanol (5 mL) in the round bottom flask then N-propylethylenediamine (0.8 mmol, 98.6 μL) was added causing the solution to become a pale orange. Then triethylamine 111 μL was added for deprotonation. In a separate vial, $FeCl_3$ (0.0648 g, 0.4 mmol) was dissolved in EtOH (3 mL). The bright orange solution was added dropwise into the HsalPren-5-OMe ligand solution. The deep blue mixture was stirred for 3 hours. The crude was then reduced to approximately 2 mL *in vacuo* and precipitated with water (30 mL). The residue was filtered, washed with water, and dried in air. **6** was collected as black microcrystals after slowly reducing from 1:2 $CH_2Cl_2$:hexane (0.130 g, 58%). Elemental analysis: cald (found) for $C_{26}H_{38}FeClN_4O_4$: C, 55.58 (55.22); H, 6.82 (6.84); N, 9.97 (9.91).

#### 3.2.2.2 Synthesis of [Fe(salPren-5-OMe)$_2$]Br 7

**7** was synthesized in a similar method to **6** using FeBr$_3$ (0.120 g, 0.4 mmol) instead of FeCl$_3$. Recrystallization after slowly reducing from 1:2 CH$_2$Cl$_2$:hexane yields black microcrystals of **7** (0.179 g, 73%). Elemental analysis: cald (found) for C$_{26}$H$_{38}$FeBrN$_4$O$_4$: C, 51.50 (51.12); H, 6.32 (6.35); N, 9.24 (9.17).

#### 3.2.2.3 Synthesis of [Fe(salPren-5-OMe)$_2$]I 8

**8** was synthesized via post-complexation anionic exchange from FeCl$_3$ (0.4 mmol, 0.0649 g) and was dissolved in EtOH (3 mL) to give a bright yellow solution to which the ligand solution was added. The solution immediately turned black and THF (4 mL) was added to improve solubility and a solution of KI (1.2 mmol, 0.2012 mg) in EtOH:H$_2$O (4 ml:1 ml) was added. The flask was heated at 60 °C overnight. After anionic exchange, the reaction mixture was allowed to cool to room temperature and reduced to approximately 2 mL *in vacuo*. Water (30 mL) was added to precipitate the product. The residue was filtered, washed with water, and dried in air. **8** was collected as black microcrystals after slowly reducing from 1:2 CH$_2$Cl$_2$:hexane (0.193 g, 76%). Elemental analysis: cald (found) for C$_{26}$H$_{38}$FeIN$_4$O$_4$: C, 47.80 (47.47); H, 5.86 (5.90); N, 8.58 (8.52).

#### 3.2.2.4 Synthesis of [Fe(salPren-5-OMe)$_2$]NO$_3$ 9

**9** was synthesized in a similar method to **6** using Fe(NO$_3$)$_3$ (0.162 g, 0.4 mmol) instead of FeCl$_3$. Recrystallization after slowly reducing from 1:2 CH$_2$Cl$_2$:hexane yields black microcrystals of **9** (0.161 g, 68%). Elemental analysis: cald (found) for C$_{26}$H$_{38}$FeN$_5$O$_7$: C, 53.07 (52.67); H, 6.51 (6.54); N, 11.90 (11.81).

#### 3.2.2.5 Synthesis of [Fe(salPren-5-OMe)$_2$]ClO$_4$ 10

**10** was synthesized in a similar method to **6** using Fe(ClO$_4$)$_3$ (0.143 g, 0.4 mmol) instead of FeCl$_3$. Recrystallization after slowly reducing from 1:2 CH$_2$Cl$_2$:hexane yields black microcrystals of **10** (0.182 g, 69%). Elemental analysis: cald (found) for C$_{26}$H$_{38}$FeN$_5$O$_7$: C, 49.89 (49.54); H, 6.12 (6.16); N, 8.95 (8.89).

## 3.3 References

Petříček, V., Palatinus, L., Plášil, J., and Dušek, M. (2023). Jana2020 – a new version of the crystallographic computing system Jana. *238*(7–8), 271–282. doi: doi:10.1515/zkri-2023-0005

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D., and Spackman, M. A. (2021). CrystalExplorer: a program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *Journal of Applied Crystallography*, *54*(3), 1006–1011. doi: 10.1107/S1600576721002910