Supporting Information

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A Straightforward Electrochemical Approach to Imine- and Amine-bisphenolate Metal Complexes with Facile Control Over Metal Oxidation State

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Supporting Information

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1. **General considerations**

Where stated, manipulations were performed under an atmosphere of dry nitrogen by means of standard Schlenk line or Glovebox techniques. Anhydrous solvents were prepared by passing the solvent over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water, via the Dow-Grubbs solvent system. Deuterated chloroform and acetonitrile were dried over CaH$_2$, cannula filtered or distilled, and then freeze-pump-thaw degassed prior to use. All other reagents and solvents were used as supplied.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX300 spectrometer or a Bruker AV500 spectrometer. The values of chemical shifts are given in ppm and values for coupling constants ($J$) in Hz. Assignment of some $^1$H NMR spectra was aided by the use of 2D $^1$H-$^1$H COSY experiments and the assignment of some $^{13}$C{$^1$H} NMR spectra was aided by $^{13}$C{$^1$H} dept 135 experiments. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Microanalyses were performed using a Carlo Erba Elemental Analyser MOD 1106 spectrometer. Atomic absorption spectroscopy (AAS) were performed using a Perkin-Elmer Atomic Absorption Spectrometer AAnalyst 400, operating with an air-acetylene flame. X-Ray fluorescence (XRF) analysis was obtained at the University of York on a Horiba XGT7000 X-ray analytical microscope instrument using a partial vacuum.

Salan ligand precursors $N,N'$-bis(3,5-tert-pentylsalicyl)-1,2-ethylenedimethylamine $^{1g}$ and $N,N'$-bis(3,5-tert-butyalsalicyl)-1,2-ethylenedimethylamine $^{1h}$ were synthesised by literature procedures\(^1\) and all other chemicals were obtained from commercial sources and used as received. Cu foil (99.9 % purity), Fe foil (99.5 % purity), Ni foil (99.5 % purity), Zn sticks (99.9 % purity, complexometric standard) and Mn/Ni foil (Mn 88/Ni 12) were used directly without further purification. Commercially available AAS standard solutions were obtained as 1000 mgmL$^{-1}$ stock and diluted as required using ultra-pure water.

A PSD 30/3B high performance digital power supply was used in constant voltage mode (CV), with current measurements made via a 15XP-B Amprobe digital multimeter, at a milliampere scale.
2. Synthesis of salen ligand precursors 1a-f

Preparation of \( N,N'\)-bis(salicylidene)ethylenediamine, 1a:

Salicylaldehyde (4.50 mL, 41.0 mmol) and ethylenediamine (1.40 mL, 20.5 mmol) were stirred vigorously in refluxing ethanol (50 mL) for 30 minutes. The resulting yellow solution was cooled to 0 °C, upon which a bright yellow precipitate formed which was collected via vacuum filtration, washed with cold ethanol (10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the title compound as a microcrystalline yellow solid. Yield: 3.45 g, 12.9 mmol, 63 %. \( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) (ppm) 13.19 (br s, 2H, O\( H \)), 8.36 (s, 2H, CH=N), 7.32 – 7.22 (m, 4H, Ar\( H \)), 6.96 – 6.83 (m, 4H, Ar\( H \)), 3.94 (s, 4H, N\( CH_2 CH_2 N \)). \( ^{13}\)C\{H\} NMR (75 MHz, CDCl\(_3\)): \( \delta \) (ppm) 166.7, 161.2, 132.5, 131.6, 118.8, 118.6, 117.1, 59.9. HR-MS (ESI\(^+\)): \( m/z \) 269.1274 [C\(_{16}\)H\(_{17}\)N\(_2\)O\(_2\)]\(^+\), calcd. [M + H]\(^+\) 269.1285. These data are in agreement with those reported in the literature.\(^2\)

Preparation of \( trans-N,N'\)-bis(salicylidene)-1,2-cyclohexanediamine, 1b:

Salicylaldehyde (4.50 mL, 41.0 mmol) and (±)-\( trans\)-1,2-diaminocyclohexane (2.50 mL, 20.5 mmol) were stirred vigorously in refluxing ethanol (50 mL) for 30 minutes. The resulting yellow solution was cooled to 0 °C, upon which a bright yellow precipitate formed which was collected via vacuum filtration, washed with cold ethanol (10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the title compound as a microcrystalline yellow solid. Yield: 6.52 g, 20.2 mmol, 99 %. \( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) (ppm) 13.30 (br s, 2H, O\( H \)), 8.26 (s, 2H, CH=N), 7.27 – 7.21 (m, 2H, Ar\( H \)), 7.16 (d, \( J = 0.6 \) Hz, 1H, Ar\( H \)), 7.13 (d, \( J = 0.6 \) Hz, 1H, Ar\( H \)), 6.89 (m, 2H, Ar\( H \)), 6.79 (td, \( J = 15.0, 7.5, 0.6 \) Hz, 2H, Ar\( H \)), 3.36 – 3.27 (m, 2H, NCH), 1.97 – 1.44 (m, 8H, cy\( H \)). \( ^{13}\)C\{H\} NMR (75 MHz, CDCl\(_3\)): \( \delta \) (ppm) 164.8, 161.1, 132.3, 131.6, 118.8, 118.7, 116.9, 72.8, 33.2, 24.3. HR-MS (ESI\(^+\)): \( m/z \) 323.1755 [C\(_{20}\)H\(_{23}\)N\(_2\)O\(_2\)]\(^+\), calcd. [M + H]\(^+\) 323.1754. These data are in agreement with those reported in the literature.\(^2\)

Preparation of \( N,N'\)-bis(salicylidene)-1,2-phenylenediamine, 1c:

Salicylaldehyde (4.50 mL, 41.0 mmol) and \( o \)-phenylenediamine (2.18 g, 20.5 mmol) were stirred vigorously in refluxing ethanol (50 mL) for 15 minutes. The resulting orange suspension was cooled
to 0 °C, upon which a bright orange precipitate formed which was collected via vacuum filtration, washed with cold ethanol (10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the title compound as a microcrystalline orange solid. Yield: 5.76 g, 18.2 mmol, 89 %. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 12.91 (br s, 2H, O\(\text{H}\)), 8.53 (s, 2H, CH=N), 7.29 – 7.21 (m, 6H, ArH), 7.16 – 7.11 (m, 2H, ArH), 6.95 – 6.93 (m, 2H, ArH), 6.81 (td, \(J = 25.0, 12.5, 1.5\) Hz, 2H, ArH). \(^{13}\)C{H} NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm) 163.8, 161.4, 142.6, 133.4, 132.4, 127.8, 119.8, 119.3, 119.1, 117.6. HR-MS (ESI\(^+\)): \(m/z\) 317.1299 \([\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2]^+\), calcd. [M + H\(^+\)] 317.1285. These data are in agreement with those reported in the literature.

Preparation of \(N,N’\)-bis(o-vanillidene)ethylenediamine, 1d:

\(O\)-vanillin (3.00 g, 19.7 mmol) and ethylenediamine (0.66 mL, 9.86 mmol) were stirred vigorously in refluxing ethanol (50 mL) for 15 minutes. The resulting yellow solution was cooled to 0 °C, upon which a bright yellow precipitate formed which was collected via vacuum filtration, washed with cold ethanol (10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the title compound as a microcrystalline yellow solid. Yield: 2.90 g, 9.86 mmol, quantitative. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 13.22 (br s, 2H, O\(\text{H}\)), 8.30 (s, 2H, CH=N), 6.89 (dd, \(J = 7.5, 1.5\) Hz, 2H, ArH), 6.83 (dd, \(J = 7.5, 1.5\) Hz, 2H, ArH), 6.77 – 6.74 (m, 2H, ArH), 3.93 (s, 4H, NCH\(_2\text{CH}_2\text{N}\)), 3.86 (s, 6H, OCH\(_3\)). \(^{13}\)C{H} NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm) 165.6, 150.4, 147.3, 122.1, 117.4, 117.0, 113.1, 58.4, 55.0. HR-MS (ESI\(^+\)): \(m/z\) 319.1400 \([\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_4]^+\), calcd. [M + H\(^+\)] 319.1496. These data are in agreement with those reported in the literature.

Preparation of \(trans-N,N’\)-bis(o-vanillidene)-1,2-cyclohexanediamine, 1e:

\(O\)-vanillin (3.00 g, 19.7 mmol) and (±)-\(trans\)-1,2-diaminocyclohexane (1.20 mL, 9.86 mmol) were stirred vigorously in refluxing ethanol (50 mL) for 30 minutes. The resulting yellow solution was cooled to 0 °C, upon which a bright yellow precipitate formed which was collected via vacuum filtration, washed with cold ethanol (10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the title compound as a microcrystalline yellow solid. Yield: 2.79 g, 8.29 mmol, 84 %. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) 13.83 (br s, 2H, O\(\text{H}\)), 8.24 (s, 2H, CH=N), 6.86 (dd, \(J = 7.8, 1.8\) Hz, 2H, ArH), 6.84 (dd, \(J = 7.8, 1.8\) Hz, 2H, ArH), 6.77 – 6.72 (m, 2H, ArH), 3.93 (s, 4H, NCH\(_2\text{CH}_2\text{N}\)), 3.85 (s, 6H, OCH\(_3\)). \(^{13}\)C{H} NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm) 165.6, 150.4, 147.3, 122.1, 117.4, 117.0, 113.1, 58.4, 55.0. HR-MS (ESI\(^+\)): \(m/z\) 329.1400 \([\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_4]^+\), calcd. [M + H\(^+\)] 329.1496. These data are in agreement with those reported in the literature.
Hz, 2H, ArH), 6.79 (dd, J = 7.8, 1.8 Hz, 2H, ArH), 6.74 – 6.69 (m, 2H, ArH), 3.86 (s, 6H, OCH3), 3.34 – 3.27 (m, 2H, NCH3), 1.97 – 1.86 (m, 4H, cyH), 1.77 – 1.70 (m, 2H, cyH), 1.57 – 1.25 (m, 2H, cyH). 13C{H} NMR (75 MHz, CDCl3): δ (ppm) 164.9, 151.7, 148.4, 123.3, 118.5, 118.0, 114.0, 72.5, 56.1, 33.2, 24.2. HR-MS (ESI+): m/z 383.1943 [C22H27N2O4]+, calcd. [M + H]+ 383.1965. These data are in agreement with those reported in the literature.3

