Crystallographic Detection of the Spin State in Fe$^{III}$ Complexes

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Table of Contents

S1 Experimental Methods...........................................................................................................................................4

S1.1 Synthesis of [Fe^{III}(4-OMe-sal_{323})]NO_{3} (1a) and [Fe^{III}(4-OMe-sal_{323})]NO_{3}·0.75MeCN·0.25MeOH (1a·S) 8

S1.2 Synthesis of [Fe^{III}(4-OMe-sal_{323})]PF_{6}·0.45H_{2}O (1b) .............................................................................8

S1.3 Synthesis of [Fe^{III}(4-OMe-sal_{323})]OTf·0.27H_{2}O (1c) .............................................................................8

S1.4 Synthesis of [Fe^{III}(4-OMe-sal_{323})]ClO_{4} (1d) ...................................................................................8

S1.5 Synthesis of [Fe^{III}(4-OMe-sal_{323})]BF_{4} (1e) ...................................................................................8

S1.6 Synthesis of [Fe^{III}(4-OMe-sal_{323})]SbF_{6}·0.31H_{2}O (1f) ...........................................................................9

S1.7 Synthesis of [Fe^{III}(4-OMe-sal_{323})]I_{2} (1g) .....................................................................................9

S1.8 Synthesis of [Fe^{III}(4-OMe-sal_{323})]Cl·EtOH·0.25H_{2}O (1h) .................................................................9

S1.9 Synthesis of [Fe^{III}(3-OMe-sal_{323})]NO_{3} (2a) .................................................................................9

S1.10 Synthesis of [Fe^{III}(3-OMe-sal_{323})]BF_{4}·H_{2}O (2b) ...........................................................................9

S1.11 Synthesis of [Fe^{III}(3-OMe-sal_{323})]PF_{6}·H_{2}O (2c) ..........................................................................10

S1.12 Synthesis of [Fe^{III}(5-OMe-sal_{323})]NO_{3} (3a) ...............................................................................10

S1.13 Synthesis of [Fe^{III}(5-OMe-sal_{323})]BF_{4} (3b) .................................................................................10

S1.14 Synthesis of [Fe^{III}(4,6-diOMe-sal_{323})]NO_{3}·MeOH (4a) .................................................................10

S1.15 Synthesis of [Fe^{III}(4,6-diOMe-sal_{323})]BF_{4}·0.5MeOH (4b) ...............................................................10

S1.16 Synthesis of [Fe^{III}(4,6-diOMe-sal_{323})]ClO_{4}·0.5MeOH (4c) .................................................................11

S1.17 Synthesis of [Fe^{III}(3-OEt-sal_{323})]PF_{6}·EtOH (5a) .............................................................................11

S1.18 Synthesis of [Fe^{III}(3-OEt-sal_{323})]BF_{4}·0.32H_{2}O (5b) ........................................................................11

S1.19 Synthesis of [Fe^{III}(4-Et_{2}N-sal_{323})]PF_{6} (6b) ...............................................................................11

S1.20 Synthesis of [Fe^{III}(4-Et_{2}N-sal_{323})]PF_{6}·0.78MeOH·0.1EtOH (6b·S) ...............................................11

S1.21 Synthesis of [Fe^{III}(4-Et_{2}N-sal_{323})]OTf (6c) .................................................................................12

S1.22 Synthesis of [Fe^{III}(4-Et_{2}N-sal_{323})]BF_{4} (6d) .................................................................................12

S1.23 Synthesis of [Fe^{III}(4-Et_{2}N-sal_{323})]BF_{4}·EtOH (6d·S) .........................................................................12

S1.24 Synthesis of [Fe^{III}(4-Et_{2}N-sal_{323})]NO_{3}·CH_{2}Cl_{2} (6e) .................................................................12

S1.25 Synthesis of [Fe^{III}(3-sal_{323})]ClO_{4} (7a) .....................................................................................13

S1.26 Synthesis of [Fe^{III}(3-Me-sal_{323})]PF_{6}·0.68H_{2}O (7b) .................................................................13
S1.27 Synthesis of [Fe\textsuperscript{III}(3-Me-sal\textsubscript{2}323)]BF\textsubscript{4} (7c) .................................................................13
S1.28 Synthesis of [Fe\textsuperscript{III}(3-Allyl-sal\textsubscript{2}323)]NO\textsubscript{3}:MeCN (8) ........................................................................................................13
S1.29 Synthesis of [Fe\textsuperscript{III}(3'-Bu-sal\textsubscript{2}323)]PF\textsubscript{6}:EtOH (9a) ........................................................................................................13
S1.30 Synthesis of [Fe\textsuperscript{III}(3'-Bu-sal\textsubscript{2}323)]BF\textsubscript{4} (9b) ........................................................................................................14
S1.31 Synthesis of [Fe\textsuperscript{III}(sal\textsubscript{2}323)]FeCl\textsubscript{4} (10e) ........................................................................................................14
S1.32 Synthesis of [Fe\textsuperscript{III}(sal\textsubscript{2}323)]BF\textsubscript{4} (10f) ........................................................................................................14
S1.33 Synthesis of [Fe\textsuperscript{III}(5-Br-sal\textsubscript{2}323)]PF\textsubscript{6} (11a) ........................................................................................................14
S1.34 Synthesis of [Fe\textsuperscript{III}(5-Br-sal\textsubscript{2}323)]BF\textsubscript{4}:EtOH (11b) ........................................................................................................14
S1.35 Synthesis of [Fe\textsuperscript{III}(5-Br-sal\textsubscript{2}323)]NO\textsubscript{3}:PrOH (11c) ........................................................................................................15
S1.36 Synthesis of [Fe\textsuperscript{III}(3,5-diBr-sal\textsubscript{2}323)]NO\textsubscript{3}:PrOH (12) ........................................................................................................15
S1.37 Synthesis of [Fe\textsuperscript{III}(3,5-diCl-sal\textsubscript{2}323)]BF\textsubscript{4}:PrOH (13a) ........................................................................................................15
S1.38 Synthesis of [Fe\textsuperscript{III}(3,5-diCl-sal\textsubscript{2}323)]PF\textsubscript{6} (13b) ........................................................................................................15
S1.39 Synthesis of [Fe\textsuperscript{III}(3,5-dil-sal\textsubscript{2}323)]PF\textsubscript{6} (14) ........................................................................................................15
S1.40 Synthesis of [Fe\textsuperscript{III}(3-NO\textsubscript{2}-sal\textsubscript{2}323)]PF\textsubscript{6}:MeCN (15a) ........................................................................................................16
S1.41 Synthesis of [Fe\textsuperscript{III}(3-NO\textsubscript{2}-sal\textsubscript{2}323)]NO\textsubscript{3} (15b) ........................................................................................................16
S1.42 Synthesis of [Fe\textsuperscript{III}(5-NO\textsubscript{2}-sal\textsubscript{2}323)]PF\textsubscript{6}:EtOH (16a) ........................................................................................................16
S1.43 Synthesis of [Fe\textsuperscript{III}(5-NO\textsubscript{2}-sal\textsubscript{2}323)]BF\textsubscript{4}:EtOH (16b) ........................................................................................................16
S1.44 Synthesis of [Fe\textsuperscript{III}(5-NO\textsubscript{2}-sal\textsubscript{2}323)]ClO\textsubscript{4}:EtOH (16c) ........................................................................................................16
S1.45 Synthesis of [Fe\textsuperscript{III}(3,5-NO\textsubscript{2}-sal\textsubscript{2}323)]ClO\textsubscript{4}:EtOH (17) ........................................................................................................17

S2 Single Crystal X-ray Diffraction Details ..................................................................................18
S2.2 Bond Lengths and Distortion Parameters ...........................................................................29
S2.3 Intermolecular Interactions ................................................................................................33
S2.4 Hirshfeld Surface Analysis ................................................................................................38

S3 Magnetic Measurements .......................................................................................................39

S4 Quantum Chemistry Calculations ..........................................................................................41

S5 Powder X-ray Diffraction .......................................................................................................44

S6 Author Contribution ...............................................................................................................44

S6 References ..............................................................................................................................45
### S1 Experimental Methods

Table S1.1. Summary of complex families 1–17 compared in this study.

| Complex | Salicylaldehyde | Molecular Formula | S.G. | T (K) | $\Sigma$(°) | $\Theta$(°) | Spin State |
|---------|-----------------|-------------------|------|-------|-------------|-------------|------------|
| 1a      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]NO$_3$ | $P2_1/2$ | 100   | 34.26       | 127.29      | SCO        |
|         |                 |                   |      | 293   | 52.06       | 200.78      |            |
| 1a-S    | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]NO$_3$·0.75MeCN·0.25MeOH | $P2_1/n$ | 100   | 24.13       | 58.94       | LS         |
|         |                 |                   |      | 293   | 25.22       | 63.53       |            |
| 1b      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]PF$_6$·0.45H$_2$O | $P2_1/c$ | 100   | 24.13       | 58.94       | LS         |
|         |                 |                   |      | 293   | 25.22       | 63.53       |            |
| 1c      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]OTf·0.27H$_2$O | $P2_1/c$ | 100   | 25.63       | 68.02       | LS         |
|         |                 |                   |      | 293   | 25.63       | 68.02       |            |
| 1d      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]ClO$_4$ | $P2_1/c$ | 100   | 21.83       | 59.15       | LS         |
|         |                 |                   |      | 200   | 27.34       | 73.46       |            |
| 1e      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]ClO$_4$ | $P2_1/c$ | 100   | 21.83       | 59.15       | LS         |
|         |                 |                   |      | 200   | 27.34       | 73.46       |            |
| 1f      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]BF$_4$·H$_2$O | $P2_1/c$ | 100   | 25.33       | 58.11       | LS         |
|         |                 |                   |      | 293   | 28.62       | 72.86       |            |
| 1g      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]BF$_4$·H$_2$O | $P2_1/c$ | 100   | 25.33       | 58.11       | LS         |
|         |                 |                   |      | 293   | 28.62       | 72.86       |            |
| 1h      | ![4-OMe](image)  | [Fe$^{III}$(4-OMe-sal$_2$323)]Cl·EtOH·0.25H$_2$O | $P2_1/c$ | 100   | 29.23       | 77.52       | LS         |
|         |                 |                   |      | 293   | 29.23       | 77.52       |            |
| 2a      | ![3-OMe](image)  | [Fe$^{III}$(3-OMe-sal$_2$323)]NO$_3$ | Pccn | 100   | 35.59       | 99.98       | LS         |
|         |                 |                   |      | 293   | 29.20       | 80.03       |            |
| 2b      | ![3-OMe](image)  | [Fe$^{III}$(3-OMe-sal$_2$323)]BF$_4$·H$_2$O | $P2_1/c$ | 100   | 26.62       | 72.86       | LS         |
|         |                 |                   |      | 293   | 28.65       | 80.74       |            |
| 2c      | ![3-OMe](image)  | [Fe$^{III}$(3-OMe-sal$_2$323)]BF$_4$·H$_2$O | $P2_1/c$ | 100   | 28.65       | 80.74       | LS         |
|         |                 |                   |      | 293   | 28.65       | 80.74       |            |
| 2d      | ![3-OMe](image)  | [Fe$^{III}$(3-OMe-sal$_2$323)]FeCl$_4$ | $P2_1/c$ | 100(II) | 29.92       | 78.11       | LS         |
|         |                 |                   |      | 293   | 29.92       | 78.11       |            |
| 2e      | ![3-OMe](image)  | [Fe$^{III}$(3-OMe-sal$_2$323)]ClO$_4$ | $P2_1$ | 100(I) | 21.94       | 50.17       | LS         |
|         |                 |                   |      | 293   | 23.86       | 61.35       |            |
| 3a      | ![5-OMe](image)  | [Fe$^{III}$(5-OMe-sal$_2$323)]NO$_3$ | $P2_1/c$ | 100(I) | 21.94       | 50.17       | LS         |
|         |                 |                   |      | 293(I) | 23.86       | 61.35       |            |
| 3b      | ![5-OMe](image)  | [Fe$^{III}$(5-OMe-sal$_2$323)]BF$_4$ | $P2_1/c$ | 100(I) | 28.51       | 79.56       | LS         |
|         |                 |                   |      | 293(I) | 29.92       | 73.33       |            |
| #  | Structure | Chemical Formula                  | Space Group | Temperature (K) | Crystallographic Data | Literature Ref. |
|----|-----------|-----------------------------------|-------------|-----------------|-----------------------|----------------|
| 4a | ![4a](image) | $\text{[Fe}^{\text{(III)}(4,6-\text{diOMe-sal}232)]\text{NO}_3\cdot\text{MeOH}}$ | $P2_1/c$   | 100             | 29.29                | LS             |
| 4b | ![4b](image) | $\text{[Fe}^{\text{(III)}(4,6-\text{diOMe-sal}232)]\text{BF}_4\cdot0.5\text{MeOH}}$ | $P2_1/n$   | 100             | 29.11                | LS             |
| 4c | ![4c](image) | $\text{[Fe}^{\text{(III)}(4,6-\text{diOMe-sal}232)]\text{ClO}_4\cdot0.5\text{MeOH}}$ | $P2_1/n$   | 100             | 28.51                | LS             |
| 5a | ![5a](image) | $\text{[Fe}^{\text{(III)}(3-\text{OEt-sal}232)]\text{PF}_6\cdot\text{EtOH}}$ | $P2_1/n$   | 100             | 25.32                | LS             |
| 5b | ![5b](image) | $\text{[Fe}^{\text{(III)}(3-\text{OEt-sal}232)]\text{BF}_4\cdot0.32\text{H}_2\text{O}}$ | $Pn$       | 100             | 24.95                | LS             |
| 6a | ![6a](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{ClO}_4$ | $P-1$      | 100             | 27.87                | LS             |
| 6b | ![6b](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{PF}_6$ | $P-1$      | 100             | 27.62                | LS             |
| 6b-S | ![6b-S](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{PF}_6\cdot0.78\text{MeCN}\cdot0.1\text{EtOH}$ | $P-1$      | 100 (I)         | 27.69                | LS             |
|     |           |                                   |             | 100 (II)        | 31.36                | LS             |
| 6c | ![6c](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{OTf}$ | $P-1$      | 100             | 28.78                | LS             |
| 6d | ![6d](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{BF}_4$ | $P2_1/n$   | 100             | 30.17                | LS             |
| 6d-S | ![6d-S](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{BF}_4\cdot\text{EtOH}$ | $P2_1/2_1$ | 100             | 26.2                 | LS             |
| 6e | ![6e](image) | $\text{[Fe}^{\text{(III)}(4-\text{NEt}_2-sal}232)]\text{NO}_3\cdot\text{CH}_2\text{Cl}_2$ | $P2_1/2_1$ | 100             | 26.07                | LS             |
| 7a | ![7a](image) | $\text{[Fe}^{\text{(III)}(3-\text{Me-sal}232)]\text{ClO}_4}$ | $P2_1/2_1$ | 100             | 26.82                | LS             |
| 7b | ![7b](image) | $\text{[Fe}^{\text{(III)}(3-\text{Me-sal}232)]\text{PF}_6\cdot0.68\text{H}_2\text{O}}$ | $C2/c$     | 100             | 24                   | LS             |
| 7c | ![7c](image) | $\text{[Fe}^{\text{(III)}(3-\text{Me-sal}232)]\text{BF}_4}$ | $P2_1/2_1$ | 100             | 27.18                | LS             |
| 8  | ![8](image) | $\text{[Fe}^{\text{(III)}(3-\text{Allyl-sal}232)]\text{NO}_3\cdot\text{MeCN}}$ | $P2_1/c$   | 100             | 25.72                | LS             |
| 9a | ![9a](image) | $\text{[Fe}^{\text{(III)}(3-\text{Bu-sal}232)]\text{PF}_6\cdot\text{EtOH}}$ | $P2_1/c$   | 100(I)          | 21.94                | LS             |
| No. | Compounds                                                                 | Formula            | Space Group | Temperature | α (°) | β (°) | γ (°) | LS    |
|-----|---------------------------------------------------------------------------|--------------------|-------------|-------------|-------|-------|-------|-------|
| 9b  | [Fe(3′-Bu-sal232)]BF₄                                                    |                    | P4_22       | 293         | 19.58 | 44.76 | LS    |       |
| 10a | [Fe(sal232)]NO₃                                                           |                    | P2_1/c       | 100         | 28.27 | 80.76 | LS    |       |
| 10b | [Fe(sal232)]BPh₄                                                          |                    | P2_1/n       | 293         | 28.43 | 74.16 | LS    |       |
| 10c | [Fe(sal232)]Cl                                                            |                    | Pccn         | 100         | 30.1  | 88.4  | LS    |       |
| 10d | [Fe(sal232)]ClO₄                                                          |                    | P2_1/c       | 100         | 27.29 | 69.38 | LS    |       |
| 10e | [Fe(sal232)]FeCl                                                          |                    | P2_2_2_1     | 100         | 30.69 | 68.49 | LS    |       |
| 10f | [Fe(sal232)]BF₄                                                           |                    | P2_1/c       | 100         | 25.3  | 63.64 | LS    |       |
| 11a | [Fe(5-Br-sal232)]PF₆                                                      |                    | P2_1         | 293         | 25.94 | 65.46 | LS    |       |
| 11b | [Fe(5-Br-sal232)]BF₄·EtOH                                                 |                    | P-1          | 100         | 22.38 | 59.2  | LS    |       |
| 11c | [Fe(5-Br-sal232)]NO₃·PrOH                                                |                    | P2_1/n       | 100 (I)     | 25.95 | 71.41 | LS    |       |
|     |                                                                           |                    |             |             |       |       |       |       |
| 12  | [Fe(3,5-diBr-sal232)]NO₃·PrOH                                            |                    | P2_1/n       | 100         | 24.74 | 63.01 | LS    |       |
| 13a | [Fe(3,5-diCl-sal232)]BF₄·PrOH                                             |                    | P2/n         | 293(I)      | 23.63 | 60.99 | LS    |       |
|     |                                                                           |                    |             |             | 293(II)| 29.9  | 78.11 | LS    |       |
| 13b | [Fe(3,5-diCl-sal232)]PF₆                                                 |                    | P2_1/n       | 100         | 24.54 | 60.26 | LS    |       |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 14 | ![Structure](image1) | [Fe$^{III}$(3,5-diI-sal$_2$323)]PF$_6$ | $P2_1/c$ | 100 | 25.7 | 64.96 | LS |
| 15a | ![Structure](image2) | [Fe$^{III}$(3-NO$_2$-sal$_2$323)]PF$_6$·MeCN | $P2_1/n$ | 293 | 27.96 | 65.59 | LS |
| 15b | ![Structure](image3) | [Fe$^{III}$(3-NO$_2$-sal$_2$323)]NO$_3$ | Cc | 100 | 29.94 | 72.17 | LS |
| 16a | ![Structure](image4) | [Fe$^{III}$(5-NO$_2$-sal$_2$323)]PF$_6$·EtOH | P-1 | 293 | 24.05 | 63.44 | LS |
| 16b | ![Structure](image5) | [Fe$^{III}$(5-NO$_2$-sal$_2$323)]BF$_4$·EtOH | P-1 | 293 | 22.36 | 58.7 | LS |
| 16c | ![Structure](image6) | [Fe$^{III}$(5-NO$_2$-sal$_2$323)]ClO$_4$·EtOH | P-1 | 100 | 21.02 | 56.65 | LS |
| 17 | ![Structure](image7) | [Fe$^{III}$(3,5-diNO$_2$-sal$_2$323)]ClO$_4$·EtOH | $P2_1/n$ | 100 | 27.75 | 76.98 | LS |

