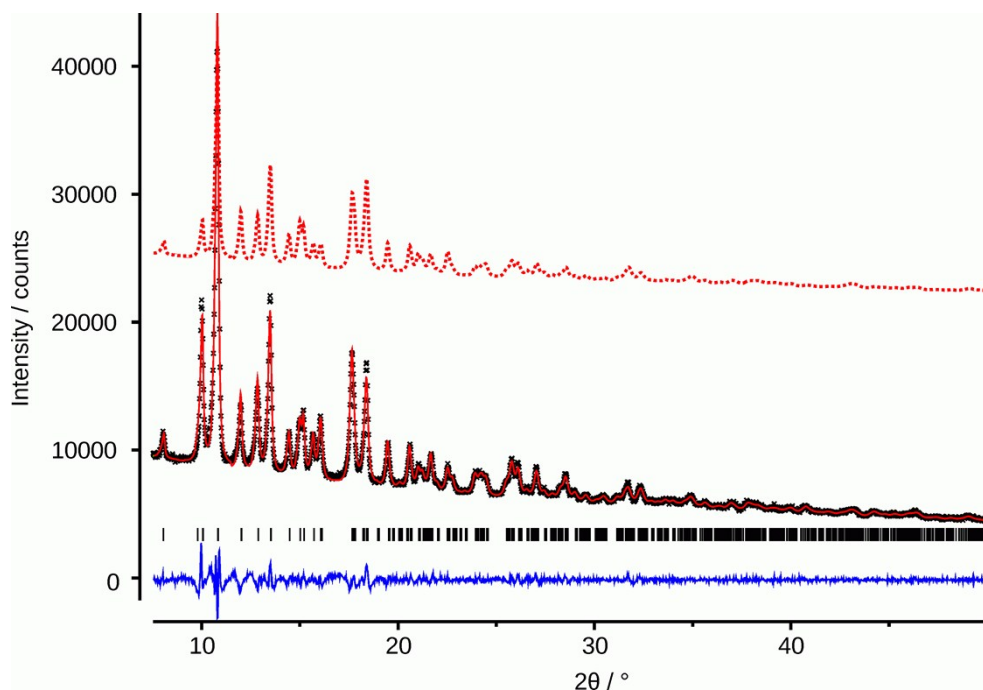


## **Supplementary material**

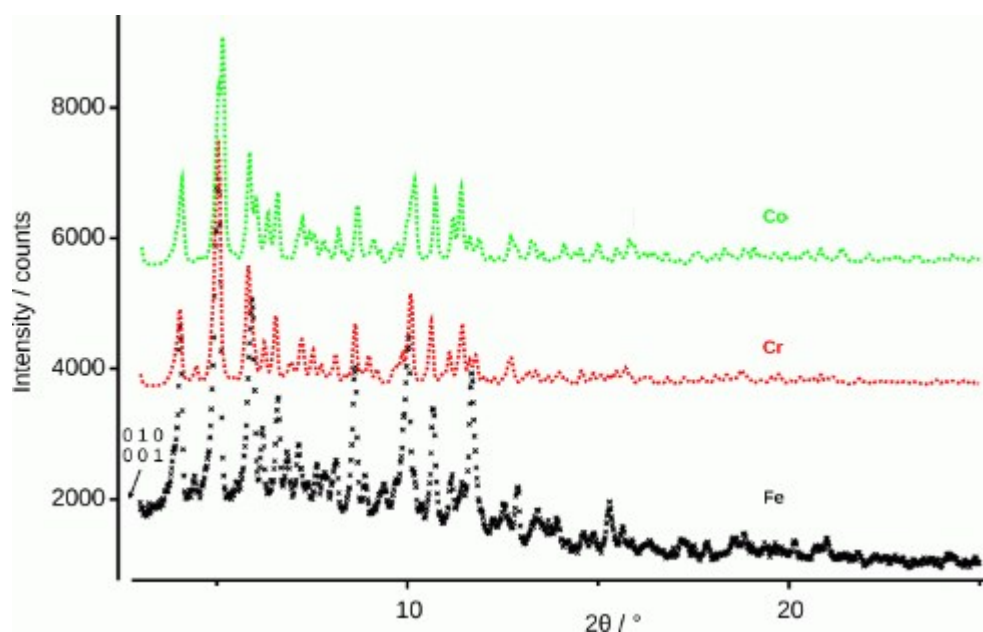
### **Ion-pair complexes of Schiff base Fe(III) cations and complex anions.**