Preparation of N,N′-bis(vanillidene)-1,2-diphenyl-1,2-ethylenediamine, 1f:

O-vanillin (3.00 g, 19.7 mmol) and (1S,2S)-(-)-1,2-diphenylethylenediamine (2.09 g, 9.86 mmol) were stirred vigorously in refluxing ethanol (50 mL) for 16 hours. The resulting yellow solution was cooled to 0 °C, upon which a bright yellow precipitate formed which was collected via vacuum filtration, washed with hot ethanol (10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the title compound as a yellow solid. Yield: 1.43 g, 3.82 mmol, 39 %. 1H NMR (300 MHz, CDCl3): δ (ppm) 13.79 (br s, 2H, OH), 8.35 (s, 2H, CH=N), 7.20 – 7.12 (m, 12H, ArH), 6.89 – 6.65 (m, 4H, ArH), 3.88 (s, 2H, NCH3), 2.16 (s, 6H, OCH3). 13C{H} NMR (75 MHz, CDCl3): δ (ppm) 207.1, 166.1, 128.5, 128.3, 128.0, 127.8, 123.6, 118.5, 114.4, 80.5, 56.2, 31.0. HR-MS (ESI+): m/z 481.2101 [C30H29N2O4]+, calcd. [M + H]+ 481.2122. These data are in agreement with those reported in the literature.4
3. **Synthesis of Cu^{II}-salen complexes, 2a-f**

**General procedure**

A three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and acetonitrile (50 mL). Two copper electrodes (30 × 10 × 1 mm) were introduced to the solution and a potential applied via an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 50.0 mA for 90 minutes. The resulting precipitate was collected via vacuum filtration, washed with dichloromethane (2 × 10 mL), water (2 × 30 mL) diethyl ether (3 × 30 mL) and dried in vacuo to deliver the corresponding Cu^{II}-salen complex as a microcrystalline solid.

**Preparation of Cu^{II}-salen complex, 2a:**

Salen precursor 1a was reacted according to the general procedure (*vide supra*), affording the product as a dark green solid. Yield: 0.26 g, 0.79 mmol, 79 %. Mp decom. >170 °C. HR-MS (ESI^+^): m/z 330.0461 [C_{16}H_{15}CuN_{2}O_{2}]^+, calcd. [M + H]^+ 330.0424. Anal. calcd. (%) for C_{16}H_{16}N_{2}O_{2}Cu·1/2CH_{2}Cl_{2}: C 54.14, H 4.10, N 7.80; found C 54.00, H 4.10, N 7.70.

**Preparation of Cu^{II}-salen complex, 2b:**

Salen precursor 1b was reacted according to the general procedure (*vide supra*), affording the product as a purple solid. Yield: 0.21 g, 0.54 mmol, 54 %. Electrochemical efficiency: 28%. Mp decom. >150 °C. HR-MS (ESI^+^): m/z 384.0909 [C_{20}H_{21}CuN_{2}O_{2}]^+, calcd. [M + H]^+ 384.0894. Anal. calcd. (%) for C_{20}H_{20}N_{2}O_{2}Cu·1/6H_{2}O: C 61.61, H 5.34, N 7.19; found C 61.21, H 5.20, N 7.00.

**Preparation of Cu^{II}-salen complex, 2c:**

Salen precursor 1c was reacted according to the general procedure (*vide supra*), affording the product as a dark brown solid. Yield: 0.31 g, 0.81 mmol, 81 %. Mp decom. >180 °C. HR-MS (ESI^+^): m/z 378.0427 [C_{20}H_{15}CuN_{2}O_{2}]^+, calcd. [M + H]^+ 378.0424. Anal. calcd. (%) for C_{20}H_{14}N_{2}O_{2}Cu: C 63.57, H 3.73, N 7.41; found C 63.40, H 3.70, N 7.30.
Preparation of Cu$^{II}$-salen complex, 2d:

Salen precursor 1d was reacted according to the general procedure (vide supra), affording the product as a dark green solid. Yield: 0.34 g, 0.86 mmol, 86 %. Mp decomp. >155 °C. HR-MS (ESI$^+$): m/z 390.0640 [C$_{18}$H$_{18}$CuN$_2$O$_4$]$^+$, calcd. [M + H]$^+$ 390.0635. Anal. calcd. (%) for C$_{18}$H$_{18}$N$_2$O$_4$Cu.H$_2$O: C 53.00, H 4.94, N 6.87; found C 52.60, H 4.90, N 6.80.

Preparation of Cu$^{II}$-salen complex, 2e:

Salen precursor 1e was reacted according to the general procedure (vide supra), affording the product as a dark purple solid. Yield: 0.35 g, 0.78 mmol, 78 %. Mp decomp. >150 °C. HR-MS (ESI$^+$): m/z 444.1109 [C$_{22}$H$_{25}$CuN$_2$O$_4$]$^+$, calcd. [M + H]$^+$ 444.1105. Anal. calcd. (%) for C$_{22}$H$_{25}$N$_2$O$_4$Cu.H$_2$O: C 57.19, H 5.67, N 6.06; found C 57.00, H 5.65, N 6.00.

Preparation of Cu$^{II}$-salen complex, 2f:

Salen precursor 1f was reacted according to the general procedure (vide supra), affording the product as a pale green solid. Yield: 0.31 g, 0.58 mmol, 58 %. Mp decomp. >180 °C. HR-MS (ESI$^+$): m/z 542.1276 [C$_{30}$H$_{27}$CuN$_2$O$_4$]$^+$, calcd. [M + H]$^+$ 542.1261. Anal. calcd. (%) for C$_{30}$H$_{26}$N$_2$O$_4$Cu.1/3CH$_2$Cl$_2$: C 63.90, H 4.71, N 4.91; found C 63.80, H 4.90, N 4.80.
4. **Synthesis of Cu$^{II}$-salan complexes, 2g, h**

General procedure

A three-necked round bottomed flask equipped with stirrer bar was charged with salan precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol), acetonitrile (50 mL) and heated to 40 °C until full dissolution was achieved, upon which the solution was allowed to cool to ambient temperature. Two copper electrodes (30 × 10 × 1 mm) were introduced to the solution and a potential applied via an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 50.0 mA for 90 minutes. The resulting precipitate was collected via vacuum filtration, washed with dichloromethane (2 × 10 mL), water (2 × 30 mL) diethyl ether (3 × 30 mL) and dried *in vacuo* to deliver the corresponding Cu$^{II}$-salan complex as a microcrystalline solid.

Preparation of Cu$^{II}$-salan complex, 2g:

Salan precursor 1g was reacted according to the general procedure (*vide supra*), affording the product as a dark green solid. Green needles suitable for X-ray crystallographic analysis were grown via slow evaporation of a concentrated CH$_2$Cl$_2$ solution of the complex. Yield: 0.53 g, 0.83 mmol, 83 %. Mp decomp. >150 °C. HR-MS (ESI$^+$): m/z 642.4202 [C$_{38}$H$_{63}$CuN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 642.4180. Anal. calcd. (%) for C$_{38}$H$_{62}$N$_2$O$_2$Cu.H$_2$O: C 69.10, H 9.77, N 4.24; found C 69.00, H 9.80, N 4.15.

Preparation of Cu$^{II}$-salen complex, 2h:

Salan precursor 1h was reacted according to the general procedure (*vide supra*), affording the product as a dark green solid. Green needles suitable for X-ray crystallographic analysis were grown via slow evaporation of a concentrated CH$_2$Cl$_2$ solution of the complex. Yield: 0.44 g, 0.75 mmol, 75 %. Mp decomp. >180 °C. HR-MS (ESI$^+$): m/z 586.3575 [C$_{34}$H$_{55}$CuN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 586.3554. Anal. calcd. (%) for C$_{34}$H$_{54}$N$_2$O$_2$Cu.2/3CH$_2$Cl$_2$: C 64.80, H 8.68, N 4.36; found C 64.40, H 8.30, N 4.10.
5. Synthesis of Ni$^{II}$-salen complexes, 3a-e

General procedure

A flame-dried three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and acetonitrile (50 mL) [N.B. product yields were much improved by use of anhydrous solvent, whilst an atmosphere of N$_2$ vs air did not affect yield]. Two nickel electrodes (30 × 10 × 1 mm) were introduced to the solution and a potential applied via an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 50.0 mA for 90 minutes. The resulting precipitate was collected via vacuum filtration, washed with dichloromethane (2 × 10 mL) followed by diethyl ether (3 × 30 mL) to give the crude product as a hygroscopic brown/red solid. Recrystallisation of the crude product from dichloromethane/diethyl ether delivered the corresponding Ni$^{II}$-salen complex as a microcrystalline solid.

Preparation of Ni$^{II}$-salen complex, 3a:

Salen precursor 1a was reacted according to the general procedure (vide supra), affording the product as a light brown solid. Yield: 0.30 g, 0.91 mmol, 91 %. Mp decomp. >300 °C. $^1$H NMR (300 MHz, CD$_3$CN): δ (ppm) 9.66 (s, 2H, CH=N), 7.50 (d, $J = 9.0$ Hz, 2H, ArH), 7.35 (t, $J = 16.8$, 9.0 Hz, 2H, ArH), 6.85 (t, $J = 16.8$, 9.0 Hz, 2H, ArH), 6.76 (d, $J = 9.0$ Hz, 2H, ArH), 3.09 (s, 4H, NCH$_2$CH$_2$N). $^{13}$C{H} NMR (75 MHz, CDCl$_3$): δ (ppm) 166.5, 162.0, 132.4, 131.5, 129.9, 118.8, 118.7, 59.8. HR-MS (ESI$^+$): m/z 325.0483 [C$_{16}$H$_{15}$NiN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 325.0482. Anal. calcd. (%) for C$_{16}$H$_{14}$NiN$_2$O$_2$: C 59.13, H 4.34, N 8.62; found C 59.10, H 4.20, N 8.40.