*Refers to the temperature of the diffraction experiment. *Structures with more than one independent Fe$^{III}$ site in the asymmetric unit are indicated as (I) and (II). *Distortion parameters $\Sigma$ and $\Theta$ are described in the main text. *Those structures previously reported in the literature are indicated with the appropriate reference. *Where OTf is CF$_3$SO$_3$. 
S1.1 Synthesis of [Fe\textsuperscript{III}(4-OMe-sal\textsubscript{2}323)]NO\textsubscript{3} (1a) and [Fe\textsuperscript{III}(4-OMe-sal\textsubscript{2}323)]NO\textsubscript{3}·0.75MeCN·0.25MeOH (1a·S)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol/acetonitrile (1:1, 5 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (40.4 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\textsubscript{24}H\textsubscript{32}N\textsubscript{5}O\textsubscript{7}Fe, Theory % (Found %): C 51.62 (51.49); H 5.78 (5.54); N 12.54 (12.52).

S1.2 Synthesis of [Fe\textsuperscript{III}(4-OMe-sal\textsubscript{2}323)]PF\textsubscript{6}·0.45H\textsubscript{2}O (1b)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and potassium hexafluorophosphate (27.6 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\textsubscript{24}H\textsubscript{32.90}N\textsubscript{4}O\textsubscript{4.45}F\textsubscript{6}PFe, Theory % (Found %): C 44.39 (44.23); H 5.11 (5.11); N 8.63 (8.55).

S1.3 Synthesis of [Fe\textsuperscript{III}(4-OMe-sal\textsubscript{2}323)]OTf·0.27H\textsubscript{2}O (1c)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and lithium trifluoromethanesulfonate (23.4 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\textsubscript{25}H\textsubscript{32.52}N\textsubscript{4}O\textsubscript{7.26}F\textsubscript{3}SFe, Theory % (Found %): C 46.18 (46.19); H 5.04 (5.01); N 8.62 (8.55).

S1.4 Synthesis of [Fe\textsuperscript{III}(4-OMe-sal\textsubscript{2}323)]ClO\textsubscript{4} (1d)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) perchlorate hexahydrate (36.3 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\textsubscript{24}H\textsubscript{32}N\textsubscript{4}O\textsubscript{8}Cl\textsubscript{Fe}, Theory % (Found %): C 48.38 (48.16); H 5.41 (5.31); N 9.40 (9.28).

S1.5 Synthesis of [Fe\textsuperscript{III}(4-OMe-sal\textsubscript{2}323)]BF\textsubscript{4} (1e)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week.
Elemental analysis, calculated for C_{24}H_{32}BN_{4}O_{4}F_{4}Fe, Theory % (Found %): C 49.43 (49.55); H 5.53 (5.50); N 9.61 (9.44).

S1.6 Synthesis of [Fe^{III}(4-OMe-sal_{323})SbF_{6}·0.31H_{2}O] (1f)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and sodium hexafluoroantimonate (38.9 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C_{24}H_{32}N_{4}O_{4.31}FeF_{6}Sb, Theory % (Found %): C 39.08 (37.97); H 4.46 (4.41); N 7.59 (7.55).

S1.7 Synthesis of [Fe^{III}(4-OMe-sal_{323})]I_{3} (1g)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and sodium iodide (22.5 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.8 Synthesis of [Fe^{III}(4-OMe-sal_{323})]Cl·EtOH·0.25H_{2}O (1h)

4-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.9 Synthesis of [Fe^{III}(3-OMe-sal_{323})]NO_{3} (2a)

3-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (40.4 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C_{24}H_{32}N_{5}O_{7}Fe, Theory % (Found %): C 51.62 (50.71); H 5.78 (5.48); N 12.54 (12.11).

S1.10 Synthesis of [Fe^{III}(3-OMe-sal_{323})]BF_{4}·H_{2}O (2b)

3-Methoxysalicylaldehyde (304 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (338 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of
solvent over a week. Elemental analysis, calculated for C_{24}H_{34}BN_{4}O_{5}F_{4}Fe, Theory % (Found %): C 47.95 (48.06); H 5.70 (5.58); N 9.32 (9.28).

S1.11 Synthesis of [Fe^{III}(3-OMe-sal_{232}3)]PF_{6}·H_{2}O (2c)
3-Methoxysalicylaldehyde (304 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C_{24}H_{34}BN_{4}O_{5}F_{4}Fe, Theory % (Found %): C 43.72 (43.60); H 5.20 (5.02); N 8.50 (8.68).

S1.12 Synthesis of [Fe^{III}(5-OMe-sal_{323}3)]NO_{3} (3a)
5-Methoxysalicylaldehyde (30.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (40.4 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C_{24}H_{32}N_{5}O_{7}Fe, Theory % (Found %): C 51.62 (51.38); H 5.78 (5.73); N 12.54 (12.38).

S1.13 Synthesis of [Fe^{III}(5-OMe-sal_{323}3)]BF_{4} (3b)
5-Methoxysalicylaldehyde (304 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (404 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C_{24}H_{32}BN_{5}O_{7}Fe, Theory % (Found %): C 49.43 (47.60); H 5.53 (5.34); N 9.61 (9.43).

S1.14 Synthesis of [Fe^{III}(4,6-diOMe-sal_{323}3)]NO_{3}·MeOH (4a)
4,6-Dimethoxysalicylaldehyde (36.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (10 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (404 mg, 1 mmol) was added, a deep red color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.15 Synthesis of [Fe^{III}(4,6-diOMe-sal_{323}3)]BF_{4}·0.5MeOH (4b)
4,6-Dimethoxysalicylaldehyde (36.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (10 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep red color was observed. The solution was briefly
stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

**S1.16 Synthesis of [Fe(4,6-diOMe-sal$_2$)$_3$]ClO$_4$·0.5MeOH (4c)**

4,6-Dimethoxysalicylaldehyde (36.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (10 mL), a yellow color was immediately observed. To this solution iron(II) perchlorate hexahydrate (36.3 mg, 0.1 mmol) was added, a deep red color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

**S1.17 Synthesis of [Fe(3-OEt-sal$_2$)$_3$]PF$_6$·EtOH (5a)**

3-Ethoxysalicylaldehyde (33.2 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (10 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and potassium hexafluorophosphate (27.6 mg, 0.15 mmol) was added, a deep red color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

**S1.18 Synthesis of [Fe(3-OEt-sal$_2$)$_3$]BF$_4$·0.32H$_2$O (5b)**

3-Ethoxysalicylaldehyde (33.2 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (10 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep red color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

**S1.19 Synthesis of [Fe(4-Et$_2$N-sal$_2$)$_3$]PF$_6$ (6b)**

4-(Diethylamino)salicylaldehyde (38.6 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and sodium hexafluorophosphate (27.6 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{30}$H$_{46}$N$_6$O$_2$F$_6$PFe, Theory % (Found %): C 49.80 (49.79); H 6.41 (6.45); N 11.62 (11.50).

**S1.20 Synthesis of [Fe(4-Et$_2$N-sal$_2$)$_3$]PF$_6$·0.78MeOH·0.1EtOH (6b·S)**

4-(Diethylamino)salicylaldehyde (38.6 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in ethanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and sodium hexafluorophosphate (27.6 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was refluxed at 110 °C for 3 hours, and subsequently filtered. The solvent was removed by
rotary evaporation. Recrystallisation of the crude solid in the minimum acetonitrile/ethanol (1:1) yielded crystals suitable for SCXRD. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

**S1.21 Synthesis of [Fe^{III}(4-Et$_2$N-sal$_2$323)]OTf (6c)**

4-(Diethylamino)salicylaldehyde (38.6 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and lithium trifluoromethanesulfonate (23.4 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for $C_{31}H_{46}N_6O_5F_3SFe$, Theory % (Found %): C 51.17 (51.07); H 6.37 (6.41); N 11.55 (11.43).

**S1.22 Synthesis of [Fe^{III}(4-Et$_2$N-sal$_2$323)]BF$_4$ (6d)**

4-(Diethylamino)salicylaldehyde (38.6 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for $C_{30}H_{46}N_6O_2F_4Fe$, Theory % (Found %): C 54.15 (54.27); H 6.97 (6.98); N 12.63 (12.56).

**S1.23 Synthesis of [Fe^{III}(4-Et$_2$N-sal$_2$323)]BF$_4$·EtOH (6d·S)**

4-(Diethylamino)salicylaldehyde (38.6 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in ethanol (5 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was refluxed at 110 °C for 3 hours, and subsequently filtered. The solvent was removed by rotary evaporation. Recrystallisation of the crude solid in the minimum acetonitrile/ethanol (1:1) yielded crystals suitable for SCXRD. Elemental analysis, calculated for $C_{32}H_{52}N_6O_3F_4Fe$, Theory % (Found %): C 54.02 (53.90); H 7.37 (7.54); N 11.81 (11.93).

**S1.24 Synthesis of [Fe^{III}(4-Et$_2$N-sal$_2$323)]NO$_3$·CH$_2$Cl$_2$ (6e)**

4-(Diethylamino)salicylaldehyde (193 mg, 1 mmol) and 1,2-bis(3-aminopropylamino)ethane (87 mg, 0.5 mmol) were briefly stirred in acetonitrile (20 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (202 mg, 0.5 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. A crude powder was collected which was recrystallized in dichloromethane. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for $C_{30}H_{46}N_7O_5Fe$, Theory % (Found %): C 56.25 (55.91); H 7.24 (7.54); N 15.31 (14.37).
S1.25 Synthesis of [Fe^{III}(3-Me-sal$_2$323)]ClO$_4$ (7a)

3-Methylsalicylaldehyde (27.2 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) perchlorate hexahydrate (36.3 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.26 Synthesis of [Fe^{III}(3-Me-sal$_2$323)]PF$_6$·0.68H$_2$O (7b)

3-Methylsalicylaldehyde (27.2 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (12.7 mg, 0.1 mmol) and potassium hexafluorophosphate (27.6 mg, 0.15 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. C$_{24}$H$_{33.36}$N$_4$O$_2$F$_{6.68}$PFe, Theory % (Found %): C 46.37 (46.74); H 5.41 (5.66); N 9.01 (8.75).

S1.27 Synthesis of [Fe^{III}(3-Me-sal$_2$323)]BF$_4$ (7c)

3-Methylsalicylaldehyde (27.2 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.28 Synthesis of [Fe^{III}(3-Allyl-sal$_2$323)]NO$_3$-MeCN (8)

3-Allylsalicylaldehyde (32.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 5 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (40.4 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.29 Synthesis of [Fe^{III}(3-Bu-sal$_2$323)]PF$_6$·EtOH (9a)

3-Tert-butyl salicylaldehyde (356 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{31}$H$_{47}$N$_4$O$_{2.5}$F$_3$PFe, Theory % (Found %): C 51.96 (51.23); H 6.61 (6.59); N 7.82 (8.19).
S1.30 Synthesis of [Fe\text{III}(3'-Bu-sal\text{2}323)]BF\text{4} (9b)

3-Tert-butyl salicylaldehyde (356 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (338 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\text{30}H\text{44}N\text{4}O\text{2}F\text{4}BFe, Theory % (Found %): C 55.03; H 5.53; N 7.77.

S1.31 Synthesis of [Fe\text{III}(sal\text{2}323)]Fe\text{Cl}\text{4} (10e)

Salicylaldehyde (244 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.32 Synthesis of [Fe\text{III}(sal\text{3}23)]BF\text{4} (10f)

Salicylaldehyde (24.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (33.8 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

S1.33 Synthesis of [Fe\text{III}(5-Br-sal\text{3}23)]PF\text{6} (11a)

5-Bromosalicylaldehyde (402 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\text{22}H\text{26}N\text{4}O\text{2}F\text{6}PF\text{6}FeBr2, Theory % (Found %): C 36.63; H 3.91; N 7.60.

S1.34 Synthesis of [Fe\text{III}(5-Br-sal\text{3}23)]BF\text{4}·EtOH (11b)

5-Bromosalicylaldehyde (402 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (338 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C\text{24}H\text{32}N\text{4}O\text{3}BF\text{4}FeBr2, Theory % (Found %): C 38.07; H 4.44; N 7.71.
**S1.35 Synthesis of [Fe^{III}(5-Br-sal$_{2}$323)]NO$_{3}$·iPrOH (11c)**

5-Bromosalicylaldehyde (402 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (404 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{25}$H$_{34}$N$_{5}$O$_{6}$FeBr$_{2}$, Theory % (Found %): C 41.92 (41.84); H 4.50 (4.33); N 9.78 (7.90).

**S1.36 Synthesis of [Fe^{III}(3,5-diBr-sal$_{2}$323)]NO$_{3}$·PrOH (12)**

3,5-Dibromosalicylaldehyde (560 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (404 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{25}$H$_{32}$N$_{5}$O$_{6}$FeBr$_{4}$, Theory % (Found %): C 34.36 (33.15); H 3.69 (3.44); N 8.01 (8.02).

**S1.37 Synthesis of [Fe^{III}(3,5-diCl-sal$_{2}$323)]BF$_{4}$·PrOH (13a)**

3,5-Dichlorosalicylaldehyde (382 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (338 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{25}$H$_{32}$N$_{4}$O$_{3}$F$_{4}$Cl$_{4}$Fe, Theory % (Found %): C 41.65 (41.27); H 4.47 (4.54); N 7.79 (7.72).

**S1.38 Synthesis of [Fe^{III}(3,5-diCl-sal$_{2}$323)]PF$_{6}$ (13b)**

3,5-Dichlorosalicylaldehyde (382 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{25}$H$_{32}$N$_{4}$O$_{3}$F$_{6}$Cl$_{4}$Fe, Theory % (Found %): C 36.75 (37.58); H 3.36 (4.47); N 7.79 (9.93).

**S1.39 Synthesis of [Fe^{III}(3,5-diI-sal$_{2}$323)]PF$_{6}$ (14)**

3,5-Diiodosalicylaldehyde (748 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained
through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{22}$H$_{24}$N$_4$O$_2$FePFeI$_4$, Theory % (Found %): C 24.36 (24.54); H 2.23 (2.28); N 5.16 (4.93).

S1.40 Synthesis of [Fe$^{III}$(3-NO$_2$-sal$_2$323)]PF$_6$·MeCN (15a)

3-Nitrosalicylaldehyde (334 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{24}$H$_{29}$N$_7$O$_6$F$_6$PFe, Theory % (Found %): C 40.47 (40.29); H 4.10 (4.06); N 13.76 (13.44).

S1.41 Synthesis of [Fe$^{III}$(3-NO$_2$-sal$_2$323)]NO$_3$ (15b)

3-Nitrosalicylaldehyde (334 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) nitrate nonahydrate (404 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{22}$H$_{26}$N$_7$O$_8$Fe, Theory % (Found %): C 44.91 (44.02); H 4.45 (4.38); N 16.67 (16.75).

S1.42 Synthesis of [Fe$^{III}$(5-NO$_2$-sal$_2$323)]PF$_6$·EtOH (16a)

5-Nitrosalicylaldehyde (334 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(III) chloride (162 mg, 1 mmol) and ammonium hexafluorophosphate (163 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{24}$H$_{32}$BN$_6$O$_7$Fe, Theory % (Found %): C 43.75 (43.60); H 4.89 (4.76); N 12.75 (12.68).

S1.43 Synthesis of [Fe$^{III}$(5-NO$_2$-sal$_2$323)]BF$_4$·EtOH (16b)

5-Nitrosalicylaldehyde (334 mg, 2 mmol) and 1,2-bis(3-aminopropylamino)ethane (174 mg, 1 mmol) were briefly stirred in IMS and acetonitrile (1:1, 20 mL), a yellow color was immediately observed. To this solution iron(II) tetrafluoroborate hexahydrate (338 mg, 1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Elemental analysis, calculated for C$_{24}$H$_{32}$BN$_6$O$_7$F$_4$Fe, Theory % (Found %): C 43.75 (43.60); H 4.89 (4.76); N 12.75 (12.68).

S1.44 Synthesis of [Fe$^{III}$(5-NO$_2$-sal$_2$323)]ClO$_4$·EtOH (16c)

5-Nitrosalicylaldehyde (33.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) perchlorate
hydrate (36.3 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.

**S1.45 Synthesis of [Fe^{III}(3,5-NO_2-sal_2)]ClO_4·EtOH (17)**

3,5-Dinitrosalicylaldehyde (42.4 mg, 0.2 mmol) and 1,2-bis(3-aminopropylamino)ethane (17.4 mg, 0.1 mmol) were briefly stirred in methanol (5 mL), a yellow color was immediately observed. To this solution iron(II) perchlorate hydrate (36.3 mg, 0.1 mmol) was added, a deep purple color was observed. The solution was briefly stirred to dissolve all solids, and subsequently filtered. Crystals were obtained through slow evaporation of solvent over a week. Too few crystals were obtained to carry out elemental analysis on the bulk sample.
# S2 Single Crystal X-ray Diffraction Details

Table S2.1. Crystallographic details for 1 – 17.