Preparation of Ni$^{II}$-salen complex, 3b:

Salen precursor 1b was reacted according to the general procedure (vide supra), affording the product as a light red solid. Pale orange needles suitable for X-ray crystallographic analysis were grown via the slow diffusion of Et$_2$O vapours into a concentrated CH$_2$Cl$_2$ solution of the complex. Yield: 0.32 g, 0.84 mmol, 84 %. Mp decomp. >300 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.32 (bs, 2H, CH=N), 7.19 (t, $J = 12.9$, 5.7 Hz, 2H, ArH), 7.02 – 6.99 (m, 4H, ArH), 6.51 (t, $J = 12.9$, 5.7 Hz, 2H, ArH),
3.24 – 3.19 (m, 2H, NCH), 2.44 – 2.38 (m, 2H, cyH), 1.96 – 1.89 (m, 2H, cyH), 1.39 – 1.27 (m, 4H, cyH). $^{13}$C{H} NMR (75 MHz, CDCl$_3$): δ (ppm) 177.3, 168.6, 139.0, 132.7, 122.6, 119.4, 110.5, 64.5, 27.7, 23.9. HR-MS (ESI$^+$): m/z 379.0940 [C$_{20}$H$_{21}$NiN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 379.0951. Anal. calcd. (%) for C$_{20}$H$_{20}$NiN$_2$O$_2$: C 61.19, H 5.52, N 7.14; found C 61.20, H 5.20, N 7.00.

Preparation of Ni$^{II}$-salen complex, 3c:

Salen precursor 1c was reacted according to the general procedure (vide supra), affording the product as a light red solid. Yield: 0.30 g, 0.80 mmol, 80 %. Mp decomp. >300 ºC. $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.27 (bs, 2H, C=H), 7.75 – 7.71 (m, 2H, ArH), 7.35 – 7.32 (m, 4H, ArH), 7.20 – 7.18 (m, 4H, ArH), 6.67 (t, J = 14.1, 7.5 Hz, 2H, ArH). $^{13}$C{H} NMR (75 MHz, CDCl$_3$): δ (ppm) 166.0, 161.8, 134.4, 131.2, 130.9, 126.9, 121.5, 119.4, 116.8, 112.0. HR-MS (ESI$^+$): m/z 373.0482 [C$_{20}$H$_{15}$NiN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 373.0482. Anal. calcd. (%) for C$_{20}$H$_{14}$N$_2$O$_2$Ni.H$_2$O: C 61.43, H 4.12, N 7.16; found C 61.20, H 3.80, N 6.95.

Preparation of Ni$^{II}$-salen complex, 3d:

Salen precursor 1d was reacted according to the general procedure (vide supra), affording the product as a light orange solid. Yield: 0.30 g, 0.77 mmol, 77 %. Mp decomp. >300 ºC. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.46 (s, 2H, C=H), 6.67 – 6.65 (m, 4H, ArH), 6.44 (t, J = 15.0, 8.0 Hz, 2H, ArH), 3.79 (s, 6H, OCH$_3$), 3.42 (s, 4H, NCH$_2$CH$_2$N). $^{13}$C{H} NMR (125 MHz, CDCl$_3$): δ (ppm) 161.6, 156.5, 151.3, 123.1, 119.5, 114.0, 112.4, 58.4, 55.3. HR-MS (ESI$^+$): m/z 385.0697 [C$_{18}$H$_{19}$NiN$_2$O$_4$]$^+$, calcd. [M + H]$^+$ 385.0693. Anal. calcd. (%) for C$_{18}$H$_{18}$N$_2$O$_4$Ni: C 56.15, H 4.71, N 7.28; found C 55.80, H 4.70, N 7.20.

Preparation of Ni$^{II}$-salen complex, 3e:

Salen precursor 1e was reacted according to the general procedure (vide supra), affording the product as a light brown solid. Pale brown needles suitable for X-ray crystallographic analysis were grown via the slow diffusion of Et$_2$O vapours into a concentrated CH$_2$Cl$_2$ solution of the complex. Yield: 0.39 g, 0.88 mmol, 88 %. Mp decomp. >300 ºC. $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.12 (s, 2H, C=H), 6.63 (dd, J = 7.5, 1.5 Hz, 2H, ArH), 6.49 (dd, J = 7.5, 1.5 Hz, 2H, ArH), 6.34 (m, 2H, ArH), 3.75 (s,
6H, OCH$_3$), 3.20 (m, 2H, NCH), 2.28 (m, 2H, cyH), 1.83 (m, 2H, cyH), 1.36 – 1.18 (m, 4H, cyH).

$^{13}$C(H) NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 168.2, 155.7, 144.1, 123.3, 120.2, 118.9, 111.0, 72.5, 55.5, 33.2, 20.2. HR-MS (ESI$^+$): $m/z$ 439.1168 [C$_{22}$H$_{35}$NiN$_2$O$_4$]$^+$, calcd. [M + H]$^+$ 439.1162. Anal. calcd. (%) for C$_{22}$H$_{35}$NiN$_2$O$_4$: C 57.80, H 5.73, N 6.13; found C 57.90, H 5.50, N 5.75.
6. **Synthesis of Zn$^{II}$-salen complexes, 4a-e**

General procedure

A three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and acetonitrile (50 mL). Two zinc electrodes (30 mm length, 6 mm dia.) were introduced to the solution and a potential applied *via* an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 50.0 mA for 90 minutes. The resulting precipitate was collected *via* vacuum filtration, washed with acetonitrile (2 $\times$ 10 mL), water (2 $\times$ 30 mL) followed by diethyl ether (3 $\times$ 30 mL) and dried *in vacuo* to deliver the corresponding Zn$^{II}$-salen complex as a hygroscopic off-white solid.

**Preparation of Zn$^{II}$-salen complex, 4a:**

Salen precursor 1a was reacted according to the general procedure (*vide supra*), affording the product as a pale yellow solid. Yield: 0.29 g, 0.88 mmol, 88 %. $^1$H NMR (500 MHz, $d_6$-DMSO): $\delta$ (ppm) 8.43 (s, 2H, CH=N), 7.15 - 7.10 (m, 4H, ArH), 6.62 (d, $J = 14.0$ Hz, 2H, ArH), 6.42 (t, $J = 9.0$, 14.0 Hz, 2H, ArH), 3.72 (s, 4H, NCH$_2$CH$_2$N). $^{13}$C{H} NMR (75 MHz, $d_6$-DMSO): $\delta$ (ppm) 171.0, 168.0, 134.8, 132.8, 122.7, 119.4, 112.2, 55.8. HR-MS (ESI$^+$): $m/z$ 331.0418 [C$_{16}$H$_{15}$ZnN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 331.0420. Anal. calcd. (%) for C$_{16}$H$_{14}$N$_2$O$_2$Zn: C 57.94, H 4.25, N 8.45; found C 57.90, H 4.30, N 8.40.

**Preparation of Zn$^{II}$-salen complex, 4b:**

Salen precursor 1b was reacted according to the general procedure (*vide supra*), affording the product as an off-white solid. Yield: 0.30 g, 0.79 mmol, 79 %. $^1$H NMR (500 MHz, $d_6$-DMSO): $\delta$ (ppm) 8.33 (s, 2H, CH=N), 7.23 (dd, $J = 2.5$, 12.0 Hz, 2H, ArH), 7.13 (td, $J = 2.5$, 12.0, 15.6 Hz, 2H, ArH), 6.63 (d, $J = 15.6$ Hz, 2H, ArH), 6.42 (t, $J = 12.0$, 15.6 Hz, 2H, ArH), 3.19 (m, 2H, cyH), 2.45 (m, 2H, cyH), 1.91 (m, 2H, cyH), 1.38 (m, 4H, cyH). $^{13}$C{H} NMR (75 MHz, $d_6$-DMSO): $\delta$ (ppm) 170.9, 164.6, 135.4, 132.7, 122.6, 119.3, 112.2, 64.5, 27.7, 23.9. HR-MS (ESI$^+$): $m/z$ 385.0887
[C_{20}H_{22}ZnN_2O_2]^+\textsuperscript{1}, calcd. [M + H]\textsuperscript{+} 385.0889. Anal. calcd. (%) for C_{20}H_{22}N_2O_2Zn\textsubscript{1/2}H_2O: C 60.85, H 5.36, N 7.10; found C 61.00, H 5.20, N 7.00.

Preparation of Zn\textsuperscript{II}-salen complex, 4c:

Salen precursor 1c was reacted according to the general procedure (vide supra), affording the product as a pale yellow solid. Yield: 0.35 g, 0.93 mmol, 93 %. \textsuperscript{1}H NMR (500 MHz, \textit{d}_6-DMSO): \(\delta\) (ppm) 9.01 (s, 2H, \(\text{C}=\text{N}\)), 7.91 – 7.89 (m, 2H, \(\text{ArH}\)), 7.42 – 7.38 (m, 4H, \(\text{ArH}\)), 7.25 (td, \(J = 1.5, 6.5, 15.0 \text{ Hz}, 2\text{H}, \text{ArH}\)), 6.72 (d, \(J = 15.0 \text{ Hz}, 2\text{H}, \text{ArH}\)), 6.51 (t, \(J = 6.5, 15.0 \text{ Hz}, 2\text{H}, \text{ArH}\)). \textsuperscript{13}C{H} NMR (75 MHz, \textit{d}_6-DMSO): \(\delta\) (ppm) 172.2, 162.8, 139.3, 136.2, 134.3, 127.2, 123.1, 119.4, 116.4, 112.9. HR-MS (ESI\textsuperscript{+}): \(m/z\) 379.0420 [C_{20}H_{17}ZnN_2O_2]^+, calcd. [M + H}\textsuperscript{+} 379.0417. Anal. calcd. (%) for C_{20}H_{17}N_2O_2Zn: C 60.30, H 4.05, N 7.04; found C 59.90, H 4.10, N 6.80.