| Complex | 1a | 1a | 1aS | 1aS | 1b |
|---------|----|----|-----|-----|----|
| CCDC No. | 2166978 | 2166979 | 2166980 | 2166981 | 2166982 |
| Molecular Formula | C₃₂H₃₂N₄O₄[NO₃]⁻ | C₃₂H₃₂N₄O₄[NO₃]⁻ | C₃₂H₃₂N₄O₄Fe⁺[NO₃]⁻ x 0.75 (C₂H₃N) x 0.25 (C₂H₆O) | C₃₂H₃₂N₄O₄Fe⁺[NO₃]⁻ x 0.73 (C₂H₃N) x 0.27 (C₂H₆O) | C₃₂H₃₂N₄O₄Fe⁺[F₆P]⁻ x 0.45 (H₂O) |
| Mᵣ (g mol⁻¹) | 558.39 | 558.39 | 597.24 | 596.99 | 649.42 |
| T (K) | 100(2) | 293(2) | 100(2) | 293(2) | 100(2) |
| Crystal System | Orthorhombic | Orthorhombic | Monoclinic | Monoclinic | Monoclinic |
| Space Group | P2₁2₁2 (#18) | P2₁2₁2 (#18) | P2₁/n (#14) | P2₁/n (#14) | P2₁/c (#14) |
| a (Å) | 7.5176(4) | 7.6624(2) | 7.50006(6) | 7.60475(5) | 7.99259(9) |
| b (Å) | 12.1717(8) | 12.2069(3) | 17.0390(2) | 17.0965(2) | 20.8108(2) |
| c (Å) | 13.336(1) | 13.5167(4) | 21.7744(2) | 22.0910(2) | 16.0625(2) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| β (°) | 90 | 90 | 138.035(8) | 128.307(6) | 135.990(7) |
| γ (°) | 90 | 90 | 90 | 90 | 90 |
| V (Å³) | 1220.27(14) | 1264.27(6) | 2752.75(5) | 2833.99(5) | 2653.02(5) |
| Z, Z' | 2, 0.5 | 2, 0.5 | 4, 1 | 4, 1 | 4, 1 |
| Radiation Type | Cu Ka | Cu Ka | Cu Kα | Cu Kα | Cu Kα |
| p (mm⁻¹) | 5.437 | 5.428 | 4.873 | 4.734 | 5.894 |
| Crystal Size | 0.080 x 0.050 x 0.020 | 0.086 x 0.036 x 0.031 | 0.295 x 0.120 x 0.110 | 0.162 x 0.127 x 0.111 | 0.295 x 0.162 x 0.043 |
| Reflections Measured, Independent Reflections | 5887, 2536 | 6555, 2628 | 56379, 5796 | 35189, 5944 | 31711, 5554 |
| Rint | 0.0457 | 0.0334 | 0.0382 | 0.0202 | 0.0324 |
| Data / Restraints / Parameters | 2536 / 0 / 184 | 2628 / 0 / 171 | 5796 / 2 / 374 | 5944 / 4 / 374 | 5554 / 0 / 421 |
| GooF on F² | 1.033 | 1.029 | 1.047 | 1.051 | 1.042 |
| Final R Indices [I>2σ(I)] | R₁ = 0.0372, wR₂ = 0.0882 | R₁ = 0.0394, wR₂ = 0.1046 | R₁ = 0.0318, wR₂ = 0.0852 | R₁ = 0.0312, wR₂ = 0.0877 | R₁ = 0.0337, wR₂ = 0.0851 |
| Apmax, Apmin (e Å⁻³) | 0.278, -0.340 | 0.299, -0.339 | 0.832, -0.482 | 0.397, -0.311 | 0.475, -0.502 |
| Flack Parameter | 0.511(8)° | 0.502(9)° | -- | -- | -- |
| Complex | 1c | 1d | 1d | 1e | 1f |
|---------|----|----|----|----|----|
| CCDC    | 2166983 | 2166984 | 2166985 | 2166986 | 2166987 |
| Molecular Formula | $\text{[C}_{24}\text{H}_{32}\text{N}_{4}\text{O}_{6}\text{Fe}]^\text{+}$ | $\text{[C}_{24}\text{H}_{32}\text{N}_{4}\text{O}_{6}\text{Fe}]^\text{-}$ | $\text{[C}_{24}\text{H}_{32}\text{N}_{4}\text{O}_{6}\text{Fe}]^\text{-}$ | $\text{[C}_{24}\text{H}_{32}\text{N}_{4}\text{O}_{6}\text{Fe}]^\text{-}$ | $\text{[C}_{24}\text{H}_{32}\text{N}_{4}\text{O}_{6}\text{Fe}]^\text{-}$ |
| $M_r$ (g mol$^{-1}$) | 650.23 | 595.83 | 595.83 | 649.42 | 737.63 |
| $T$ (K) | 100(2) | 100(2) | 200(2) | 293(2) | 100(2) |
| Crystal System | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space Group | $P2_1/c$ (#14) | $P2_1/c$ (#14) | $P2_1/c$ (#14) | $P2_1/c$ (#14) | $P2_1/c$ (#14) |
| $a$ (Å) | 8.05017(5) | 7.39852(9) | 7.47123(5) | 7.4540(9) | 8.13318(5) |
| $b$ (Å) | 20.9777(2) | 16.1939(2) | 17.5694(2) | 17.537(2) | 21.0366(2) |
| $c$ (Å) | 16.2883(1) | 21.4358(3) | 20.5528(2) | 20.521(3) | 16.0425(1) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 97.8371(6) | 95.064(1) | 96.1464(6) | 96.344(2) | 96.3820(5) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 2724.98(4) | 2558.22(6) | 2682.35(4) | 1640.96(2) | 2727.77(4) |
| $Z, Z'$ | 4, 1 | 4, 1 | 4, 1 | 4, 1 | 4, 1 |
| Radiation Type | Cu $K\alpha$ | Cu $K\alpha$ | Cu $K\alpha$ | Mo $K\alpha$ | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 5.818 | 6.183 | 5.897 | 0.631 | 12.856 |
| Crystal Size | 0.193 × 0.118 × 0.071 | 0.207 × 0.104 × 0.045 | 0.252 × 0.149 × 0.114 | 0.40 × 0.10 × 0.10 | 0.119 × 0.085 × 0.028 |
| Reflections Measured, Independent Reflections | 55717, 5729 | 26655, 5372 | 54881, 5654 | 14397, 3260 | 37818, 5744 |
| $R_{int}$ | 0.0543 | 0.0354 | 0.0309 | 0.0347 | 0.0327 |
| Data / Restraints / Parameters | 5729 / 0 / 394 | 5372 / 0 / 345 | 5654 / 0 / 364 | 3260 / 0 / 354 | 5744 / 0 / 404 |
| GooF on $F^2$ | 1.066 | 1.037 | 1.075 | 1.031 | 1.040 |
| Final $R$ Indices / $I$>2$s(I)$ | $R_1 = 0.0347$, $wR_2 = 0.0947$ | $R_1 = 0.0281$, $wR_2 = 0.0728$ | $R_1 = 0.0344$, $wR_2 = 0.0942$ | $R_1 = 0.0444$, $wR_2 = 0.1020$ | $R_1 = 0.0243$, $wR_2 = 0.0588$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.707, -0.654 | 0.284, -0.433 | 0.607, -0.435 | 0.469, -0.397 | 0.562, -1.474 |
| Complex | 1g | 1h | 2a | 2a | 2b |
|---------|----|----|----|----|----|
| CCDC    | 2166988 | 2166989 | 2166990 | 2166991 | 2166992 |
| Molecular Formula | [C$_{24}$H$_{32}$N$_{4}$O$_{4}$Fe]$^{+}$[I$_{3}$$^{-}$] x C$_{2}$H$_{4}$O x 0.25 (H$_{2}$O)$_{p}$ | [C$_{24}$H$_{32}$N$_{4}$O$_{4}$Fe]$^{+}$[Cl$^{-}$] | [C$_{24}$H$_{32}$N$_{4}$O$_{4}$Fe]$^{+}$[N O$_{3}$$^{-}$] | [C$_{24}$H$_{32}$N$_{4}$O$_{4}$Fe]$^{+}$[N O$_{3}$$^{-}$] | [C$_{24}$H$_{32}$N$_{4}$O$_{4}$Fe]$^{+}$[B F$_{4}$$^{-}$] x H$_{2}$O |
| $M_r$ (g mol$^{-1}$) | 877.08 | 582.41 | 558.39 | 558.39 | 601.21 |
| $T$ (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal System | Monoclinic | Monoclinic | Orthorhombic | Orthorhombic | Monoclinic |
| Space Group | P2$_1$/c (#14) | P2$_1$/c (#14) | Pccn (#56) | Pccn (#56) | P2$_1$/c (#14) |
| a (Å) | 18.8904(5) | 7.3320(1) | 8.2203(2) | 7.5246(1) | 7.6802(7) |
| b (Å) | 8.0120(1) | 16.5758(2) | 17.9327(3) | 18.3978(2) | 20.4717(19) |
| c (Å) | 20.1289(4) | 22.3775(3) | 17.1866(3) | 19.1075(3) | 16.5641(15) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 108.588(3) | 90.404(2) | 90 | 90 | 99.897(2) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 2887.59(11) | 2719.55(6) | 2533.51(9) | 2645.17(6) | 2565.64(9) |
| $Z, Z'$ | 4, 1 | 4.1 | 4, 0.5 | 4, 0.5 | 4, 1 |
| Radiation Type | Mo Ka | Cu Ka | Cu K$\alpha$ | Cu K$\alpha$ | Mo Ka |
| $\mu$ (mm$^{-1}$) | 3.766 | 5.720 | 5.237 | 5.016 | 0.661 |
| Crystal Size | 0.143 x 0.060 x 0.042 | 0.321 x 0.048 x 0.036 | 0.272 x 0.050 x 0.042 | 0.158 x 0.103 x 0.064 | 1.00 x 0.60 x 0.50 |
| Reflections Measured, Independent Reflections | 57637, 5893 | 27639, 5665 | 24801, 2660 | 12686, 2772 | 29091, 7471 |
| $R_{int}$ | 0.0779 | 0.0428 | 0.0980 | 0.0295 | 0.0399 |
| Data / Restraints / Parameters | 5893 / 0 / 327 | 5665 / 0 / 309 | 2660 / 0 / 170 | 2772 / 0 / 171 | 7471 / 0 / 488 |
| Goof on F$^2$ | 1.093 | 1.049 | 1.070 | 1.038 | 1.035 |
| Final R Indices [I>2σ(I)] | $R_I = 0.0391$, wR$_2 = 0.0996$ | $R_I = 0.0325$, wR$_2 = 0.0849$ | $R_I = 0.0636$, wR$_2 = 0.1564$ | $R_I = 0.0316$, wR$_2 = 0.0877$ | $R_I = 0.0358$, wR$_2 = 0.0853$ |
| $\Delta$p$_{max}$, $\Delta$p$_{min}$ (e Å$^{-3}$) | 1.981, -1.475 | 0.479, -0.583 | 1.368, -1.265 | 0.265, -0.223 | 0.488, -0.471 |
| Complex | 2c | 3a | 3a | 3b | 4a |
|---------|----|----|----|----|----|
| CCDC    | 2166993 | 2166994 | 2166995 | 2166996 | 2166997 |
| Molecular Formula | [C$_{24}$H$_{32}$N$_4$O$_4$Fe]·[F$_6$P]·xH$_2$O | [C$_{24}$H$_{32}$N$_4$O$_4$Fe]·[N O$_3$]· | [C$_{24}$H$_{32}$N$_4$O$_4$Fe]·[N O$_3$]· | [C$_{26}$H$_{36}$N$_4$O$_6$Fe]·[N O$_3$]··x(H$_2$O) | [C$_{26}$H$_{38}$N$_4$O$_6$Fe]·[N O$_3$]··x(H$_2$O) |
| $M_r$ (g mol$^{-1}$) | 659.37 | 558.39 | 558.39 | 583.20 | 650.49 |
| $T$ (K) | 293(2) | 100(2) | 293(2) | 100(2) | 100(2) K |
| Crystal System | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space Group | P2$_1$/c (#14) | P2/c (#13) | P2/c (#13) | P2/c (#13) | P2$_1$/c (#14) |
| $a$ (Å) | 7.9224(6) | 17.2266(3) | 17.44550(10) | 17.5340(15) | 7.3600(2) |
| $b$ (Å) | 20.7034(15) | 8.2713(2) | 8.33440(10) | 8.408(7) | 25.3852(5) |
| $c$ (Å) | 17.0178(12) | 17.9701(4) | 17.91840(10) | 17.3701(15) | 15.8505(4) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 101.514(1) | 101.129(2) | 100.5440(10) | 96.424(2) | 102.530(2) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 2735.1(3) | 2512.34(9) | 2561.30(4) | 2544.4(4) | 2890.90(12) |
| $Z, Z'$ | 4, 1 | 4, 1 | 4, 1 | 4, 1 | 4, 1 |
| Radiation Type | Mo Kα | Mo Kα | Cu Kα | Mo Kα | Cu Kα |
| $\mu$ (mm$^{-1}$) | 0.694 | 0.655 | 5.180 | 0.661 | 4.754 |
| Crystal Size | 0.60 × 0.50 × 0.40 | 0.237 × 0.149 × 0.111 | 0.214 × 0.077 × 0.052 | 0.80 × 0.20 × 0.20 | 0.090 × 0.060 × 0.040 |
| Reflections Measured, Independent Reflections | 44903, 5975 | 36039, 8644 | 51335, 5380 | 16401, 6169 | 32913, 6025 |
| F$_{int}$ | 0.0234 | 0.0344 | 0.0196 | 0.0271 | 0.0734 |
| Data / Restraints / Parameters | 5975 / 1 / 543 | 8644 / 0 / 337 | 5380 / 0 / 337 | 6169 / 0 / 472 | 6025 / 0 / 374 |
| Goof on F$^2$ | 1.059 | 1.072 | 1.057 | 1.057 | 1.045 |
| Final $R$ Indices | $R_f = 0.0336$, w$R_2 = 0.0868$ | $R_f = 0.0372$, w$R_2 = 0.0821$ | $R_f = 0.0286$, w$R_2 = 0.0827$ | $R_f = 0.0422$, w$R_2 = 0.1005$ | $R_f = 0.0515$, w$R_2 = 0.1181$ |
| $\Delta$min, $\Delta$max (e Å$^{-3}$) | 0.397, -0.171 | 0.524, -0.495 | 0.29, -0.31 | 0.728, -0.319 | 0.658, -0.583 |
| Complex | 4a | 4b | 4b | 4c | 5a |
|----------|----|----|----|----|----|
| CCDC     | 2166998 | 2167009 | 2167010 | 2167011 | 2167012 |
| Molecular Formula | [C\(_{26}\)H\(_{36}\)N\(_4\)O\(_6\)Fe]\(^+\)\([N O\(_3\)]\)\(^-\) \times C\(_4\)H\(_4\)O\(_2\)\) | [C\(_{26}\)H\(_{36}\)N\(_4\)O\(_6\)Fe]\(^+\)\([B F\(_4\)]\)\(^-\) \times C\(_4\)H\(_4\)O\(_2\)\) | [C\(_{26}\)H\(_{36}\)N\(_4\)O\(_6\)Fe]\(^+\)\([B F\(_4\)]\)\(^-\) \times C\(_4\)H\(_4\)O\(_2\)\) | [C\(_{26}\)H\(_{36}\)N\(_4\)O\(_6\)Fe]\(^+\)\([O_4\)Cl\)]\(^-\) \times C\(_4\)H\(_4\)O\(_2\)\) | [C\(_{26}\)H\(_{36}\)N\(_4\)O\(_6\)Fe]\(^+\)\([F_6P\)]\(^-\) \times C\(_2\) |
| \(M_r\) (g mol\(^{-1}\)) | 638.47 | 659.27 | 659.27 | 715.47 | 715.47 |
| \(T\) (K) | 298(2) K | 100(2) K | 100(2) K | 100(2) K | 100(2) K |
| Crystal System | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space Group | P2\(_1\)/c (#14) | P2\(_1\)/n (#14) | P2\(_1\)/n (#14) | P2\(_1\)/n (#14) | P2\(_1\)/n (#14) |
| \(a\) (Å) | 7.4389(3) | 7.3608(1) | 7.4703(2) | 7.3704(1) | 20.0400(2) |
| \(b\) (Å) | 25.334(1) | 25.5467(5) | 25.783(1) | 25.957(1) | 7.70456(7) |
| \(c\) (Å) | 16.0847(9) | 15.9111(4) | 16.1483(5) | 15.8498(7) | 20.7074(2) |
| \(\alpha\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(\beta\) (°) | 102.361(6) | 103.313(2) | 103.353(3) | 102.906(4) | 96.5038(8) |
| \(\gamma\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(V\) (Å\(^3\)) | 2961.0(2) | 2911.58(10) | 3026.19(17) | 2955.7(2) | 3176.63(5) |
| \(Z, Z'\) | 4, 4 | 4, 1 | 4 | 1 | 4, 1 |
| Radiation Type | Cu Ka | Cu Ka | Cu Ka | Cu Ka | Cu Ka |
| \(\mu\) (mm\(^{-1}\)) | 4.621 | 4.823 | 4.641 | 5.485 | 4.990 |
| Crystal Size | 0.090 × 0.060 × 0.040 | 0.180 × 0.040 × 0.020 | 0.180 × 0.040 × 0.020 | 0.150 × 0.050 × 0.020 | 0.256 × 0.204 × 0.185 |
| Reflections Measured, Independent Reflections | 14246, 4533 | 23209, 6013 | 28967, 5205 | 20771, 6204 | 37576, 6685 |
| \(R_{int}\) | 0.0493 | 0.0462 | 0.0490 | 0.0735 | 0.0295 |
| Data / Restraints / Parameters | 4533 / 0 / 374 | 6013 / 0 / 397 | 5205 / 28 / 407 | 6204 / 0 / 382 | 6685 / 0 / 407 |
| GoF on \(F^2\) | 1.020 | 1.058 | 1.039 | 1.052 | 1.082 |
| Final \(R\) Indices \([I>2\sigma(I)]\) | \(R_I = 0.0557, wR_I = 0.1370\) | \(R_I = 0.0479, wR_I = 0.1287\) | \(R_I = 0.0596, wR_I = 0.1659\) | \(R_I = 0.0758, wR_I = 0.2043\) | \(R_I = 0.0720, wR_I = 0.1962\) |
| \(\Delta \rho_{max}, \Delta \rho_{min} \) (e Å\(^{-3}\)) | 0.521, -0.372 | 0.729, -0.846 | 0.435, -0.550 | 0.871, -0.643 | 1.623, -0.850 |
| Complex | 5b | 6b | 6b-S | 6c | 6c |
|---------|----|----|------|----|----|
| CCDC    | 2167013 | 2044253 | 2167014 | 2044252 | 2167015 |
| Molecular Formula | [C$_{26}$H$_{36}$N$_4$O$_4$Fe]·[BF$_4$]·x(H$_2$O) | 0.315 (H$_2$O) | [C$_{30}$H$_{46}$N$_6$O$_2$Fe]·[BF$_4$]·y(P$_6$F$_6$) | 0.78(C$_2$H$_2$N) x 0.1(C$_2$H$_6$O) | [C$_{30}$H$_{46}$N$_6$O$_2$Fe]·[BF$_4$]·y(P$_6$F$_6$) | 0.78(C$_2$H$_2$N) x 0.1(C$_2$H$_6$O) |
| $M_r$ (g mol$^{-1}$) | 616.92 | 723.55 | 759.94 | 727.65 | 727.65 |
| $T$ (K) | 100(2) | 100(2) | 100(2) | 100(2) | 293(2) |
| Crystal System | Monoclinic | Triclinic | Triclinic | Triclinic | Triclinic |
| Space Group | Pn (#7) | P-1 (#2) | P-1 (#2) | P-1 (#2) | P-1 (#2) |
| $a$ (Å) | 7.46133(5) | 7.80570(7) | 13.0164(2) | 14.6609(2) | 14.0529(1) |
| $b$ (Å) | 11.00091(7) | 13.8253(2) | 16.1629(2) | 14.6609(2) | 14.0529(1) |
| $c$ (Å) | 17.2247(1) | 16.6288(2) | 17.6941(2) | 16.2660(2) | 17.4409(1) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 102.4789(6) | 85.2660(7) | 80.0716(8) | 99.1600(7) | 82.0484(7) |
| $\gamma$ (°) | 90 | 88.3907(7) | 89.3125(7) | 91.9331(7) | 89.7708(7) |
| $V$ (Å$^3$) | 1380.427(5) | 1664.92(4) | 3587.04(8) | 1690.88(3) | 1775.88(2) |
| $Z, Z'$ | 2, 1 | 2, 1 | 2, 1 | 2, 1 | 2, 1 |
| Radiation Type | Cu Ka | Mo Ka | Cu Ka | Cu Ka | Cu Ka |
| $\mu$ (mm$^{-1}$) | 4.984 | 0.572 | 4.412 | 4.712 | 4.487 |
| Crystal Size | 0.216 x 0.157 x 0.073 | 0.327 x 0.220 x 0.151 | 0.209 x 0.110 x 0.028 | 0.344 x 0.093 x 0.069 | 0.328 x 0.103 x 0.066 |
| Reflections Measured, Independent Reflections | 27616, 5557 | 106699, 11880 | 91164, 15049 | 53375, 7090 | 69770, 7455 |
| $R_{int}$ | 0.0191 | 0.0338 | 0.0485 | 0.0370 | 0.0418 |
| Data / Restraints / Parameters | 5557 / 2 / 376 | 11880 / 0 / 419 | 15049 / 0 / 907 | 7090 / 0 / 428 | 7455 / 0 / 428 |
| Goof on $F^2$ | 1.048 | 1.071 | 1.067 | 1.080 | 1.102 |
| Final $R$ Indices [I>2σ(I)] | $R_I = 0.0208$, w$R_2 = 0.0548$ | $R_I = 0.0316$, w$R_2 = 0.0767$ | $R_I = 0.0466$, w$R_2 = 0.1277$ | $R_I = 0.0273$, w$R_2 = 0.0735$ | $R_I = 0.0391$, w$R_2 = 0.1132$ |
| Δρ$_{max}$/Δρ$_{min}$ (e Å$^{-3}$) | 0.166, -0.253 | 0.525, -0.485 | 0.975, -0.651 | 0.423, -0.391 | 0.444, -0.417 |
| Flack Parameter | -0.0095(11) | --- | --- | --- | --- |
| Complex | 6d | 6d-S | 6e | 7a | 7b |
|---------|----|------|----|----|----|
| CCDC    | 2044257 | 2167016 | 2167017 | 2167018 | 2167019 |
| Molecular Formula | [C_{30}H_{46}N_{6}O_{2}Fe]\cdot[BF_4]- | [C_{30}H_{46}N_{6}O_{2}Fe]\cdot[BF_4]- x C_{2}H_{4}O\cdot | [C_{30}H_{46}N_{6}O_{2}Fe]\cdot[N O_{3}]- x C H_{2}Cl_{2} | [C_{24}H_{32}N_{4}O_{2}Fe]\cdot[BF_4]- | [C_{24}H_{32}N_{4}O_{2}Fe]\cdot[BF_4]- x 0.68 (H_{2}O) |
| M_r (g mol^{-1}) | 665.39 | 711.45 | 725.51 | 563.83 | 621.69 |
| T (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal System | Monoclinic | Orthorhombic | Orthorhombic | Orthorhombic | Monoclinic |
| Space Group | P2_{1}/n (#14) | P2_{1}2_{1}2_{1} (#19) | P2_{1}2_{1}2_{1} (#19) | P2_{1}2_{1}2_{1} (#19) | C2/c (#14) |
| a (Å) | 7.6682(1) | 7.6914(2) | 7.65722(8) | 8.42810(9) | 13.3659(2) |
| b (Å) | 19.6632(4) | 19.7983(4) | 19.4470(2) | 16.5915(2) | 11.2845(2) |
| c (Å) | 21.3813(4) | 23.0219(4) | 23.1185(3) | 17.8926(2) | 17.3363(2) |
| a (°) | 90 | 90 | 90 | 90 | 90 |
| β (°) | 91.087(2) | 90 | 90 | 90 | 100.708(1) |
| γ (°) | 90 | 90 | 90 | 90 | 90 |
| V (Å^3) | 3223.32(10) | 3505.70(13) | 3442.57(7) | 2502.01(5) | 2569.26(7) |
| Z, Z' | 4, 1 | 4, 1 | 4, 1 | 4 | 4, 0.5 |
| Radiation Type | Cu Kα | Cu Kα | Cu Kα | Cu Kα | Cu Kα |
| μ (mm^{-1}) | 4.2470 | 3.981 | 5.348 | 6.225 | 6.003 |
| Crystal Size | 0.248 × 0.073 × 0.050 | 0.178 × 0.039 × 0.023 | 0.305 × 0.047 × 0.038 | 0.144 × 0.037 × 0.023 | 0.204 × 0.188 × 0.084 |
| Reflections Measured, Independent Reflections | 35206, 6776 | 17939, 7309 | 18331, 7175 | 26098, 5239 | 12503, 2674 |
| R_{int} | 0.0627 | 0.0616 | 0.0346 | 0.0705 | 0.0191 |
| Data / Restraints / Parameters | 6776 / 0 / 401 | 7309 / 0 / 401 | 7175 / 0 / 425 | 5239 / 0 / 327 | 2674 / 0 / 192 |
| GoF on F^2 | 1.040 | 0.967 | 1.051 | 1.019 | 1.124 |
| Final R Indices [I>2σ(I)] | R_I = 0.0487, wR_I = 0.1254 | R_I = 0.0381, wR_I = 0.0743 | R_I = 0.0608, wR_I = 0.1709 | R_I = 0.0339, wR_I = 0.0778 | R_I = 0.0259, wR_I = 0.0718 |
| Δρ_{max}, Δρ_{min} (e Å^{-3}) | 1.077, -0.659 | 0.246, -0.272 | 1.016, -1.380 | 0.264, -0.289 | 0.351, -0.448 |
| Flack Parameter | --- | -0.006(3) | 0.212(7)\* | -0.023(3) | --- |
| Complex | 7c | 8 | 9a | 9b | 10e |
|---------|----|---|----|----|-----|
| CCDC    | 2167020 | 2167021 | 2167022 | 2167023 | 2167024 |
| Molecular Formula | [C_{24}H_{32}N_4O_2Fe]([BF_4]) | [C_{30}H_{44}N_4O_2Fe]([NO_3])[F_6P]_2 | [C_{30}H_{44}N_4O_2Fe]([BF_4]) | [C_{22}H_{30}N_4O_2Fe]([Cl_4Fe]) |
| $M_r$ (g mol$^{-1}$) | 551.19 | 619.52 | 1433.09 | 635.35 | 633.98 |
| $T$ (K) | 100(2) | 100(2) | 293(2) | 100(2) | 100(2) |
| Crystalline System | Orthorhombic | Monoclinic | Monoclinic | Tetragonal | Orthorhombic |
| Space Group | P2_12_1_2 (#19) | P2_1/c (#14) | P2_1/c (#14) | P4_2_2_2 (#95) | P2_12_1_2 (#19) |
| $a$ (Å) | 8.2990(1) | 7.90357(9) | 11.1204(9) | 8.7437(16) | 8.7437(16) |
| $b$ (Å) | 16.6365(2) | 17.0622(2) | 34.653(3) | 17.4070(3) | 17.4070(3) |
| $c$ (Å) | 17.9173(2) | 22.6549(3) | 17.6469(15) | 42.142(15) | 19.7425(3) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 96.780(1) | 103.925(2) | 90 | 90 |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 2473.78(5) | 3033.70(6) | 6600.4(10) | 3221.8(16) | 2647.95(7) |
| $Z, Z'$ | 4, 1 | 4, 1 | 4, 2 | 4, 0.5 | 4, 1 |
| Radiation Type | Cu Ka | Mo Ka | Mo Ka | Mo Ka | Mo Ka |
| $\mu$ (mm$^{-1}$) | 5.419 | 0.546 | 0.576 | 0.524 | 1.527 |
| Crystal Size | 0.515 x 0.046 x 0.039 | 0.284 x 0.191 x 0.069 | 0.80 x 0.30 x 0.20 | 0.50 x 0.50 x 0.40 | 0.285 x 0.111 x 0.075 |
| Reflections Measured, Independent Reflections | 25661, 5188 | 52588, 7801 | 10341, 10341 | 17421, 3800 | 18710, 6338 |
| $R_{int}$ | 0.0578 | 0.0259 | 0.0481 | 0.0625 | 0.0260 |
| Data / Restraints / Parameters | 5188 / 0 / 335 | 7801 / 0 / 390 | 10341 / 0 / 855 | 3800 / 0 / 195 | 6338 / 0 / 312 |
| Goof on $F^2$ | 1.014 | 1.051 | 1.091 | 1.166 | 1.091 |
| Final $R$ Indices [$I>2\sigma(I)$] | $R_f = 0.0315, wR_f = 0.0775$ | $R_f = 0.0458, wR_f = 0.1291$ | $R_f = 0.0487, wR_f = 0.1094$ | $R_f = 0.0839, wR_f = 0.1875$ | $R_f = 0.0295, wR_f = 0.0645$ |
| $\Delta P_{max}, \Delta P_{min}$ (e Å$^{-3}$) | 0.267, -0.475 | 0.496, -0.703 | 0.606, -0.499 | 0.67, -1.08 | 0.648, -0.458 |
| Flack Parameter | -0.017(2) | --- | --- | 0.44(6)$^a$ | -0.017(12)$^a$ |
| Complex | 10f | 11a | 11b | 11c | 12 |
|---------|-----|-----|-----|-----|----|
| CCDC    | 2167025 | 2167026 | 2167027 | 2167028 | 2166999 |
| Molecular Formula | [C\textsubscript{22}H\textsubscript{28}N\textsubscript{4}O\textsubscript{2}Fe\textsubscript{2}]\textsuperscript{+}B\textsubscript{F}_4\textsuperscript{-} | [C\textsubscript{22}H\textsubscript{28}N\textsubscript{4}O\textsubscript{2}FeBr\textsubscript{2}]\textsuperscript{+}Fe\textsubscript{2}P\textsuperscript{-} | [C\textsubscript{22}H\textsubscript{28}N\textsubscript{4}O\textsubscript{2}FeBr\textsubscript{2}]\textsuperscript{+}N\textsubscript{O}\textsubscript{3}\textsuperscript{-} | [C\textsubscript{22}H\textsubscript{28}N\textsubscript{4}O\textsubscript{2}FeBr\textsubscript{2}]\textsuperscript{+}N\textsubscript{O}\textsubscript{3}\textsuperscript{-} | [C\textsubscript{22}H\textsubscript{28}N\textsubscript{4}O\textsubscript{2}FeBr\textsubscript{2}]\textsuperscript{+}N\textsubscript{O}\textsubscript{3}\textsuperscript{-} |
| \(M\) (g mol\(^{-1}\)) | 523.14 | 739.11 | 727.02 | 716.24 | 874.05 |
| \(T\) (K) | 100(2) | 293(2) | 293(2) | 100(2) | 100(2) |
| Crystal System | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space Group | P\textsubscript{2}1/c (#14) | P\textsubscript{2}1 (#4) | P\textsubscript{1} (#2) | P\textsubscript{2}1/n (#14) | P\textsubscript{2}1/n (#14) |
| \(a\) (Å) | 7.4795(2) | 7.889(4) | 8.5033(6) | 18.7006(18) | 10.6549(13) |
| \(b\) (Å) | 15.2664(4) | 17.883(9) | 9.8037(7) | 8.0056(8) | 14.3738(17) |
| \(c\) (Å) | 20.2861(6) | 9.483(5) | 17.5760(13) | 38.606(4) | 20.851(3) |
| \(\alpha\) (°) | 90 | 90 | 84.3930(10) | 90 | 90 |
| \(\beta\) (°) | 93.155(3) | 92.588(8) | 81.8850(10) | 96.466(2) | 103.324(2) |
| \(\gamma\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(V\) (Å\(^3\)) | 2312.86(11) | 1336.6(12) | 1431.44(18) | 5742.9(10) | 3107.4(6) |
| \(Z, Z'\) | 4 | 2.1 | 2.1 | 4.2 | 4.1 |
| Radiation Type | Mo Ka | Mo Ka | Mo Ka | Mo Ka | Mo Ka |
| \(\mu\) (mm\(^{-1}\)) | 0.712 | 3.684 | 3.378 | 3.356 | 5.676 |
| Crystal Size | 0.291 x 0.188 x 0.177 | 0.50 x 0.30 x 0.20 | 0.50 x 0.30 x 0.10 | 0.80 x 0.80 x 0.30 | 0.60 x 0.50 x 0.40 |
| Reflections Measured, Independent Reflections | 25697, 5944 | 22230, 6194 | 30801, 7599 | 104961, 13870 | 27008, 6785 |
| \(R_{int}\) | 0.0323 | 0.0222 | 0.0244 | 0.0599 | 0.0742 |
| Data / Restraints / Parameters | 5944 / 0 / 324 | 6194 / 1 / 344 | 7599 / 0 / 362 | 13870 / 0 / 731 | 6785 / 0 / 391 |
| GooF on \(F^2\) | 1.054 | 1.040 | 1.032 | 1.103 | 1.029 |
| Final \(R\) Indices \([I \geq 2\sigma(I)]\) | \(R_I = 0.0330, wR_2 = 0.0767\) | \(R_I = 0.0329, wR_2 = 0.0854\) | \(R_I = 0.0387, wR_2 = 0.1041\) | \(R_I = 0.0409, wR_2 = 0.0960\) | \(R_I = 0.0447, wR_2 = 0.1025\) |
| \(\Delta\rho_{max}, \Delta\rho_{min}\) (e Å\(^{-3}\)) | 0.387, -0.496 | 0.820, -0.302 | 0.941, -0.639 | 1.180, -0.899 | 1.270, -1.027 |
| Flack Parameter | --- | 0.497(6)* | --- | --- | --- |
| Complex   | 13a  | 13b  | 14   | 15a   | 15b   |
|-----------|------|------|------|-------|-------|
| CCDC      | 2167000 | 2167001 | 2167002 | 2167003 | 2167004 |
| Molecular Formula | $[\text{C}_{32} \text{H}_{30} \text{N}_4 \text{O}_2 \text{Cl}_4 \text{Fe}^2]^+ \cdot [\text{B} \text{F}_4]^-$ | $[\text{C}_{32} \text{H}_{30} \text{N}_4 \text{O}_2 \text{Cl}_4 \text{Fe}^2]^+ \cdot [\text{F}_6 \text{P}_3]^-$ | $[\text{C}_{32} \text{H}_{30} \text{N}_4 \text{O}_2 \text{Cl}_4 \text{Fe}^2]^+ \cdot [\text{F}_6 \text{P}_3]^-$ | $[\text{C}_{22} \text{H}_{26} \text{N}_6 \text{O}_6 \text{Fe}]^+ \cdot [\text{B} \text{F}_4]^-$ | $[\text{C}_{22} \text{H}_{26} \text{N}_6 \text{O}_6 \text{Fe}]^+ \cdot [\text{F}_6 \text{P}_3]^-$ |
| $M_r$ (g mol$^{-1}$) | 721.01 | 719.07 | 1084.87 | 712.36 | 588.35 |
| $T$ (K) | 293(2) | 100(2) | 100(2) | 293(2) | 100(2) |
| Crystal System | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space Group | P2/n (#13) | P2/n (#14) | P21/c (#14) | P21/n (#14) | Cc (#9) |
| $a$ (Å) | 17.633(4) | 10.8760(8) | 9.0211(7) | 8.8737(7) | 10.3078(14) |
| $b$ (Å) | 8.4837(17) | 18.6961(13) | 17.5555(14) | 13.9089(11) | 12.9869(17) |
| $c$ (Å) | 21.240(4) | 13.6869(9) | 18.4041(15) | 24.3218(19) | 17.856(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 96.596(4) | 95.7120(10) | 96.692(2) | 93.6640(10) | 99.035(2) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 3156.2(11) | 2769.3(3) | 2894.8(4) | 2995.7(4) | 2360.7(5) |
| $Z, Z'$ | 4, 1 | 4, 1 | 4, 1 | 4, 1 | 4, 1 |
| Radiation Type | Mo Ka | Mo Ka | Mo Ka | Mo Ka | Mo Ka |
| $\mu$ (mm$^{-1}$) | 0.874 | 1.059 | 4.911 | 2.995(74) | 2.3607(5) |
| Crystal Size | 1.00 x 0.50 x 0.30 | 0.60 x 0.50 x 0.02 | 0.30 x 0.10 x 0.03 | 0.60 x 0.30 x 0.03 | 0.50 x 0.40 x 0.02 |
| Reflections Measured, Independent Reflections | 56846, 6890 | 62599, 8081 | 64939, 8443 | 49140, 6531 | 10803, 5513 |
| $R_{int}$ | 0.0204 | 0.0325 | 0.0335 | 0.0238 | 0.0324 |
| Data / Restraints / Parameters | 6890 / 0 / 479 | 8081 / 0 / 457 | 8443 / 0 / 361 | 6531 / 0 / 440 | 5513 / 2 / 352 |
| Goof on F$^2$ | 1.034 | 1.058 | 1.114 | 1.036 | 1.016 |
| Final R Indices [I>2σ(I)] | $R_I = 0.0402$, $wR_2 = 0.1055$ | $R_I = 0.0413$, $wR_2 = 0.1008$ | $R_I = 0.0332$, $wR_2 = 0.0803$ | $R_I = 0.0465$, $wR_2 = 0.1237$ | $R_I = 0.0404$, $wR_2 = 0.0836$ |
| $\Delta \rho_{max}$ / $\Delta \rho_{min}$ (e Å$^{-3}$) | 0.472, -0.367 | 1.421, -0.647 | 2.429, -0.855 | 0.547, -0.398 | 0.749, -0.324 |
| Flack Parameter | --- | --- | --- | --- | 0.015(14) |
The structure was refined as a two-component inversion twin. The solvent could not be modelled in terms of atomic sites. PLATON SQUEEZE was used to compensate for the spread electron density. The hydrogen atoms of the water molecules could not be detected.
### S2.2 Bond Lengths and Distortion Parameters

Table S2.2. Summary of bond lengths and distortion parameters for 1 – 17.

| Complex | 1a | 1a·S | 1b | 1c | 1d | 1e | 1f | 1g | 1h |
|---------|----|------|----|----|----|----|----|----|----|
| Temperature (K) | 100 | 293 | 100 | 293 | 100 | 100 | 200 | 293 | 100 |

**Bond Lengths (Å)**

| | Fe–Ophen | Fe–Nimin | Fe–Namine |
|---|---|---|---|
| Fe–Ophen | 1.908(2) | 1.923(3) | 1.8785(11) | 1.8768(10) | 1.878(1) | 1.879(1) | 1.881(1) | 1.8748(12) | 1.875(2) | 1.874(1) | 1.877(3) | 1.878(11) |
| Fe–Nimin | 1.982(2) | 2.048(4) | 1.9514(12) | 1.9487(12) | 1.958(2) | 1.961(2) | 1.956(1) | 1.9568(16) | 1.950(3) | 1.947(2) | 1.945(4) | 1.9567(14) |
| Fe–Namine | 2.051(3) | 2.102(4) | 2.0154(12) | 2.0166(12) | 2.020(1) | 2.025(1) | 2.023(1) | 2.0221(15) | 2.017(3) | 2.022(2) | 2.023(4) | 2.0142(13) |