Preparation of Zn\textsuperscript{II}-salen complex, 4d:

Salen precursor 1d was reacted according to the general procedure (vide supra), affording the product as a colourless solid. Yield: 0.30 g, 0.77 mmol, 77 %. \textsuperscript{1}H NMR (500 MHz, \textit{d}_6-DMSO): \(\delta\) (ppm) 8.42 (s, 2H, \(\text{C}=\text{N}\)), 6.78 – 6.76 (m, 4H, \(\text{ArH}\)), 6.36 – 6.33 (m, 2H, \(\text{ArH}\)), 3.72 (s, 6H, OC\textsubscript{3}H\textsubscript{3}), 3.71 (s, 4H, N\textsubscript{3}C\textsubscript{3}H\textsubscript{2}C\textsubscript{3}H\textsubscript{2}N). \textsuperscript{13}C{H} NMR (75 MHz, \textit{d}_6-DMSO): \(\delta\) (ppm) 168.0, 162.1, 152.5, 126.1, 118.5, 113.0, 111.9, 110.9, 56.0, 55.0. HR-MS (ESI\textsuperscript{+}): \(m/z\) 469.0772 [C_{18}H_{20}N_2O_4 + DMSO]\textsuperscript{+}, calcd. [M + H]\textsuperscript{+} 469.0770. Anal. calcd. (%) for C_{18}H_{20}N_2O_4Zn: C 52.76, H 4.92, N 6.84; found C 52.40, H 4.90, N 6.70.

Preparation of Zn\textsuperscript{II}-salen complex, 4e:

Salen precursor 1e was reacted according to the general procedure (vide supra), affording the product as an off-white solid. Colourless blocks suitable for X-ray crystallographic analysis were grown upon standing of a concentrated DMSO solution of the complex. Yield: 0.42 g, 0.94 mmol, 94 %. \textsuperscript{1}H NMR (500 MHz, \textit{d}_6-DMSO): \(\delta\) (ppm) 8.32 (s, 2H, \(\text{C}=\text{N}\)), 6.84 (d, \(J = 8.0 \text{ Hz}, 2\text{H}, \text{ArH}\)), 7.78 (d, \(J = 8.0 \text{ Hz}, 2\text{H}, \text{ArH}\)), 6.34 (t, \(J = 8.0, 15.0 \text{ Hz}, 2\text{H}, \text{ArH}\)), 3.72 (s, 6H, OCH\textsubscript{3}), 3.20 – 3.18 (m, 2H, cyH), 2.45 – 2.43 (m, 2H, cyH), 1.91 – 1.90 (m, 2H, cyH), 1.43 – 1.30 (m, 4H, cyH). \textsuperscript{13}C{H} NMR (75 MHz, \textit{d}_6-DMSO): \(\delta\) (ppm) 164.7, 151.9, 126.5, 118.2, 114.8, 111.4, 64.9, 63.9, 27.8, 23.9, 14.6. HR-MS
(ESI\(^+\)): \textit{m/z} 445.1109 \ [C_{22}H_{25}ZnN_2O_4]^+, \text{ calcd.} \ [M + H]^+ \ 445.1100. \text{ Anal. calcd. (\%) for}
\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{Zn}\cdot1/4\text{H}_2\text{O}: \text{C 56.42, H 5.70, N 5.98; found C 56.20, H 5.90, N 5.60.}
7. Synthesis of Fe$^{III}$-salen complexes, 5a-e

General procedure

A three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and acetonitrile (50 mL). Two iron electrodes ($30 \times 10 \times 1$ mm) were introduced to the solution and a potential applied via an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 50.0 mA for 90 minutes. The resulting precipitate was collected via vacuum filtration, washed with acetonitrile ($2 \times 10$ mL), water ($2 \times 30$ mL), diethyl ether ($3 \times 30$ mL) and dried in vacuo to deliver the corresponding Fe$^{III}$-salen complex as a microcrystalline solid.

Preparation of Fe$^{III}$-salen complex, 5a:

Salen precursor 1a was reacted according to the general procedure (vide supra), affording the product as a dark red solid. Dark red needles suitable for X-ray crystallographic analysis were grown via the slow diffusion of Et$_2$O vapours into a concentrated CH$_2$Cl$_2$ solution of the complex. Yield: 0.20 g, 0.30 mmol, 59 %. Mp decomp. >180 °C. HR-MS (ESI$^+$): $m/z$ 661.0828 [C$_{32}$H$_{28}$Fe$_2$N$_4$O$_5$]$^+$, calcd. [M + H]$^+$ 661.0831. Anal. calcd. (%) for C$_{32}$H$_{29}$N$_4$O$_5$Fe$_2$: C 56.83, H 4.17, N 8.28; found C 56.80, H 4.20, N 8.10.

Preparation of Fe$^{III}$-salen complex, 5b:

Salen precursor 1b was reacted according to the general procedure (vide supra), affording the product as a red solid. Yield: 0.28 g, 0.37 mmol, 74 %. Mp decomp. >200 °C. HR-MS (ESI$^+$): $m/z$ 769.1777 [C$_{40}$H$_{41}$Fe$_2$N$_4$O$_5$]$^+$, calcd. [M + H]$^+$ 769.1770. Anal. calcd. (%) for C$_{40}$H$_{40}$N$_4$O$_5$Fe$_2$: C 62.15, H 5.28, N 7.25; found C 61.85, H 5.20, N 7.20.

Preparation of Fe$^{III}$-salen complex, 5c:

Salen precursor 1c was reacted according to the general procedure (vide supra), affording the product as a dark red/brown solid. Yield: 0.26 g, 0.35 mmol, 69 %. Mp decomp. >200 °C. HR-MS (ESI$^+$): $m/z$
757.1090 [C\textsubscript{40}H\textsubscript{28}Fe\textsubscript{2}N\textsubscript{4}O\textsubscript{5}]^\textsuperscript{+}, calcd. [M + H]^\textsuperscript{+} 757.0831. Anal. calcd. (%) for C\textsubscript{40}H\textsubscript{28}N\textsubscript{4}O\textsubscript{5}Fe\textsubscript{2}.H\textsubscript{2}O: C 59.43, H 3.99, N 6.93; found C 59.30, H 3.80, N 6.60.

Preparation of Fe\textsuperscript{III}-salen complex, 5d:

Salen precursor 1d was reacted according to the general procedure (vide supra), affording the product as a red/brown solid. Yield: 0.30 g, 0.39 mmol, 78 %. Mp decomps. >180 °C. HR-MS (ESI\textsuperscript{+}): m/z 781.1888 [C\textsubscript{36}H\textsubscript{37}Fe\textsubscript{2}N\textsubscript{4}O\textsubscript{9}]^\textsuperscript{+}, calcd. [M + H]^\textsuperscript{+} 781.1254. Anal. calcd. (%) for C\textsubscript{36}H\textsubscript{36}N\textsubscript{4}O\textsubscript{9}Fe\textsubscript{2}.1\textsubscript{1/2}H\textsubscript{2}O: C 50.84, H 4.98, N 6.59; found C 50.80, H 4.90, N 6.50.

Preparation of Fe\textsuperscript{III}-salen complex, 5e:

Salen precursor 1e was reacted according to the general procedure (vide supra), affording the product as a dark brown solid. Yield: 0.28 g, 0.32 mmol, 64 %. Mp decomps. >200 °C. HR-MS (ESI\textsuperscript{+}): m/z 889.2180 [C\textsubscript{44}H\textsubscript{49}Fe\textsubscript{2}N\textsubscript{4}O\textsubscript{9}]^\textsuperscript{+}, calcd. [M + H]^\textsuperscript{+} 889.2193. Anal. calcd. (%) for C\textsubscript{44}H\textsubscript{48}N\textsubscript{4}O\textsubscript{9}Fe\textsubscript{2}: C 61.54, H 5.14, N 7.14; found C 61.85, H 5.20, N 7.20.

Preparation of Fe\textsuperscript{III}-salen complex, 5, from Fe(OAc)\textsubscript{2}:\textsuperscript{5a,b}

Salen precursor 1b (0.20 g, 0.62 mmol) and anhydrous Fe(OAc)\textsubscript{2} (0.11 g, 0.62 mmol) were charged to a flame-dried Schlenk flask and stirred in anhydrous ethanol (10 mL) at 75 °C for 1 hour under an inert atmosphere. Upon slow cooling to room temperature, a dark purple microcrystalline solid precipitated from solution, which was collected via filtration under N\textsubscript{2} and washed with anhydrous hexane (2 × 15 mL). The solid was further purified by suspension in refluxing ethanol under N\textsubscript{2}, followed by filtration and washing with additional hexane (3 × 20 mL) to give the Fe\textsuperscript{III}(salen)(OAc) complex 5 as a microcrystalline dark purple solid. Anal. calcd. (%) for C\textsubscript{22}H\textsubscript{23}N\textsubscript{2}O\textsubscript{4}Fe: C 60.71, H 5.33, N 6.64; found C 60.80, H 5.15, N 7.00.
8. **Synthesis of Fe$^{II}$-salen complexes, 6a, b, e**

General procedure

A flame-dried three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and further dried *in vacuo*. Anhydrous (anoxic) acetonitrile (50 mL) was added *via* cannula and the solution further degassed *via* bubbling a stream of N$_2$ or Ar for ca. 30 minutes through the solution. Two iron electrodes (30 × 10 × 1 mm) were introduced to the solution and a potential applied *via* an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 50.0 mA for 90 minutes. The suspended violet precipitate was isolated *via* cannula filtration and washed with anhydrous (anoxic) acetonitrile (2 × 15 mL), followed by rinsing with anhydrous (anoxic) diethyl ether (3 × 15 mL) before drying *in vacuo* to deliver the corresponding Fe$^{II}$-salen complex as a (highly air- and moisture-sensitive) light violet powder [N. B. upon exposure to an atmosphere of air, the products rapidly become an orange powder, which is likely due to oxidation of the Fe centre].

Preparation of Fe$^{II}$-salen complex, 6a:

Salen precursor 1a was reacted according to the general procedure (*vide supra*), affording the product as a light violet solid. Yield: 0.28 g, 0.88 mmol, 88 %. $\mu_{\text{eff}} = 5.0 \mu_B$. HR-MS (ESI$^+$): $m/z$ 323.1761 [C$_{16}$H$_{15}$FeN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 323.0477. Anal. calcd. (%) for C$_{16}$H$_{14}$N$_2$O$_2$Fe: C 59.66, H 4.38, N 8.70; found C 59.90, H 4.30, N 8.60.