**Distortion Parameters (°)**

| | Σ | Θ | α | τ |
|---|---|---|---|---|
| 1a | 34.26 | 52.06 | 24.13 | 25.22 | 25.78 | 25.63 | 21.83 | 27.34 | 26.62 | 27.79 | 25.33 | 29.23 |
| 1a·S | 127.29 | 200.78 | 58.94 | 63.53 | 71.98 | 68.02 | 59.15 | 73.46 | 72.86 | 71.75 | 58.11 | 77.52 |
| 1b | 49.39 | 50.93 | 44.29 | 45.89 | 45.55 | 39.50 | 40.91 | 41.24 | 40.89 | 41.92 | 43.77 | 40.73 |
| 1c | 30.80 | 30.02 | 26.04 | 25.17 | 31.78 | 32.27 | 29.08 | 29.35 | 29.19 | 30.74 | 25.25 | 28.61 |
| 1d | 26.84 | 26.10 | 26.88 | 26.13 | 27.39 | 29.28 | 30.21 | 26.13 | 25.44 | 29.24 |
| Complex | 2a   | 2b   | 2c   | 2d   | 2e   | 3a   | 3b   |
|---------|------|------|------|------|------|------|------|
| Temperature (K) | 100 | 293 | 100 | 293 | 100 | 100 | 100 | 293 | 100 |
| Comment | Site I | Site II | Site I | Site II | Site I | Site II |
| Bond Lengths (Å) | | | | | | | | |
| Fe–O\textsubscript{phen} | 1.870(1) | 1.8778(10) | 1.855(1) | 1.877(1) | 1.861(2) | 1.893(1) | 1.876(1) | 1.874(1) | 1.8767(10) | 1.8798(10) | 1.873(1) | 1.875(1) |
| Fe–N\textsubscript{iminie} | 1.959(2) | 1.9578(14) | 1.953(1) | 1.954(1) | 1.944(2) | 1.945(1) | 1.943(1) | 1.944(1) | 1.9420(12) | 1.9514(11) | 1.951(2) | 1.959(2) |
| Fe–N\textsubscript{amine} | 2.017(2) | 2.0170(14) | 2.024(1) | 2.019(1) | 2.012(2) | 2.025(1) | 2.014(1) | 2.012(1) | 2.0188(13) | 2.0180(12) | 2.010(2) | 2.014(2) |
| Bond Lengths (Å) | | | | | | | | | |
| Fe–O\textsubscript{phen} | 1.8922(19) | 1.889(2) | 1.881(2) | 1.883(3) | 1.885(4) | 1.862(2) | 1.879(15) | 1.884(2) | 1.878(1) | 1.8802(15) | 1.8728(14) | 1.878(1) |
| Fe–N\textsubscript{iminie} | 1.955(2) | 1.947(3) | 1.963(5) | 1.946(4) | 1.947(5) | 1.950(3) | 1.952(18) | 1.952(3) | 1.952(1) | 1.9438(17) | 1.9416(18) | 1.954(1) |
| Fe–N\textsubscript{amine} | 2.020(2) | 2.016(3) | 2.019(3) | 2.012(4) | 2.012(5) | 2.016(3) | 2.0258(19) | 2.020(3) | 2.023(1) | 2.026(2) | 2.0157(19) | 2.024(1) |
| Distortion Parameters (°) | | | | | | | | | |
| Σ | 35.59 | 29.20 | 28.65 | 28.27 | 30.71 | 29.90 | 21.94 | 24.24 | 29.92 | 23.86 | 28.51 | 26.47 |
| θ | 99.98 | 80.03 | 80.74 | 78.45 | 79.62 | 78.11 | 50.17 | 58.49 | 73.33 | 61.35 | 79.56 | 70.26 |
| α | 66.64 | 40.95 | 40.66 | 39.22 | 45.97 | 36.79 | 38.15 | 38.86 | 37.71 | 37.49 | 35.47 | 32.41 |
| τ | 28.33 | 28.88 | 36.52 | 28.17 | 35.02 | 27.90 | 33.43 | 30.52 | 26.18 | 30.18 | 27.84 | 29.56 |
| Distortion Parameters (°) | | | | | | | | | |
| Σ | 29.29 | 27.79 | 29.11 | 27.26 | 28.51 | 25.32 | 24.95 | 27.87 | 27.62 | 27.69 | 31.36 | 28.78 |
| θ | 83.14 | 73.82 | 79.30 | 70.69 | 77.47 | 70.20 | 76.39 | 72.14 | 71.25 | 67.81 | 81.93 | 77.34 |
| α | 38.96 | 40.07 | 40.77 | 41.63 | 41.89 | 45.55 | 50.55 | 57.75 | 51.24 | 50.24 | 50.97 | 56.33 |
| τ | 31.37 | 28.44 | 28.66 | 27.99 | 28.75 | 27.49 | 29.82 | 29.38 | 30.23 | 21.19 | 19.43 | 29.03 |
| Complex | 6c | 6d | 6dS | 6e | 7a | 7b | 7c | 8 | 9a | 9b | 10a |
|---------|----|----|-----|----|----|----|----|---|----|----|-----|
| Temperature | 293 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 293 | 100 |
| Comment | | | | | | | | | | | |

### Bond Lengths (Å)

| Complex | 6c | 6d | 6dS | 6e | 7a | 7b | 7c | 8 | 9a | 9b | 10a |
|---------|----|----|-----|----|----|----|----|---|----|----|-----|
| Fe–Ophen | 1.8768(13) | 1.8671(16) | 1.884(2) | 1.885(3) | 1.869(3) | 1.878(1) | 1.873(2) | 1.8845(13) | 1.904(2) | 1.896(3) | 1.919(6) | 1.873(3) |
| Fe–Namin | 1.9551(16) | 1.9463(18) | 1.946(3) | 1.951(4) | 1.946(3) | 1.950(1) | 1.943(2) | 1.9821(15) | 1.920(3) | 1.921(2) | 1.924(8) | 1.944(4) |
| Fe–Namine | 1.9564(16) | 1.9479(18) | 1.952(3) | 1.967(4) | 1.949(3) | 1.948(2) | 1.9833(15) | 1.924(2) | 1.917(2) | 1.926(7) | 1.957(4) |

### Distortion Parameters (°)

| Complex | 6c | 6d | 6dS | 6e | 7a | 7b | 7c | 8 | 9a | 9b | 10a |
|---------|----|----|-----|----|----|----|----|---|----|----|-----|
| Site I | 27.53 | 30.17 | 26.20 | 26.07 | 26.82 | 24.00 | 27.18 | 25.72 | 21.94 | 24.24 | 19.58 | 28.27 |
| Site II | 25.70 | 79.92 | 68.86 | 68.45 | 65.95 | 61.26 | 65.94 | 76.93 | 50.17 | 58.49 | 44.76 | 80.76 |
| α | 52.66 | 54.14 | 51.90 | 52.24 | 48.97 | 40.11 | 49.46 | 31.74 | 32.46 | 32.08 | 49.39 | |
| τ | 26.43 | 25.00 | 26.26 | 26.00 | 26.00 | 17.73 | 27.28 | 25.49 | 25.55 | 22.94 | 16.47 | 20.29 | 28.16 |
| Σ | 26.38 | 29.50 | 25.80 | 30.81 | 26.89 | 28.44 | 28.50 | 28.61 | 27.38 | 24.87 | 28.50 | 28.84 |
| Complex | 13b | 14 | 15a | 15b | 16a | 16b | 16c | 17 |
|---------|-----|----|-----|-----|-----|-----|-----|----|
| Temperature (K) | 100 | 100 | 293 | 100 | 293 | 293 | 100 | 100 |
| Comment |     |     |     |     |     |     |     |     |

**Bond Lengths (Å)**

|        | Fe–O_phen | Fe–N_amine | Fe–N_imine | Fe–N_amine | Fe–N_imine | Fe–N_amine | Fe–N_amine | Fe–N_amine | Fe–N_amine | Fe–N_amine | Fe–N_amine | Fe–N_amine | Fe–N_amine |
|--------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
|        | 1.874(1)  | 1.879(2)   | 1.880(1)   | 1.887(2)   | 1.881(2)   | 1.886(3)   | 1.887(2)   | 1.889(1)   |            |            |            |            |            |
|        | 1.863(1)  | 1.874(2)   | 1.884(1)   | 1.890(2)   | 1.890(2)   | 1.900(3)   | 1.896(2)   | 1.891(1)   |            |            |            |            |            |
|        | 1.946(2)  | 1.950(3)   | 1.941(2)   | 1.950(3)   | 1.955(2)   | 1.959(3)   | 1.957(2)   | 1.951(1)   |            |            |            |            |            |
|        | 1.949(2)  | 1.945(3)   | 1.933(2)   | 1.957(2)   | 1.959(2)   | 1.956(2)   | 1.958(2)   | 1.955(1)   |            |            |            |            |            |
|        | 2.021(2)  | 2.011(3)   | 2.005(2)   | 2.008(2)   | 2.001(2)   | 1.999(3)   | 2.006(2)   | 2.008(1)   |            |            |            |            |            |
|        | 2.016(2)  | 2.007(3)   | 2.006(2)   | 2.004(3)   | 2.007(2)   | 2.017(3)   | 2.009(2)   | 2.003(1)   |            |            |            |            |            |

**Distortion Parameters (°)**

|        | Σ        | Φ        | α        | τ        |
|--------|----------|----------|----------|----------|
|        | 24.54    | 25.70    | 27.96    | 29.94    |
|        | 24.05    | 22.36    | 21.02    | 27.75    |
|        | 60.26    | 64.96    | 65.59    | 72.17    |
|        | 63.44    | 58.70    | 56.65    | 76.98    |
|        | 45.13    | 20.18    | 34.51    | 44.74    |
|        | 26.07    | 26.67    | 26.66    | 21.29    |
|        | 27.62    | 26.12    | 19.42    | 29.06    |
|        | 26.34    | 26.24    | 30.54    | 27.21    |
|        | 22.40    | 25.80    | 26.06    | 29.30    |
|        | 28.88    | 25.58    | 24.98    |          |
### S2.3 Intermolecular Interactions

**Table S2.3.** Intermolecular hydrogen bonds for all complexes. Symmetry operations used to generate equivalent atoms are shown beneath each set of hydrogen bonds.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|--------|----------|----------|--------|
| 1b [Fe(4-OH-Me$_2$-sal)$_3$]PF$_6$·0.45H$_2$O | | | | |
| O(5)–H(205)···O(4) | 0.84 | 2.18 | 2.96(4) | 155.6 |
| O(5)–H(105)···F(5B) | 0.84 | 2.17 | 2.91(2) | 174.7 |
| O(5)–H(105)···F(4B) | 0.84 | 2.22 | 2.95(6) | 145.3 |
| N(2)–H(2)···O(5)#1 | 1.00 | 2.35 | 3.15(5) | 160.7 |
| N(2)–H(2)···F(4A)#1 | 1.00 | 2.40 | 3.15(4) | 131.6 |
| #1 x,1-y,z; #2 1-x,1-y,2-z |
| 1c [Fe(4-OH-Me$_2$-sal)$_3$]OTf·0.27H$_2$O | | | | |
| N(2)–H(1N2)···O(6A)#1 | 0.87(2) | 2.44(2) | 3.04(8) | 127.3(19) |
| N(2)–H(1N2)···O(6B)#1 | 0.87(2) | 2.44(2) | 3.14(7) | 138(2) |
| N(3)–H(1N3)···O(9)#2 | 0.91(2) | 2.31(2) | 3.20(6) | 167.3(19) |
| #1 x,1-y,3/2,z-1/2; #2 x,-y+3/2,z-1/2 |
| 1d [Fe(4-OH-Me$_2$-sal)$_3$]ClO$_4$ | | | | |
| N(3)–H(3)···O(5)#1 | 1.00 | 2.22 | 3.07(4) | 143.1 |
| 100 K – #1 x,y,z+1 |
| N(3)–H(3)···O(5)#1 | 1.00 | 2.26 | 3.07(5) | 138.0 |
| N(2)–H(1N2)···O(5)#2 | 1.00 | 2.21 | 3.06(3) | 142.1 |
| 200 K – #1 x,y,z+1; #2 x,1-y,2-z |
| 1e [Fe(4-OH-Me$_2$-sal)$_3$]BF$_4$ | | | | |
| N(3)–H(1N3)···F(1)#1 | 0.91 | 2.29 | 3.07(2) | 144.4 |
| N(2)–H(1N2)···F(1)#2 | 0.91 | 2.30 | 3.05(5) | 140.7 |
| #1 x,1-y,z; #2 1-x,1-y,2-z |
| 1f [Fe(4-OH-Me$_2$-sal)$_3$]SbF$_6$·0.31H$_2$O | | | | |
| N(3)–H(1N3)···F(5A)#1 | 1.00 | 2.35 | 3.13(2) | 134.9 |
| N(3)–H(1N3)···O(7)#2 | 1.00 | 2.44 | 3.39(2) | 158.4 |
| N(2)–H(1N2)···O(5) | 1.00 | 2.50 | 3.47(8) | 166.9 |
| #1 x,1/2+y,1/2-z; #2 1-x,y,z |
| 1g 1373 [Fe(4-OH-Me$_2$-sal)$_3$]I$_3$ | | | | |
| N(2)–H(2)···I(2)#1 | 1.00 | 2.98 | 3.86(1) | 147.3 |
| N(3)–H(3)···I(2)#2 | 1.00 | 2.93 | 3.73(3) | 137.6 |
| #1 x,1+y,1/2-z; #2 1-x,1-y,2-z |
| 1h [Fe(4-OH-Me$_2$-sal)$_3$]Cl·EtOH·0.25H$_2$O | | | | |
| N(3)–H(1N3)···Cl#1 | 1.00 | 2.54 | 3.25(14) | 127.9 |
| N(2)–H(1N2)···Cl | 1.00 | 2.39 | 3.17(14) | 134.8 |
| #1 x,1+y,z |