Preparation of Fe$^{II}$-salen complex, 6b:

Salen precursor 1b was reacted according to the general procedure (*vide supra*), affording the product as a violet solid. Yield: 0.34 g, 0.90 mmol, 90 %. $\mu_{\text{eff}} = 4.9 \mu_B$. HR-MS (ESI$^+$): $m/z$ 376.0870 [C$_{20}$H$_{21}$FeN$_2$O$_2$]$^+$, calcd. [M + H]$^+$ 376.0874. Anal. calcd. (%) for C$_{16}$H$_{14}$N$_2$O$_2$Fe.$^3$I$_4$H$_2$O: C 61.63, H 5.56, N 7.19; found C 61.50, H 5.20, N 7.10.
Preparation of Fe$^{II}$-salen complex, 6e:

Salen precursor 1e was reacted according to the general procedure (*vide supra*), affording the product as a light violet solid. Violet blocks suitable for X-ray crystallographic analysis were grown *via* slow diffusion of Et$_2$O vapours into a weak CH$_2$Cl$_2$ solution of the complex. Yield: 0.41 g, 0.93 mmol, 93\% $\mu_{\text{eff}} = 4.9 \ \mu_B$. HR-MS (ESI$^+$): $m/z$ 437.1160 [C$_{22}$H$_{25}$FeN$_2$O$_4$]$^+$. calcd. [M + H]$^+$ 437.1158. Anal. calcd. (%) for C$_{22}$H$_{24}$N$_2$O$_4$Fe: C 60.43, H 5.66, N 8.25; found C 60.50, H 5.40, N 8.30.
9. **Synthesis of Mn IV-salen complexes, 7a-e**

**General procedure**

A three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and acetonitrile (50 mL). Two manganese/nickel (80:20 weight %) electrodes (25 × 10 × 0.25 mm) were introduced to the solution and a potential applied via an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 20.0 mA for 90 minutes. The resulting precipitate was collected via vacuum filtration, washed with acetonitrile (2 × 10 mL) followed by diethyl ether (3 × 30 mL) and dried in vacuo to deliver the corresponding Mn IV-salen complex as a microcrystalline solid.

**Preparation of Mn IV-salen complex, 7a:**

Salen precursor 1a was reacted according to the general procedure (vide supra), affording the product as a brown powder. Pale brown blocks suitable for X-ray crystallographic analysis were grown via either (i) slow diffusion of Et₂O vapours into a concentrated binary CH₂Cl₂/DMSO solution of the complex, or (ii) standing of a weak MeCN solution of the complex to give two different solvent-dependent solid-state structures of 7a (see section 18, Crystallographic details). Yield: 0.30 g, 0.44 mmol, 87 %. Mp decomp. >300 °C. HR-MS (ESI⁺): m/z 675.0845 [C₃₂H₂₉Mn₂N₄O₆]⁺, calcd. [M + H]⁺ 675.0843. Anal. calcd. (%) for C₃₂H₂₉N₄O₆Mn₂: C 57.99, H 4.18, N 8.31; found C 58.10, H 4.25, N 8.40.

**Preparation of Mn IV-salen complex, 7b:**

Salen precursor 1b was reacted according to the general procedure (vide supra), affording the product as a brown powder. Yield: 0.39 g, 0.45 mmol, 90 %. Mp decomp. >300 °C. HR-MS (ESI⁺): m/z 783.1780 [C₄₀H₄₁Mn₂N₄O₆]⁺, calcd. [M + H]⁺ 783.1782. Anal. calcd. (%) for C₄₀H₄₁N₄O₆Mn₂: C 61.39, H 5.15, N 7.16; found C 61.20, H 5.20, N 7.20.
Preparation of Mn\textsuperscript{IV}-salen complex, 7c:

Salen precursor 1c was reacted according to the general procedure (\textit{vide supra}), affording the product as a brown powder. Yield: 0.38 g, 0.49 mmol, 95 %. Mp decomp. \textgreater 300 °C. HR-MS (ESI\textsuperscript{+}): \textit{m/z} 771.0840 \textit{[C\textsubscript{40}H\textsubscript{28}Mn\textsubscript{2}N\textsubscript{4}O\textsubscript{6}]}\textsuperscript{+}, calcd. [M + H\textsuperscript{+}] 771.0843. Anal. calcd. (%) for C\textsubscript{40}H\textsubscript{28}N\textsubscript{4}O\textsubscript{6}Mn\textsubscript{2}: C 62.35, H 3.66, N 7.27; found C 62.30, H 3.99, N 7.00.

Preparation of Mn\textsuperscript{IV}-salen complex, 7d:

Salen precursor 1d was reacted according to the general procedure (\textit{vide supra}), affording the product as a brown powder. Yield: 0.39 g, 0.49 mmol, 98 %. Mp decomp. \textgreater 300 °C. HR-MS (ESI\textsuperscript{+}): \textit{m/z} 795.1271 \textit{[C\textsubscript{36}H\textsubscript{37}Mn\textsubscript{2}N\textsubscript{4}O\textsubscript{10}]}\textsuperscript{+}, calcd. [M + H\textsuperscript{+}] 795.1265. Anal. calcd. (%) for C\textsubscript{36}H\textsubscript{36}N\textsubscript{4}O\textsubscript{10}Mn\textsubscript{2}.H\textsubscript{2}O: C 53.21, H 4.71, N 6.89; found C 53.30, H 4.61, N 6.95.

Preparation of Mn\textsuperscript{IV}-salen complex, 7e:

Salen precursor 1e was reacted according to the general procedure (\textit{vide supra}), affording the product as a brown powder. Pale brown blocks suitable for X-ray crystallographic analysis were grown \textit{via} slow diffusion of Et\textsubscript{2}O vapours into a concentrated binary CH\textsubscript{2}Cl\textsubscript{2}/DMSO solution of the complex. Yield: 0.35 g, 0.39 mmol, 78 %. Mp decomp. \textgreater 300 °C. HR-MS (ESI\textsuperscript{+}): \textit{m/z} 903.2225 \textit{[C\textsubscript{44}H\textsubscript{49}Mn\textsubscript{2}N\textsubscript{4}O\textsubscript{10}]}\textsuperscript{+}, calcd. [M + H\textsuperscript{+}] 903.2204. Anal. calcd. (%) for C\textsubscript{44}H\textsubscript{48}N\textsubscript{4}O\textsubscript{10}Mn\textsubscript{2}.\textsubscript{\textfrac{1}{2}}H\textsubscript{2}O: C 57.96, H 5.42, N 6.14; found C 57.65, H 5.20, N 6.10.

Preparation of Mn\textsuperscript{III}-salen polymer, 7, from Mn(OAc)\textsubscript{2}:\textsuperscript{5a}

Salen precursor 1a (0.17 g, 0.62 mmol) and anhydrous Mn(OAc)\textsubscript{2} (0.11 g, 0.62 mmol) were charged to a flame-dried Schlenk flask and stirred in anhydrous ethanol (10 mL) at 75 °C for 1 hour under an inert atmosphere. Upon slow cooling to room temperature, a dark brown microcrystalline solid precipitated from solution, which was collected \textit{via} filtration under N\textsubscript{2} and washed with anhydrous hexane (2 \times 15 mL). The solid was further purified by suspension in refluxing ethanol under N\textsubscript{2}, followed by filtration and washing with additional hexane (3 \times 20 mL) to give the [Mn\textsuperscript{III}(salen)(OAc)]
polymer 7 as a microcrystalline dark brown solid. Anal. calcd. (%) for C_{18}H_{17}N_{2}O_{4}Mn: C 56.85, H 4.51, N 7.37; found C 56.50, H 4.50, N 7.20.
10. **Synthesis of Mn$^{II}$-salen complexes, 8a, b, e**

A flame-dried three-necked round bottomed flask equipped with stirrer bar was charged with salen precursor (1.0 mmol), tetrabutylammonium tetrafluoroborate (0.03 mmol) and further dried *in vacuo*. Anhydrous (anoxic) acetonitrile (50 mL) was added *via* cannula and the solution further degassed *via* bubbling a stream of N$_2$ or Ar for *ca.* 30 minutes through the solution. Two manganese/nickel (80:20 weight %) electrodes (25 × 10 × 0.25 mm) were introduced to the solution and a potential applied *via* an external power supply (22.0 – 25.0 V, operating in CV mode) to maintain a constant current of 20.0 mA for 90 minutes. The suspended pale orange precipitate was isolated *via* cannula filtration and washed with anhydrous (anoxic) acetonitrile (2 × 15 mL), followed by rinsing with anhydrous (anoxic) diethyl ether (3 × 15 mL) before drying *in vacuo* to deliver the corresponding Mn$^{II}$-salen complex as a (highly air- and moisture-sensitive) pale orange powder.

**Preparation of Mn$^{II}$-salen complex, 8a:**

Salen precursor 1a was reacted according to the general procedure (*vide supra*), affording the product as a pale orange microcrystalline powder. Yield: 0.25 g, 0.77 mmol, 77 %. $\mu_{\text{eff}} = 5.9$ $\mu_B$. HR-MS (ESI$^+$): $m/z$ 321.0460 [C$_{16}$H$_{14}$MnN$_2$O$_2$]$^+$, calcd. [M]$^+$ 321.0436. Anal. calcd. (%) for C$_{16}$H$_{14}$N$_2$O$_2$Mn: C 59.82, H 4.39, N 8.72; found C 60.20, H 4.10, N 8.75.

**Preparation of Mn$^{II}$-salen complex, 8b:**

Salen precursor 1b was reacted according to the general procedure (*vide supra*), affording the product as a pale orange microcrystalline powder. Yield: 0.27 g, 0.71 mmol, 71 %. $\mu_{\text{eff}} = 5.7$ $\mu_B$. HR-MS (ESI$^+$): $m/z$ 375.0903 [C$_{20}$H$_{20}$MnN$_2$O$_2$]$^+$, calcd. [M]$^+$ 375.0905. Anal. calcd. (%) for C$_{20}$H$_{20}$N$_2$O$_2$Mn: C 64.00, H 5.37, N 7.46; found C 64.22, H 5.00, N 7.75.

**Preparation of Mn$^{II}$-salen complex, 8e:**

Salen precursor 1e was reacted according to the general procedure (*vide supra*), affording the product as a pale orange microcrystalline powder. Bright yellow blocks suitable for X-ray crystallographic analysis were grown *via* slow diffusion of Et$_2$O vapours into a concentrated binary CH$_2$Cl$_2$/DMSO
solution of the complex. Yield: 0.33 g, 0.78 mmol, 78 %. $\mu_{\text{eff}} = 5.8 \mu_B$. HR-MS (ESI$^+$): $m/z$ 429.0647 [C$_{22}$H$_{18}$MnN$_2$O$_4$]$^+$, calcd. [M]$^+$ 429.0647. Anal. calcd. (%) for C$_{22}$H$_{24}$N$_2$O$_4$Mn: C 60.69, H 5.56, N 6.43; found C 60.40, H 5.10, N 6.80.
11. $^1$H NMR spectra of Ni$^{II}$-salen complexes, 3a-e

Figure S1. $^1$H NMR spectrum of complex 3a (300 MHz, CD$_3$CN).

Figure S2. $^1$H NMR spectrum of complex 3b (300 MHz, CDCl$_3$).
Figure S3. $^1$H NMR spectrum of complex 3c (300 MHz, CDCl$_3$).

Figure S4. $^1$H NMR spectrum of complex 3d (500 MHz, CDCl$_3$).
**Figure S5.** $^1$H NMR spectrum of complex 3e (300 MHz, CDCl$_3$).
12. $^1$H NMR spectra of Zn$^{II}$-salen complexes, 4a-e

**Figure S6.** $^1$H NMR spectrum of complex 4a (500 MHz, d$_6$-DMSO).

**Figure S7.** $^1$H NMR spectrum of complex 4b (500 MHz, d$_6$-DMSO).
Figure S8. $^1$H NMR spectrum of complex 4c (500 MHz, d$_6$-DMSO).

Figure S9. $^1$H NMR spectrum of complex 4d (500 MHz, d$_6$-DMSO).
Figure S10. $^1$H NMR spectrum of complex 4e (500 MHz, d$_6$-DMSO).
13. Cyclic voltammetry measurements

Electrochemical measurements were conducted using an Autolab PGSTAT20 voltammetric analyser under an argon atmosphere, solvated in pre-dried/degassed CH$_3$CN containing 0.10 M [$^n$Bu$_4$N]BF$_4$ as supporting electrolyte at room temperature. Voltammetric experiments utilised a Pt disk working electrode, a Pt rod auxiliary electrode and an Ag/AgCl reference electrode. All potentials quoted are referenced to an internal ferrocene/ferrocenium standard and were obtained at a scan rate ($\nu$) of 400 mVs$^{-1}$. The ferrocene/ferrocenium couple under these conditions was observed at $+0.40 \leq E_{1/2} \leq +0.55$ V vs Ag/AgCl.

![Figure S11](image.png)

**Figure S11.** Full cyclic voltammogram of salen ligand 1c (left) and cathodic sweep of salen ligands 1a, b, d, e (right), illustrating regions of reduction potential in acetonitrile. [Salen ligand] = [Fc] = 1.0 mM; media = (CH$_3$CN/$^n$Bu$_4$N]BF$_4$ 0.10 M); $\nu = 400$ mVs$^{-1}$; $T = 298$ K; $E_{pa}$ ascribed to phenolate oxidation band.

| Entry | Salen ligand precursor | $E_{\text{red vs Fc/Fc}^+}$ (V) |
|-------|------------------------|---------------------------------|
| 1     | 1a                     | -2.12                           |
| 2     | 1b                     | -2.04                           |
| 3     | 1c                     | -2.13                           |
| 4     | 1d                     | -2.45                           |
| 5     | 1e                     | -2.55                           |

**Table S1.** Reduction potentials (*versus* Fc/Fc$^+$) of salen ligand precursors 1a-e.
14. Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) was used to determine the presence (or absence) of elements (Mn and Ni) within bulk samples of 7a-c, which were dissolved in 30% nitric/10% hydrochloric acid solution.

![Image of atomic absorbance calibration profiles for Mn and Ni](image1.png)

**Figure S12.** Atomic absorbance calibration profiles (1, 5, 10, 15 ppm stock solutions, diluted from 1000 ppm standard solutions using ultra-pure water) for Mn (left, correlation coefficient 0.98) and Ni (right, correlation coefficient 0.98).

![Image of atomic absorbance data for Ni](image2.png)

**Figure S13.** Atomic absorbance of Ni (Sample 009 = 7a, 010 = 7b, 011 = 7c, 012 = 7a at 10-fold concentration).
AAS analysis indicates trace quantities of Ni within bulk samples 7a-c (Figure S13, 7a = 0.076, 7b = 0.043, 7c = 0.075 ppm), which are consistent with quantities observed within blank solvent. A 10-fold increase in concentration of compound 7a does not lead to a 10-fold increase in Ni absorbance (Figure S13, 7a = 0.106 ppm), indicating that these readings lie within error associated with this instrument (i.e. no Ni above 1 ppm in any sample was accurately detected).
15. X-ray fluorescence analysis

All samples were run as solids on a Horiba XGT7000 X-ray analytical microscope instrument using a partial vacuum (X-ray voltage = 30 kV; preset time = 60 s; current set to auto; process time = 6; XGT beam size = 1.2 mm with no filter (F4) or Nb filter (F3). Solid samples were mounted on a glass slide and sealed using sellotape.

The first reference sample was benzylmanganese(I) pentacarbonyl (Figure S14) – data was collected at three separate positions to ensure that the sample was homogeneous.

![Graph](image)

**Figure S14.** XRF analysis of benzylmanganese(I) pentacarbonyl (F4).

The second reference sample was Ni(NO$_3$)$_2$·6H$_2$O (Figure S15) – as the material was crystalline, one sample point was recorded with no filter (F4).
The presence of Ni is indicated by characteristic K lines at 7.478 and 8.627 KeV (not present in the BnMn(CO)$_5$ reference sample).

Sample 7a was analysed under the same conditions as for the reference samples (Figure S16). In total, six independent measurements were made to examine for sample homogeneity (with F3 applied). In all cases, Mn was the strongest element present and no Ni was detected (to the limits of detection ~ 10 ppm). For one sample point, trace Ca was detected (K lines at 4.013/3.690 KeV), when no filter (F4) was used.
Sample 7b was analysed under the same conditions as for the reference samples. In total, six independent measurements were made to examine the sample homogeneity. It was found that Ca and Cl (K lines at 2.816/2.621 KeV) were present in trace amounts when no filter (F4) was used (Figure S17). The Ca and Cl signals were lost using the F3 filter, with only Mn being visible (Figure S18). Ni was not found within this sample, to the limits of detection.

**Figure S17.** XRF analysis of sample 7b (F4).

**Figure S18.** XRF analysis of sample 7b (F3).
The analysis would indicate that trace CaCl is present in the sample. For quantification, it would be necessary to calibrate the analysis sample using authentic CaCl samples.

Sample 7c was analysed under the same conditions as for the reference samples. In total, five independent measurements were made to examine the sample homogeneity. For two of the five samples, a trace signal that may be indicative of Ca, was observed when no filter (F4) was used in the measurement (Figure S19), which was lost when the Nb filter (F3) was used (Figure S20). In all cases, the Mn signal was dominant. Ni was not found within this sample, to the limits of detection.
16. Magnetic susceptibility measurements

The solution magnetic susceptibility measurements were made by NMR methods on a Bruker AV500 spectrometer at 298 K using a modified Evans method. A flame-sealed coaxial insert containing a deuterated reference solvent (C₆D₆/C₆H₆, 50:50) was placed in a Young’s NMR tube under an inert atmosphere. An anhydrous (anoxic) C₆D₆ (100 %) solution of the paramagnetic complex was added to the tube and ¹H{¹³C} NMR spectra recorded. The volume magnetic susceptibility (χ) of the paramagnetic compound was calculated from the following equation:

\[ \chi = \chi_0 + \frac{3000 \Delta \nu}{4\pi \nu_0 c M} \]

where χ₀ is the volume magnetic susceptibility of pure solvent; Δν (Hz) is the separation of the reference solvent peaks from the inner and outer tubes; ν₀ is the operating frequency of the spectrometer; c is the concentration of the complex in molL⁻¹ and M is the molecular weight of the complex. The molar susceptibility (χₘ₀) and magnetic moment (μₑffective) were calculated from χ at 298 K, taking account of the diamagnetic correction from the sum of Pascal constants.
17. Electrochemical reactor configuration
**Inert procedure:**

A pair of oven-dried metal electrodes are each independently attached to standard electrical wire (a). Each electrode is independently connected to a positive and negative terminal of a power supply (b). A flame-dried three-necked flask is charged with salen precursor, and further dried in vacuo for 30 minutes (c). Anhydrous (and anoxic) acetonitrile is added to the flask, and further degassed via bubbling a flow of argon through the solution for 30 minutes (d). Whilst under an inert atmosphere, the two electrodes are introduced to the solution (e) and a potential applied to the cell (f) to maintain a constant current (20 – 50 mA).

**Hydrous procedure:**

A pair of metal electrodes are prepared as above. A three-necked flask is charged with salen precursor, dissolved with HPLC-grade acetonitrile and both electrodes are introduced to the solution. Whilst under an atmosphere of air, a potential is applied to the cell (see above).
18. Crystallographic details

X-Ray diffraction data were collected on an Agilent SuperNova diffractometer fitted with an Atlas CCD detector with Mo Kα radiation (\(\lambda = 0.7107 \, \text{Å}\)) or Cu Kα radiation (\(\lambda = 1.5418 \, \text{Å}\)). Crystals were mounted under oil on nylon fibres. Data sets were corrected for absorption using a multiscan method, and the structures were solved by direct methods using SHELXS-97/SHELXT and refined by full-matrix least squares on \(F^2\) using ShelXL-97, interfaced through the program Olex2.8 Molecular graphics for all structures were generated using POV-RAY in the X-Seed program.