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|--------|----------|----------|--------|
| 2a [Fe(3-OH-Me$_2$-sal)$_3$]NO$_3$ | | | | |
| N(2)–H(1N2)···O(3)#1 | 1.00 | 2.30 | 3.09(4) | 149.0 |
| N(2)–H(1N2)···O(4)#2 | 1.00 | 2.19 | 3.092(5) | 149.2 |
| 100 K – #1 x,1/2-y,1/2-z; #2 2-x+1/2,y,z-1/2 |
| N(2)–H(1N2)···O(4) | 0.98 | 2.01 | 2.907(16) | 150.7 |
| 293 K |
| 2b [Fe(3-OH-Me$_2$-sal)$_3$]BF$_4$·H$_2$O | | | | |
| O(5)–H(1O5)···O(1)#1 | 0.76(3) | 2.10(3) | 2.83(16) | 163(2) |
| O(5)–H(1O5)···F(3) | 0.81(3) | 2.90(3) | 2.87(6) | 162(2) |
| #1 x,1+y,1/2,-z+3/2 |
| 2c [Fe(3-OH-Me$_2$-sal)$_3$]PF$_6$·H$_2$O | | | | |
| O(5)–H(1O5)···O(1) | 0.91(3) | 2.08(4) | 2.86(4) | 143(4) |
| O(5)–H(1O5)···F(3A) | 0.93(3) | 2.11(5) | 2.99(12) | 156(2) |
| #1 x,1+y,1/2,z+3/2 |
| 3a [Fe(4-OH-Me$_2$-sal)$_3$]NO$_3$ | | | | |
| N(4)–H(1N4)···O(7)#1 | 1.00 | 2.10 | 2.99(7) | 148.4 |
| #1 x,1+y,1/2,z+3/2 |
| 3b [Fe(5-OH-Me$_2$-sal)$_3$]BF$_4$ | | | | |
| N(2)–H(1N2)···F(1)#1 | 0.78(2) | 2.16(3) | 2.89(2) | 158(2) |
| #1 x,1+y,1/2,z+3/2 |
| 4a [Fe(4,6-diOH-Me$_2$-sal)$_3$]NO$_3$·MeOH | | | | |
| N(2)–H(1N2)···O(7)#1 | 1.00 | 2.17 | 2.95(4) | 139.1 |
| N(3)–H(1N3)···O(7)#2 | 1.00 | 2.05 | 2.98(4) | 154.9 |
| 100 K – #1 x,1-y,3/2,z+1/2; #2 x,1-y,3/2,z+1/2 |
| N(2)–H(1N2)···O(7)#1 | 0.98 | 2.18 | 2.99(6) | 140.1 |
| N(3)–H(1N3)···O(7)#2 | 0.98 | 2.09 | 2.97(6) | 148(8) |
| 293 K – #1 x,1-y,3/2,z+1/2; #2 x,1-y,3/2,z+1/2 |
| 4b [Fe(4,6-diOH-Me$_2$-sal)$_3$]BF$_4$·0.5MeOH | | | | |
| N(2)–H(1N2)···F(1) | 1.00 | 2.21 | 3.01(7) | 136.5 |
| N(3)–H(1N3)···F(1)#1 | 1.00 | 2.10 | 3.014(3) | 151.3 |
| 100 K – #1 x,1+y,z |
| N(2)–H(1N2)···F(1) | 0.98 | 2.28 | 3.067(6) | 137.0 |
| N(3)–H(1N3)···F(1)#1 | 0.98 | 2.16 | 3.039(6) | 147.8 |
| 293 K – #1 x,1+y,z |
| D–H...A | d(D–H) | d(H...A) | d(D...A) | <(DHA) |
|--------|--------|----------|----------|--------|
| 4c [FeIII(4,6-diOMe-sal323)]ClO4·0.5MeOH | N(3)–H(1N3)...O(7)#1 | 1.00 | 2.15 | 3.050(7) | 148.3 |
|        |        | #1 x+y,z |
| 5a [FeIII(3-OEt-sal323)]PF6·EtOH | N(2)–H(3)...O(5)#1 | 1.00 | 2.38 | 3.209(5) | 140.2 |
|        | N(3)–H(3)...O(5)#1 | 1.00 | 2.28 | 3.257(5) | 166.9 |
|        | #1 –x+1,–y+1,z |
| 5b [FeIII(3-OEt-sal323)]BF4·0.32H2O | O(5)–H(2O5)...F(2)#1 | 0.84 | 1.80 | 2.609(7) | 161.2 |
|        | O(5)–H(1O5)...O(3) | 0.84 | 2.17 | 2.986(6) | 164.9 |
|        | N(3)–H(3)...F(1)#1 | 1.00 | 2.22 | 3.142(2) | 153.3 |
|        | N(2)–H(2)...F(1) | 1.00 | 2.29 | 3.086(2) | 135.3 |
|        | #1 x+y,z |
| 6b [FeIII(4-NEt-sal323)]PF6 | N(3)–H(3)...F(2) | 1.00 | 2.35 | 3.174(1) | 138.5 |
|        | N(4)–H(4)...F(1)#1 | 1.00 | 2.37 | 3.331(1) | 161.3 |
|        | #1 x+y,z |
| 6bS [FeIII(4-NEt-sal323)]PF6·0.78MeCN·0.1EtOH | N(3)–H(3)...F(1) | 1.00 | 2.15 | 3.100(3) | 157.8 |
|        | N(4)–H(4)...F(7)#1 | 1.00 | 2.44 | 3.221(3) | 134.8 |
|        | N(9)–H(9)...F(9A) | 1.00 | 2.10 | 3.097(3) | 176.9 |
|        | N(10)–H(10)...F(5) | 1.00 | 2.30 | 3.126(2) | 139.4 |
|        | #1 x+y,z |
| 6c [FeIII(4-NEt-sal323)]OTf | N(4)–H(4)...O(5)#1 | 1.00 | 2.14 | 3.039(15) | 149.2 |
|        | #100 K – #1 –x+2,–y+1,z+1 |
|        | N(4)–H(4)...O(4)#1 | 0.98 | 2.39 | 3.180(2) | 137.8 |
|        | 297 K – #1 –x+1,–y+1,z+1 |
| 6d [FeIII(4-NEt-sal323)]BF4 | N(3)–H(1N3)...F(4)#1 | 1.00 | 2.20 | 3.050(2) | 142.1 |
|        | #1 +x+3/2,y–1/2,z+1/2 |
| 6dS [FeIII(4-NEt-sal323)]BF4·EtOH | N(3)–H(1N3)...F(1) | 1.00 | 2.20 | 3.118(4) | 152.3 |
|        | N(4)–H(1N4)...F(1)#1 | 1.00 | 2.08 | 3.020(4) | 154.8 |
|        | #1 x+y,z |
| 6e [FeIII(4-NEt-sal323)]NO3·CH3Cl | N(3)–H(1N3)...O(3)#1 | 1.00 | 2.05 | 2.970(7) | 152.2 |
|        | N(4)–H(1N4)...O(3)#2 | 1.00 | 2.09 | 3.035(7) | 156.4 |
|        | #1 x,y+1,z #2 x–1,y+1,z |

| D–H...A | d(D–H) | d(H...A) | d(D...A) | <(DHA) |
|--------|--------|----------|----------|--------|
| 7a [FeIII(3-Me-sal323)]ClO4 | N(2)–H(1N2)...O(3)#1 | 1.00 | 2.11 | 3.061(4) | 158.5 |
|        | N(3)–H(1N1)...O(4)#2 | 1.00 | 2.18 | 3.049(4) | 144.4 |
|        | #1 x,1–y,–1,z #2 x,y–1,z |
| 7b [FeIII(3-Me-sal323)]PF6·0.68H2O | N(2)–H(1N2)...F(3)#1 | 0.87(2) | 2.46(2) | 3.279(2) | 157(2) |
|        | #1 x,1–y,–1/2+z |
| 7b [FeIII(3-Me-sal323)]BF4 | N(2)–H(1N2)...F(4)#1 | 0.85(4) | 2.18(4) | 2.993(3) | 160(4) |
|        | N(3)–H(1N3)...F(2)#2 | 0.93(5) | 2.22(5) | 3.013(3) | 142(4) |
|        | #1 –x,y+1/2,z+1/2 #2 –x+1,y+1/2,z–1/2 |
| 80982 [FeIII(3-Allyl-sal323)]NO3·MeCN | N(2)–H(1N2)...O(3) | 0.93 | 2.25 | 3.145(2) | 162.2 |
|        | N(3)–H(1N3)...O(3)#1 | 0.93 | 2.18 | 3.033(2) | 151.2 |
|        | #1 x+y,z |
| 9a [FeIII(3-Bu-sal323)]PF6·EtOH | N(6)–H(6)...O(5A)#1 | 0.93 | 2.07 | 2.930(6) | 152.7 |
|        | N(6)–H(6)...O(5B)#1 | 0.93 | 2.07 | 2.749(18) | 128.8 |
|        | O(5A)–H(5A)...F(1) | 0.84 | 2.00 | 2.838(5) | 172.0 |
|        | O(5B)–H(5B)...F(1) | 0.84 | 1.92 | 2.711(17) | 156.1 |
|        | N(2)–H(2)...F(5) | 0.93 | 2.44 | 3.227(3) | 142.1 |
|        | N(7)–H(7)...F(3) | 0.93 | 2.36 | 3.229(4) | 155.3 |
|        | N(7)–H(7)...F(6) | 0.93 | 2.54 | 3.204(4) | 128.1 |
|        | #1 –x,–y+1,z |
| 9b [FeIII(3-Bu-sal323)]BF4 | N(2)–H(1N2)...F(2)#1 | 0.91 | 2.07 | 2.913(9) | 154.6 |
|        | N(3)–H(1N3)...F(1)#2 | 0.91 | 2.07 | 2.925(9) | 155.3 |
|        | #1 x–1,y+1,z #2 x–1,y,z |
| 10e [FeIII(sal323)]FeCl3 | N(2)–H(2)...Cl(3B)#1 | 0.93 | 2.55 | 3.365(7) | 147.3 |
|        | N(3)–H(3)...Cl(3B)#2 | 0.93 | 2.41 | 3.287(6) | 157.2 |
|        | N(2)–H(2)...Cl(3A)#1 | 0.93 | 2.54 | 3.398(2) | 154.2 |
|        | N(3)–H(3)...Cl(3A)#2 | 0.93 | 2.47 | 3.304(2) | 148.9 |
|        | #1 –x+1,y+1/2,z+1/2 #2 –x+1,y+1/2,z–1/2 |
| 10f [FeIII(sal323)]BF4 | N(3)–H(3)...F(3)#1 | 1.00 | 2.13 | 2.935(2) | 136.4 |
|        | N(2)–H(2)...F(3)#2 | 1.00 | 2.26 | 3.069(2) | 136.9 |
|        | #1 –x,y+1,z+1 #2 –x+1,y–1,z+1 |
| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|---------|---------|---------|---------|
| 11a [Fe(II)(5-Br-sal)]PF₆ | N(2)-H(N2)...Br(2)#1 | 0.91 | 2.99 | 3.784(3) | 146.0 |
|         | N(3)-H(N3)...Br(2)#2 | 0.91 | 2.95 | 3.635(3) | 133.8 |
| #1 -x,-2+y,1-z; #2 1-x,-1/2+y,1-z |
| 11b [Fe(II)(5-Br-sal)]BF₃ EtOH | O(3)-H(O3)...F(3)#1 | 0.82 | 2.12 | 2.902(4) | 158.6 |
|         | N(3)-H(N3)...O(3) | 0.83(4) | 2.08(4) | 2.899(4) | 168(3) |
|         | N(2)-H(N2)...F(3)#2 | 0.82(4) | 2.24(3) | 3.021(4) | 159(3) |
| #1 x,y,-1,x #2 1+x,-1+y,z |
| 11c [Fe(II)(5-Br-sal)]NO₃ PrOH | N(2)-H(N2)...O(9)#1 | 0.84(3) | 2.20(4) | 2.980(3) | 155(3) |
|         | N(6)-H(N6)...O(7) | 0.85(4) | 2.16(4) | 2.978(3) | 163(3) |
|         | O(11)-H(O11)...O(10) | 0.78(4) | 2.03(4) | 2.812(3) | 179(4) |
|         | O(12)-H(O12)...O(5)#2 | 0.83(5) | 2.00(5) | 2.827(4) | 173(4) |
|         | N(3)-H(N3)...O(10)#1 | 0.84(3) | 2.36(3) | 3.036(3) | 138(3) |
|         | N(7)-H(N7)...O(5)#3 | 0.82(4) | 2.41(4) | 3.067(3) | 138(3) |
| #1 -x,-y,-z+1; #2 -x+1,-y+1,-z+1; #3 x,1+y,z |
| 12 [Fe(III)(5-diBr-sal)]NO₃ PrOH | O(6B)-H(6B)...O(3)#1 | 0.84 | 2.18 | 2.879(5) | 140.7 |
|         | O(6A)-H(6A)...O(3)#1 | 0.84 | 2.04 | 2.879(5) | 175.8 |
|         | N(3)-H(N3)...O(5) | 0.82(6) | 2.17(6) | 2.961(5) | 161(5) |
|         | N(2)-H(N2)...O(4)#2 | 0.77(6) | 2.33(6) | 3.064(5) | 159(6) |
| #1 -x+1/2,y+1/2,-z+3/2; #2 3/2-x,-1/2+y,3/2-z |
| 13a [Fe(III)(5-diCl-sal)]BF₃ PrOH | O(3)-H(O3)...F(1)#1 | 0.82 | 1.99 | 2.801(3) | 167.3 |
|         | N(4)-H(N4)...O(3) | 0.88(3) | 2.15(3) | 2.933(3) | 148(2) |
|         | N(2)-H(N2)...F(2)#2 | 0.81(3) | 2.17(3) | 2.863(2) | 144(2) |
| #1 -x+1,-y,-z+1; #2 x+1/2,-y+1,z,-1/2 |
| 13b [Fe(III)(5-diCl-sal)]PF₆ | N(3)-H(N3)...F(4) | 0.82(3) | 2.50(3) | 3.269(3) | 157(3) |
|         | N(3)-H(N3)...F(4) | 0.82(3) | 2.50(3) | 3.269(3) | 157(3) |
|         | N(2)-H(N2)...F(5)#1 | 0.80(3) | 2.49(3) | 3.263(3) | 163(3) |
| #1 1/2+x,1/2-y,-1/2+z |
| 14 [Fe(III)(3,5-di-sal)]PF₆ | N(2)-H(N2)...I(3)#1 | 0.93 | 3.11 | 3.989(3) | 157.9 |
|         | N(3)-H(N3)...I(3)#2 | 0.93 | 3.08 | 3.947(3) | 156.4 |
| #1 x,1+y,z; #2 -x,y,1/2,-z+1/2 |

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------|---------|---------|---------|---------|
| 15a [Fe(III)(5-NO₂-sal)]PF₆ MeCN | N(4)-H(N4)...O(6)#1 | 0.81(3) | 2.25(3) | 3.000(3) | 155(3) |
|         | N(3)-H(N3)...O(7) | 0.93 | 2.05 | 2.927(3) | 157.8 |
| #1 -x+2,-y+1,-x+2 |
| 15b [Fe(III)(5-NO₂-sal)]NO₃ | N(3)-H(N3)...O(7) | 0.93 | 2.00 | 2.922(3) | 172.5 |
| #1 x-1/2,y+1/2,x |
| 16a [Fe(III)(5-NO₂-sal)]BF₃ EtOH | N(3)-H(3)...O(7)#1 | 0.77(3) | 2.24(3) | 2.995(3) | 167(3) |
|         | O(7)-H(7)...F(5A)#2 | 0.82 | 2.33 | 3.117(6) | 160.2 |
|         | N(4)-H(4)...F(5A)#1 | 0.81(3) | 2.42(3) | 3.209(5) | 166(2) |
| #1 x+1,y,z; #2 x,y-1,z; #3 x,1+y,z |
| 16b [Fe(III)(5-NO₂-sal)]BF₃ EtOH | O(7)-H(7)...F(3) | 0.82 | 2.16 | 2.945(7) | 161.6 |
|         | N(3)-H(3)...O(7)#1 | 0.91 | 2.03 | 2.933(6) | 171.4 |
|         | N(4)-H(4)...F(3) | 0.91 | 2.12 | 3.010(6) | 164.1 |
| #1 x+1,y,z |
| 16c [Fe(III)(5-NO₂-sal)]ClO₄ EtOH | N(3)-H(1N3)...O(11) | 1.00 | 1.91 | 2.905(3) | 170.5 |
|         | N(4)-H(1N4)...O(7)#1 | 1.00 | 2.03 | 3.021(3) | 172.6 |
|         | O(11)-H(11)...O(7)#2 | 0.84 | 2.05 | 2.860(3) | 163.0 |
| #1 x-1,y+1,z; #2 x,y+1,z |
| 17 [Fe(III)(3,5-diNO₂-sal)]ClO₄ EtOH | O(15)-H(15).O(13)#1 | 0.82(3) | 2.04(3) | 2.8485(19) | 171(2) |
|         | N(5)-H(5)...O(15)#2 | 0.87(2) | 2.03(2) | 2.8496(17) | 156(2) |
|         | N(4)-H(4)...O(12)# | 0.85(2) | 2.44(2) | 3.035(2) | 128(2) |
|         | N(4)-H(4)...O(6)# | 0.85(2) | 2.55(2) | 3.283(2) | 146(2) |
| #1 -x+1,-y+1,-z+1; #2 x+1/2,-y+1/2,z+1/2; #3 x-1/2,-y+1/2,z-1/2 |
Figure S2.1. Molecular structure of 3a showing the two unique cations, and the N–H…O hydrogen bonding existing between the amine N(2) and O(7) of the NO$_3^-$ anion. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms, except those involved in hydrogen bonding have been omitted for clarity. A similar motif is observed in 3b.