Crystallographic details for 2g:

| Identification code | SEH30_Cu |
|---------------------|----------|
| Empirical formula   | \(\text{C}_{38}\text{H}_{62}\text{CuN}_{2}\text{O}_{2}\) |
| Formula weight      | 642.44 |
| Temperature/K       | 120.3(7) |
| Crystal system      | orthorhombic |
| Space group         | Pbca |
| \(a/\AA\)           | 17.7387(4) |
| \(b/\AA\)           | 11.6590(2) |
| \(c/\AA\)           | 34.8626(6) |
| \(\alpha/\^\circ\)  | 90.00 |
| \(\beta/\^\circ\)   | 90.00 |
| \(\gamma/\^\circ\)  | 90.00 |
| Volume/\(\AA^3\)    | 7210.2(2) |
| \(Z\)               | 8 |
| \(\rho_{\text{calc}}/\text{g/cm}^3\) | 1.184 |
| \(\mu/\text{mm}^{-1}\) | 1.096 |
| \(F(000)\)          | 2792.0 |
| Crystal size/\(\text{mm}^3\) | 0.33 \times 0.04 \times 0.03 |
| Radiation           | CuKα (\(\lambda = 1.54184\)) |
| 2\(\Theta\) range for data collection/\(^\circ\) | 7.1 to 134.06 |
| Index ranges        | \(-20 \leq h \leq 21, \ -13 \leq k \leq 13, \ -41 \leq l \leq 29\) |
| Reflections collected | 18677 |
| Independent reflections | 6424 [\(R_{\text{int}} = 0.0321, R_{\text{sigma}} = 0.0325\)] |
| Data/restraints/parameters | 6424/0/402 |
| Goodness-of-fit on \(F^2\) | 1.036 |
| Final R indexes [\(I>2\sigma(I)\)] | \(R_1 = 0.0548, wR_2 = 0.1465\) |
| Final R indexes [all data] | \(R_1 = 0.0649, wR_2 = 0.1563\) |
| Largest diff. peak/hole / e \(\AA^{-3}\) | 1.76/-0.66 |
Figure S22. Molecular structure of complex 2g.

Crystallographic details for 2h:

- **Identification code**: SEH31_Cu
- **Empirical formula**: C₃₄H₅₄CuN₂O₂
- **Formula weight**: 586.33
- **Temperature/K**: 121(1)
- **Crystal system**: orthorhombic
- **Space group**: Pbca
- **a/Å**: 17.3203(10)
- **b/Å**: 10.9924(11)
- **c/Å**: 34.278(2)
- **α/°**: 90.00
- **β/°**: 90.00
- **γ/°**: 90.00
- **Volume/Å³**: 6526.2(9)
- **Z**: 8
- **ρ calc g/cm³**: 1.193
- **μ/mm⁻¹**: 1.166
- **F(000)**: 2536.0
- **Crystal size/mm³**: 0.27 × 0.03 × 0.02
- **Radiation**: CuKα (λ = 1.54184)
- **2Θ range for data collection/°**: 7.26 to 134.12
- **Index ranges**: -18 ≤ h ≤ 20, -13 ≤ k ≤ 12, -28 ≤ l ≤ 40
- **Reflections collected**: 15600
- **Independent reflections**: 5824 [R int = 0.1069, R sigma = 0.1173]
- **Data/restraints/parameters**: 5824/0/366
Goodness-of-fit on $F^2$ 0.974
Final R indexes [$I>=2\sigma (I)$] $R_1 = 0.0643$, $wR_2 = 0.1401$
Final R indexes [all data] $R_1 = 0.1223$, $wR_2 = 0.1713$
Largest diff. peak/hole / e Å$^{-3}$ 0.79/-0.75

Figure S23. Molecular structure of complex 2h.

Crystallographic details for 3b:

| Identification code    | MRC236_Cu               |
|------------------------|--------------------------|
| Empirical formula      | C$_{20}$H$_{20}$N$_2$NiO$_2$ |
| Formula weight         | 379.09                   |
| Temperature/K          | 120.01(13)               |
| Crystal system         | orthorhombic             |
| Space group            | Pnna                     |
| $a$/Å                  | 6.8080(4)                |
| $b$/Å                  | 13.6311(7)               |
| $c$/Å                  | 17.8457(11)              |
| $\alpha$/°             | 90.00                    |
| $\beta$/°              | 90.00                    |
| $\gamma$/°             | 90.00                    |
| Volume/Å$^3$           | 1656.10(16)              |
| Z                      | 4                        |
| $\rho_{calc}$/g/cm$^3$ | 1.520                    |
| $\mu$/mm$^{-1}$        | 1.818                    |
| $F(000)$               | 792.0                    |
| Crystal size/mm$^3$    | 0.3738 × 0.117 × 0.03    |
| Radiation              | CuKα ($\lambda = 1.54184$) |
| 2θ range for data collection/° | 8.16 to 146.82        |
Index ranges $\quad -8 \leq h \leq 4, \quad -16 \leq k \leq 15, \quad -21 \leq l \leq 14$

Reflections collected $\quad 3881$

Independent reflections $\quad 1630 \quad [R_{int} = 0.0406, \quad R_{sigma} = 0.0431]$

Data/restraints/parameters $\quad 1630/0/114$

Goodness-of-fit on $F^2$ $\quad 1.038$

Final R indexes [$I>2\sigma (I)$] $\quad R_1 = 0.0442, \quad wR_2 = 0.1150$

Final R indexes [all data] $\quad R_1 = 0.0586, \quad wR_2 = 0.1258$

Largest diff. peak/hole / e Å$^{-3}$ $\quad 0.48/-0.45$

**Figure S24.** Molecular structure of complex 3b.

**Crystallographic details for 3e:**

Identification code $\quad$ seh38_cu_sqd
Empirical formula $\quad$ C$_{23.75}$H$_{23}$N$_2$NiO$_{4.5}$
Formula weight $\quad$ 467.15
Temperature/K $\quad$ 120.2(5)
Crystal system $\quad$ orthorhombic
Space group $\quad$ Cmcm
a/Å $\quad$ 18.9750(12)
b/Å $\quad$ 16.8021(10)
c/Å $\quad$ 6.8430(5)
$\alpha/°$ $\quad$ 90.00
$\beta/°$ $\quad$ 90.00
$\gamma/°$ $\quad$ 90.00
Volume/Å$^3$ $\quad$ 2181.7(2)
Z $\quad$ 4
$\rho_{calc}$/g/cm$^3$ $\quad$ 1.422
μ/mm$^{-3}$ 0.925  
F(000) 974.0  
Crystal size/mm$^3$ 0.1390 × 0.0333 × 0.0220  
Radiation MoK$\alpha$ ($\lambda = 0.71073$)  
2$\Theta$ range for data collection/$^\circ$ 3.24 to 52.56  
Index ranges -21 ≤ h ≤ 22, -20 ≤ k ≤ 19, -8 ≤ l ≤ 7  
Reflections collected 4067  
Independent reflections 1225 [R$\text{int} = 0.0565$, R$\text{sigma} = 0.0420$]  
Data/restraints/parameters 1225/0/97  
Goodness-of-fit on F$^2$ 1.124  
Final R indexes [I=] R$_1 = 0.0621$, wR$_2 = 0.1723$  
Final R indexes [all data] R$_1 = 0.0708$, wR$_2 = 0.1810$  
Largest diff. peak/hole / e Å$^{-3}$ 0.78/-0.37

Figure S25. Molecular structure of complex 3e.

Crystallographic details for 4e:

| Identification code | MRC240 |
|---------------------|--------|
| Empirical formula   | C$_{24}$H$_{30}$N$_2$O$_5$S$_2$Zn |
| Formula weight      | 523.93 |
| Temperature/K       | 120.01(10) |
| Crystal system      | triclinic |
| Space group         | P-1 |
| a/Å                 | 9.6395(10) |
| b/Å                 | 11.5180(6) |
Crystallographic details for 5a:

| Identification code  | MRC35(2_Cu) |
|----------------------|-------------|
| Empirical formula    | C₆₄H₅₆Fe₄N₈O₁₀ |
| Formula weight       | 1320.57     |

**Figure S26.** Molecular structure of complex 4e.
Temperature/K 120.1(4)
Crystal system triclinic
Space group P-1
a/Å 10.8736(5)
b/Å 11.0146(5)
c/Å 13.7145(7)
α/° 67.507(5)
β/° 72.885(4)
γ/° 76.765(4)
Volume/Å³ 1437.75(11)
Z 1
ρ calc g/cm³ 1.525
μ/mm⁻¹ 8.500
F(000) 680.0
Crystal size/mm³ 0.3853 × 0.1701 × 0.0575
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 8.58 to 147.66
Index ranges -13 ≤ h ≤ 13, -12 ≤ k ≤ 10, -17 ≤ l ≤ 13
Reflections collected 10707
Independent reflections 5434 [Rint = 0.0418, Rsigma = 0.0485]
Data/restraints/parameters 5434/0/388
Goodness-of-fit on F² 1.031
Final R indexes [I>=2σ (I)] R₁ = 0.0530, wR₂ = 0.1458
Final R indexes [all data] R₁ = 0.0568, wR₂ = 0.1507
Largest diff. peak/hole / e Å⁻³ 1.57/-0.53

Figure S27. Molecular structure of complex 5a.
Crystallographic details for 6e:

| Property                        | Value                          |
|--------------------------------|--------------------------------|
| Identification code            | MRC250_Cu(3)_twin1_hklf4       |
| Empirical formula              | C$_{22}$H$_{28}$FeN$_2$O$_5$   |
| Formula weight                 | 456.31                         |
| Temperature/K                  | 120.01(14)                     |
| Crystal system                 | monoclinic                     |
| Space group                    | P2$_1$/n                       |
| a/Å                            | 13.356(4)                      |
| b/Å                            | 7.725(2)                       |
| c/Å                            | 19.505(5)                      |
| α/°                            | 90                             |
| β/°                            | 93.71(3)                       |
| γ/°                            | 90                             |
| Volume/Å$^3$                   | 2008.3(9)                      |
| Z                              | 4                              |
| ρ$_{calc}$/g/cm$^3$             | 1.509                          |
| μ/mm$^3$                       | 0.789                          |
| F(000)                         | 960.0                          |
| Crystal size/mm$^3$            | 0.211 × 0.0601 × 0.0395        |
| Radiation                      | MoKα (λ = 0.71073)             |
| 2θ range for data collection/° | 3.59 to 44.198                 |
| Index ranges                   | -14 ≤ h ≤ 14, -8 ≤ k ≤ 8, -19 ≤ l ≤ 20 |
| Reflections collected          | 3516                           |
| Independent reflections        | 3516 [R$_{int}$ = ?, R$_{sigma}$ = 0.1667] |
| Data/restraints/parameters     | 3516/330/313                   |
| Goodness-of-fit on F$^2$        | 0.978                          |
| Final R indexes [I>=2σ (I)]    | R$_1$ = 0.0898, wR$_2$ = 0.2015 |
| Final R indexes [all data]     | R$_1$ = 0.1594, wR$_2$ = 0.2268 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.00/-0.42          |
Figure S28. Molecular structure of complex 6e.

Crystallographic details for 7a:

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | exp_1330                                   |
| Empirical formula               | C_{17}H_{16}Cl_{2}MnN_{2}O_{3}             |
| Formula weight                  | 422.16                                     |
| Temperature/K                    | 120.00(10)                                 |
| Crystal system                   | monoclinic                                 |
| Space group                      | P2_{1}/c                                   |
| a/Å                              | 9.7531(3)                                  |
| b/Å                              | 8.3562(2)                                  |
| c/Å                              | 21.8483(6)                                 |
| α/°                             | 90.00                                      |
| β/°                             | 100.943(3)                                 |
| γ/°                             | 90.00                                      |
| Volume/Å³                        | 1748.24(8)                                 |
| Z                                | 4                                          |
| ρ_{calc} g/cm³                   | 1.604                                      |
| μ/mm⁻¹                           | 1.080                                      |
| F(000)                           | 860.0                                      |
| Crystal size/mm³                 | 0.0829 × 0.0653 × 0.0414                    |
| Radiation                        | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°  | 4.26 to 52.56                              |
| Index ranges                     | -12 ≤ h ≤ 11, -5 ≤ k ≤ 10, -21 ≤ l ≤ 26   |
| Reflections collected            | 6574                                       |
| Independent reflections          | 3411 [R_{int} = 0.0420, R_{sigma} = 0.0468] |
Data/restraints/parameters 3411/0/226
Goodness-of-fit on $F^2$ 1.197
Final R indexes [$I>=2\sigma(I)$] $R_1 = 0.1234$, $wR_2 = 0.2728$
Final R indexes [all data] $R_1 = 0.1298$, $wR_2 = 0.2845$
Largest diff. peak/hole / e Å$^{-3}$ 1.99/-0.81

Figure S29. Molecular structure of complex 7a.

Crystallographic details for 7a:

Identification code MRC258_bis salen
Empirical formula $C_{36}H_{40}Mn_2N_4O_8S_2$
Formula weight 830.72
Temperature/K 120.01(10)
Crystal system monoclinic
Space group $P2_1/n$
a/Å 6.2918(2)
b/Å 14.1567(5)
c/Å 20.0004(7)
$\alpha$/° 90.00
$\beta$/° 92.700(3)
$\gamma$/° 90.00
Volume/Å$^3$ 1779.47(11)
Z 2
$\rho_{calc}$/g/cm$^3$ 1.550
$\mu$/mm$^{-1}$ 0.886
$F(000)$ 860.0
Crystal size/mm$^3$ 0.281 × 0.242 × 0.0318
Radiation MoK$\alpha$ ($\lambda = 0.71073$)
2$d$ range for data collection/° 6.7 to 62.64
Index ranges \(-6 \leq h \leq 9, -19 \leq k \leq 13, -28 \leq l \leq 28\)

Reflections collected \(13057\)

Independent reflections \(5065 \ [R_{int} = 0.0433, R_{sigma} = 0.0571]\)

Data/restraints/parameters \(5065/0/244\)

Goodness-of-fit on \(F^2\) \(1.032\)

Final R indexes \([I>=2\sigma (I)]\) \(R_1 = 0.0474, wR_2 = 0.0970\)

Final R indexes [all data] \(R_1 = 0.0685, wR_2 = 0.1059\)

Largest diff. peak/hole / e Å\(^{-3}\) \(0.52/-0.48\)

Figure S30. Molecular structure of complex 7a.

Crystallographic details for 7e:

Identification code MRC265

Empirical formula \(C_{52}H_{60}Mn_2N_8O_{10}\)

Formula weight \(1066.96\)

Temperature/K \(120.01(10)\)

Crystal system monoclinic

Space group C2\(\bar{c}\)

\(a/\text{Å}\) \(21.6125(3)\)

\(b/\text{Å}\) \(15.41812(18)\)

\(c/\text{Å}\) \(16.4514(2)\)

\(\alpha/°\) \(90.00\)

\(\beta/°\) \(110.1828(16)\)

\(\gamma/°\) \(90.00\)

Volume/Å\(^3\) \(5145.37(12)\)

\(Z\) \(4\)

\(\rho_{calc} \ g/cm^3\) \(1.377\)
Figure S31. Molecular structure of complex 7e.

Crystallographic details for 8e:

Identification code MRC267_Cu
Empirical formula C_{24}H_{31}MnN_{2}O_{5}S
Formula weight 514.51
Temperature/K 120.03(10)
Crystal system triclinic
Space group P-1
a/Å 9.6974(4)
b/Å 11.4783(4)
**Table 1: Crystallographic Data**

| Parameter         | Value                        |
|-------------------|------------------------------|
| c/Å               | 11.9218(5)                  |
| α/°               | 73.001(4)                   |
| β/°               | 66.826(4)                   |
| γ/°               | 87.881(3)                   |
| Volume/Å³         | 1162.03(8)                  |
| Z                 | 2                            |
| ρcalc g/cm³       | 1.470                        |
| μ/mm⁻¹            | 5.785                        |
| F(000)            | 540.0                        |
| Crystal size/mm³  | 0.1473 × 0.0993 × 0.0539     |
| Radiation         | CuKα (λ = 1.54184)          |
| 2Θ range for data collection/° | 8.08 to 147.7               |
| Index ranges      | -11 ≤ h ≤ 10, -14 ≤ k ≤ 13, -14 ≤ l ≤ 13 |
| Reflections collected | 8887                        |
| Independent reflections | 4372 [Rint = 0.0475, Rsigma = 0.0608] |
| Data/restraints/parameters | 4372/0/320                  |
| Goodness-of-fit on F² | 1.022                        |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0596, wR₂ = 0.1468    |
| Final R indexes [all data] | R₁ = 0.0665, wR₂ = 0.1534    |
| Largest diff. peak/hole / e Å⁻³ | 1.35/-1.05                 |

**Figure S32.** Molecular structure of complex 8e.
Crystallographic details for 5:

- **Identification code**: MRC223
- **Empirical formula**: C_{22}H_{23}FeN_{2}O_{4}
- **Formula weight**: 435.27
- **Temperature/K**: 120.01(15)
- **Crystal system**: monoclinic
- **Space group**: P2_1/c
- **a/Å**: 10.7886(16)
- **b/Å**: 9.8899(12)
- **c/Å**: 18.666(3)
- **α/°**: 90.00
- **β/°**: 101.890(14)
- **γ/°**: 90.00
- **Volume/Å³**: 1948.9(5)
- **Z**: 4
- **ρ_{calc} g/cm³**: 1.483
- **μ/mm⁻¹**: 0.806
- **F(000)**: 908.0
- **Crystal size/mm³**: 0.162 × 0.0514 × 0.0299
- **Radiation**: MoKα (λ = 0.71073)
- **2Θ range for data collection/°**: 6.36 to 62.5
- **Index ranges**: -14 ≤ h ≤ 14, -13 ≤ k ≤ 13, -26 ≤ l ≤ 27
- **Reflections collected**: 13843
- **Independent reflections**: 5531 [R_{int} = 0.0794, R_{sigma} = 0.1368]
- **Data/restraints/parameters**: 5531/0/263
- **Goodness-of-fit on F²**: 1.095
- **Final R indexes [I>=2σ (I)]**: R₁ = 0.0877, wR₂ = 0.1389
- **Final R indexes [all data]**: R₁ = 0.1512, wR₂ = 0.1605
- **Largest diff. peak/hole / e Å⁻³**: 0.98/-0.51

![Figure S33. Molecular structure of complex 5.](image)
Crystallographic details for 7:

Identification code          MRC258
Empirical formula           C₉H₆Mn₀.₅NO₂
Formula weight              187.62
Temperature/K               110.01(10)
Crystal system              orthorhombic
Space group                 Pmmn
a/Å                         6.5251(2)
b/Å                         16.1505(4)
c/Å                         7.4488(2)
α/°                         90.00
β/°                         90.00
γ/°                         90.00
Volume/Å³                   784.98(4)
Z                            4
ρcalc g/cm³                 1.588
μ/mm⁻¹                       7.080
F(000)                      382.0
Crystal size/mm³             0.0918 × 0.0692 × 0.0278
Radiation                   CuKα (λ = 1.54184)
2Θ range for data collection/° 10.96 to 147.96
Index ranges                -7 ≤ h ≤ 8, -7 ≤ k ≤ 19, -8 ≤ l ≤ 8
Reflections collected       1936
Independent reflections     859 [Rint = 0.0387, Rsigma = 0.0374]
Data/restraints/parameters  859/0/79
Goodness-of-fit on F²        1.191
Final R indexes [I>=2σ (I)] R₁ = 0.0905, wR₂ = 0.2631
Final R indexes [all data]  R₁ = 0.0911, wR₂ = 0.2634
Largest diff. peak/hole / e Å⁻³ 1.63/-1.22

Figure S34. Molecular structure of complex 7.
19. References

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