Figure S2.2. Partial packing diagram showing the formations of hydrogen bonding dimers through N–H…O interactions. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms, except those involved in hydrogen bonding have been omitted for clarity.
Table S2.4 Summary of bond lengths and distortion parameters of high spin Fe$^{III}$ cations with similar hexadentate ligands of differing backbone lengths.$^{7,9}$

| Complex                  | [Fe(5-Me-sal$_2$222)]PF$_6$ | [Fe(4,6-diOMe-sal$_2$322)]ClO$_4$ | [Fe(5-F-sal$_3$333)]Cl |
|--------------------------|-----------------------------|-----------------------------------|------------------------|
| Refcode                  | WOBWOA                     | ELANOV                            | FONFAS                 |
| Bond Length (Å)          |                             |                                   |                        |
| Fe–O$_{phen}$            | 1.9315(13)                  | 1.906(2)                          | 1.9426(9)              |
| Fe–N$_{imine}$           | 2.1245(14)                  | 2.045(3)                          | 2.1398(11)             |
| Fe–N$_{amine}$           | 2.2179(15)                  | 2.144(3)                          | 2.1837(11)             |
| Distortion Parameters (°) |                             |                                   |                        |
| $\Sigma$                 | 93.87                       | 74.62                             | 57.97                  |
| $\Theta$                 | 325.88                      | 301.84                            | 230.34                 |
S2.4 Hirshfeld Surface Analysis

Table S2.5. Relative contribution (%) of the various intermolecular interactions to the Hirshfeld surface in 1a – 1h.

| Complex | 1a | 1aS | 1b | 1c | 1d | 1e | 1f | 1g | 1h |
|---------|----|-----|----|----|----|----|----|----|----|
| T (K)   | 100| 293 | 100| 293| 100| 100| 100| 100| 100|
| H···H   | 54.5| 56.7| 55.2| 55.8| 48 | 44.2| 53.2| 52.6| 46.6| 55.9| 65.2|
| O···O   | 24 | 21.9| 19.4| 19.2| 12.2| 25.5| 26.4| 9.5 | 11.3| 8.6 | 10.4|
| C···H   | 18.9| 18.5| 18.2| 17.9| 15.9| 14.4| 18.3| 17.5| 15.8| 15.9| 16.2|
| O···O   | 1.3 | 1.3 | 0.1 | 0.2 | 0.2 | 0.7 | 0.4 | 0  | 0.2 | 0  | 0  |
| N···H   | 0.8 | 1   | 5.6 | 5.6 | 0.4 | 0.3 | 0.1 | 0.3 | 0.4 | 0  | 0  |
| C···C   | 0.1 | 0.2 | 0.7 | 0.7 | 1.1 | 1.2 | 0.1 | 0  | 0.8 | 0.7 | 0  |
| C···O   | 0.4 | 0.5 | 0.8 | 0.6 | 1.1 | 1.9 | 1.4 | 1.3 | 0.8 | 1.1 | 0  |
| F···H   | 0  | 0   | 0   | 0   | 21.2| 11.6| 0   | 18.8| 23.9| 0  | 0  |
| I···H   | 0  | 0   | 0   | 0   | 0   | 0   | 0   | 0  | 0   | 0  | 0  |
| O···I   | 0  | 0   | 0   | 0   | 0   | 0   | 0   | 0  | 0   | 0  | 0  |
| Cl···H  | 0  | 0   | 0   | 0   | 0   | 0   | 0   | 0  | 0   | 0  | 8  |

Figure S2.3. Hirshfeld surface analysis for 1a (i) and 1a-S (ii) at 293 K with two views of the cation for both. The surface is mapped with $d_{	ext{norm}}$ values of -0.4374 to 1.3143 a.u. (i) and -0.4014 to 1.3143 a.u. (ii). Contacts which are shorter than the van der Waals (vdW) radii of the contact atoms are shown in red on the surface and contacts longer than the vdW radii in blue. Contacts which are shorter than the vdW radii are indicated with a dashed blue line and labelled according to the contact atoms inside (white) and outside the surface (colored). Two-dimensional fingerprint plots delineated into H···O, H···C and C···H contacts, with $d_e$ on the x-axis (distance from the surface to the closest internal atom) and $d_i$ on the y-axis (distance from the surface to the closest external atom). The dashed lines on the plots refer to the vdW radii of the selected atoms.\(^{10}\)
S3 Magnetic Measurements

Figure S3.1. Magnetic susceptibility of 1a (black circles) and fitted to the Boltzmann equation (red line), which reveals a $T_1/2$ of 265 K.

Figure S3.2. EPR spectrum of a polycrystalline sample of 1a. The multi-line spectrum was obtained as the sample was polycrystalline and not ground.
Figure S3.3. $^1$H NMR spectra of 1a (a) and 1d (b) showing the shift in the DMSO-$d_6$ peaks. The peaks are labelled with their chemical shift in Hz.
## S4 Quantum Chemistry Calculations

### Table S4.1. XYZ coordinates of the optimized geometries of the $[\text{Fe}^{\text{III}}(\text{sal233})]^+$ and $[\text{Fe}^{\text{III}}(4\text{-OMe-sal233})]^+$ cations.

|        | Spin Sextet (S = 5/2, HS) | Spin Doublet (S = 1/2, LS) |
|--------|---------------------------|-----------------------------|
| **Fe** | 0.753843003               | 11.3530522                  | Fe | 0.754629586 | 11.36497342 | 11.83157739 |
| **O**  | 1.564473465               | 9.594799204                 | O  | 1.714348933 | 9.801990325 | 11.41333129 |
| **C**  | 2.231623391               | 8.872033774                 | C  | 2.235046663 | 9.004601609 | 12.313942   |
| **H**  | 2.250860061               | 7.463809671                 | C  | 2.472918117 | 7.650576837 | 12.00621678 |
| **H**  | 1.71580756                | 7.009617282                 | H  | 2.228810088 | 7.314639728 | 10.99791359 |
| **C**  | 2.935033898               | 6.682765715                 | C  | 2.982328274 | 6.77224674 | 12.95234917 |
| **H**  | 2.926869141               | 5.597111369                 | H  | 3.135310184 | 5.726160248 | 12.68358647 |
| **C**  | 3.641729985               | 7.271286844                 | C  | 3.307189359 | 7.213882943 | 14.24872211 |
| **H**  | 4.177398339               | 6.649168254                 | H  | 3.711006655 | 6.516445476 | 14.98138754 |
| **C**  | 3.659161845               | 8.651969099                 | C  | 3.133828903 | 8.548200169 | 14.5710333 |
| **H**  | 4.219855565               | 9.126726498                 | H  | 3.421918128 | 8.91712783 | 15.55386287 |
| **C**  | 2.960446988               | 9.475171379                 | C  | 2.598154405 | 10.864539  | 13.93720682 |
| **H**  | 3.087241479               | 10.8994208                  | H  | 3.24332112  | 11.18924058 | 14.76599929 |
| **N**  | 2.433772564               | 11.79420145                 | N  | 1.99181937  | 11.78798387 | 13.24471196 |
| **C**  | 2.852935303               | 13.1894081                 | C  | 2.453456402 | 13.17027604 | 13.4139586  |
| **H**  | 3.617295664               | 13.29593639                 | H  | 3.080219908 | 13.23646519 | 14.31648182 |
| **H**  | 1.983480706               | 13.80172168                 | H  | 1.593540958 | 13.83725998 | 13.5487496  |
| **C**  | 3.427521662               | 13.68190653                 | C  | 3.26819453  | 13.58947523 | 12.18735557 |
| **H**  | 3.84041564                | 14.68972452                 | H  | 3.689759732 | 14.59592796 | 12.38173086 |
| **H**  | 4.278206144               | 13.04062856                 | H  | 4.123268026 | 12.9147215 | 12.05385467 |
| **C**  | 2.428642999               | 13.7736193                 | C  | 2.453486654 | 13.68400967 | 10.90177418 |
| **H**  | 1.560090753               | 14.37713799                 | H  | 1.593788011 | 14.35190596 | 11.04591414 |
| **H**  | 2.911609519               | 14.27107637                | H  | 3.037398111 | 14.09742974 | 10.0887822 |
| **N**  | 1.899601938               | 12.45458575                 | N  | 1.898252343 | 12.3745516 | 10.47253674 |
| **C**  | 2.686677681               | 11.82146821                | C  | 2.667517511 | 11.71405756 | 10.30435341 |
| **C**  | 1.059156956               | 12.5403566                 | C  | 1.08978286  | 12.30525381 | 9.23466718  |
| **C**  | 1.645965177               | 12.83722213                | C  | 1.717587509 | 12.76071181 | 8.366179384 |
| **C**  | 0.313804719               | 13.33441334                | C  | 0.384486357 | 13.33215721 | 9.400663137 |
| **C**  | 0.368192837               | 11.21013882                | C  | 0.34303081 | 11.20676005 | 9.00996884 |
| **C**  | -0.242936427              | 11.2410689                 | C  | -0.309328395 | 11.26900413 | 8.12401745 |
| **H**  | 1.114337489               | 10.41065252                | H  | 1.048254413 | 10.37740387 | 8.856343517 |
| **N**  | -0.439888809              | 10.8681815                 | N  | -0.431004559 | 10.89136194 | 10.23657284 |
| **H**  | -1.227783535              | 11.52275807                | H  | -1.200666061 | 11.56576881 | 10.33197718 |
| **C**  | -0.965491777              | 9.481363169                | C  | -0.981777752 | 9.512272947 | 10.19379732 |
| **H**  | -0.092740554              | 8.814917454                | H  | -0.12215229 | 8.840186819 | 10.0696476 |
| **H**  | -1.470075397              | 9.315266363                | H  | -1.626624408 | 9.408199856 | 9.304966501 |
| **C**  | -1.930516727              | 9.159384917                | C  | -1.760206275 | 9.137144274 | 11.44957222 |
| Spin Sextet (S = 5/2, HS) | Spin Doublet (S = 1/2, LS) |
|---------------------------|---------------------------|
| Fe                        | -1.095538255              | Fe                        | -1.099611924              |
|                           | 5.351638493               |                           | 5.370314373               |
|                           | 16.5790609                |                           | 16.6153123                |
| O                         | -2.506513973              | O                         | -2.467439498              |
|                           | 6.483064688               |                           | 6.515649925               |
|                           | 16.0416698                |                           | 15.81167197               |
| C                         | -3.084968733              | C                         | -3.167015288              |
|                           | 6.402125567               |                           | 6.328411195               |
|                           | 14.85581829               |                           | 14.71339884               |
| C                         | -3.732873252              | C                         | -3.658245382              |
|                           | 7.547033755               |                           | 7.46628319                |
|                           | 14.34628164               |                           | 14.00764237               |
| H                         | -3.7285427                | H                         | -3.447411206              |
|                           | 8.445065451               |                           | 8.433070489               |
|                           | 14.95980818               |                           | 14.41436832               |
| C                         | -4.340294818              | C                         | -4.395145506              |
|                           | 7.514027552               |                           | 7.275124487               |
|                           | 13.08914813               |                           | 12.83180158               |
| O                         | -4.958670596              | O                         | -4.889286276              |
|                           | 8.569274533               |                           | 8.29011699                |
|                           | 12.51364267               |                           | 12.0897535                |
| C                         | -5.029789274              | C                         | -4.668054309              |
|                           | 9.79795049                |                           | 9.63371932                |
|                           | 13.24787185               |                           | 12.5390101                |
| H                         | -5.57248741               | H                         | -5.11912661               |
|                           | 9.65904125                |                           | 9.7961095                |
|                           | 14.19555437               |                           | 13.52007395               |
| H                         | -5.578876655              | H                         | -5.158048093              |
|                           | 10.49327413               |                           | 10.27532644               |
|                           | 12.60596219               |                           | 11.80048079               |
| H                         | -4.02244983               | H                         | -3.591913494              |
|                           | 10.19517699               |                           | 9.864176935               |
|                           | 13.44830359               |                           | 12.57434281               |
| C                         | -4.338569277              | C                         | -4.67581263               |
|                           | 6.329680135               |                           | 5.976799279               |
|                           | 11.3451647               |                           | 12.3384152               |
| H                         | -4.827210436              | H                         | -5.256900934              |
|                           | 6.329680135               |                           | 5.877814118               |
|                           | 11.3451647               |                           | 11.42310561               |
| C                         | -3.748664184              | C                         | -4.22232806               |
|                           | 5.19224566               |                           | 4.881339352               |
|                           | 12.83013427               |                           | 13.03634298               |
| H                         | -3.777557581              | H                         | -4.451376089              |
|                           | 4.262865256              |                           | 3.87790421                |
|                           | 12.25089626               |                           | 12.6716635               |
| C                         | -3.099490802              | C                         | -3.456990487              |
|                           | 5.19134094               |                           | 5.011296057               |
|                           | 14.0915383               |                           | 14.22268335               |
| C                         | -2.670524029              | C                         | -3.09430955               |
|                           | 3.961384999               |                           | 3.835768162               |
|                           | 14.668313               |                           | 14.9430301               |
| H                         | -3.057638957              | H                         | -3.555413948              |
|                           | 3.03958188               |                           | 2.897016061               |
|                           | 14.21165632               |                           | 14.5924488               |
| N                         | -1.938558362              | N                         | -2.30703995               |
|                           | 3.83927948               |                           | 3.773319373               |
|                           | 15.74514971               |                           | 15.98289848               |
| C                         | -1.972218233              | C                         | -2.24789324               |
|                           | 2.5504948               |                           | 2.522755918               |
|                           | 16.44130280               |                           | 16.73341192               |
| H                         | -0.952283387              | H                         | -1.198715163              |
|                           | 2.230839441              |                           | 2.20782917                |
|                           | 16.68980239               |                           | 16.82701749               |
| H                         | -2.413742777              | H                         | -2.798556645              |
|                           | 1.789846651              |                           | 1.731277489               |
|                           | 15.77874149               |                           | 16.19653982               |

[Fe\textsuperscript{II}(4-OMe-sal:323)]\textsuperscript{+}
Table S4.2. Calculated Gibbs free energies ($\Delta G_{SCO}$) upon SCO from the LS to HS state for the [Fe$^{III}$(sal$_2$323)]$^+$ and [Fe$^{III}$(4-OMe-sal$_2$323)]$^+$ cations.

|                  | [Fe$^{III}$(sal$_2$323)]$^+$ | [Fe$^{III}$(4-OMe-sal$_2$323)]$^+$ |
|------------------|-----------------------------|---------------------------------|
| $\Delta E$       | +40.7                       | +40.2                           |
| $\Delta G_{corr}$| $-21.9$                     | $-21.8$                         |
| $\Delta G_{SCO}$ (HS-LS) | +18.8                 | +18.4                           |

S5 Powder X-ray Diffraction

Figure S5.1 Micro-powder XRD spectrum of 1a/1a-S recorded on the sample used in the magnetic susceptibility measurement. The simulated spectra for 1a and 1a-S from the single crystal XRD data are provided in red and grey respectively.

S6 Author Contribution

Conor T. Kelly: Conceptualization, Formal Analysis, Investigation, Data Curation, Writing – Original Draft, Writing – Review & Editing, Visualization. Michael Griffin: Conceptualization, Formal Analysis, Investigation. Kane Esien: Investigation. Solveig Felton: Resources, Supervision. Helge Müller-Bunz: Formal Analysis, Investigation. Grace G. Morgan: Conceptualization, Resources, Writing – Review & Editing, Supervision, Project Administration, Funding Acquisition.
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