Ivan Nemec,<sup>a,b\*</sup>, Pavel Zoufalý,<sup>a</sup> Pawel Jewula,<sup>b</sup> Peter Antal,<sup>a</sup> Wolfgang Linert,<sup>c</sup> and Radovan Herchel

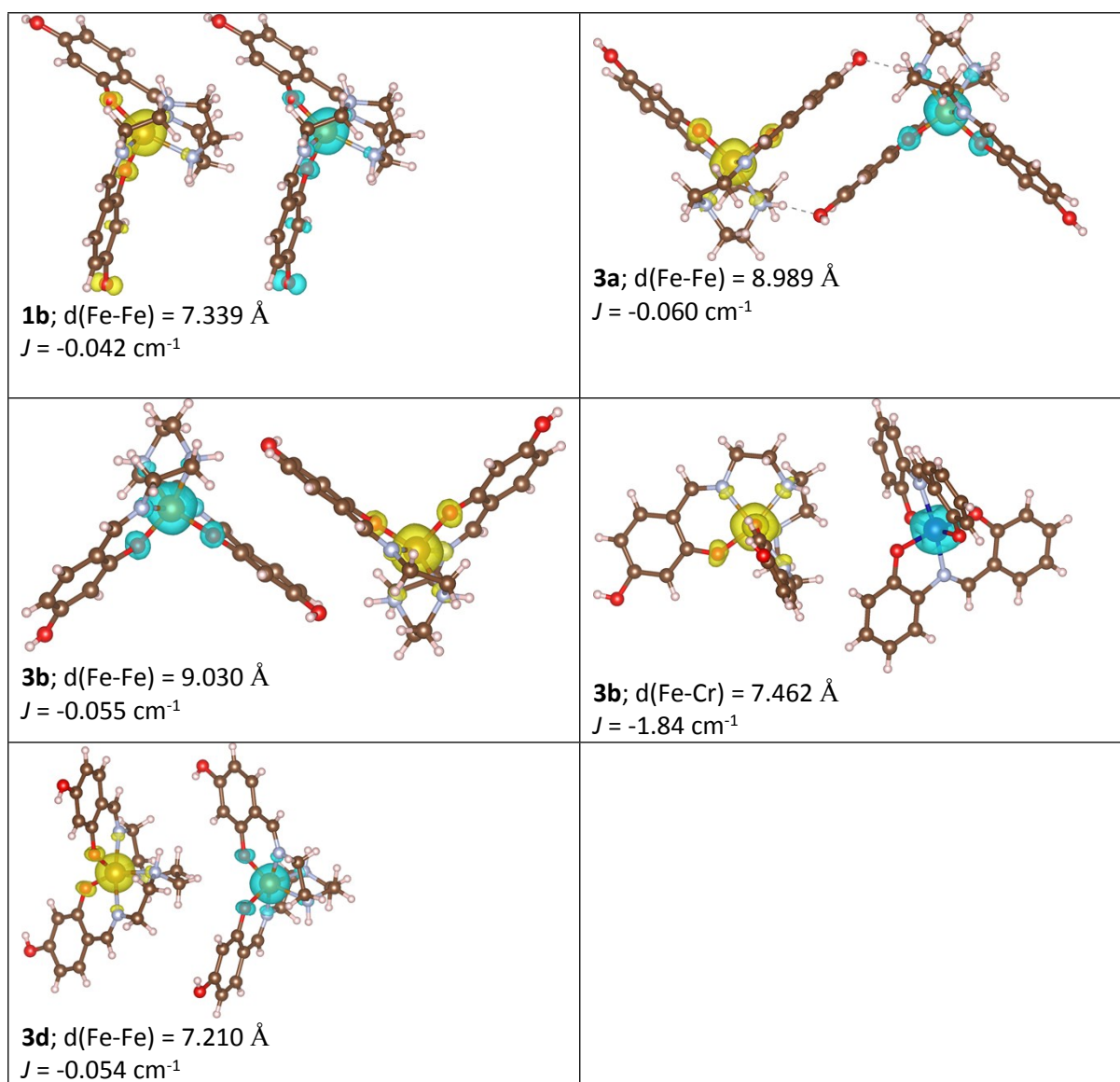
## X-ray powder diffraction



**Figure S1** Bottom: Le Bail fitted powder pattern (×...observed, red line...fit,  $\lambda = \text{Cu K}\alpha_{1,2}$ ) of **1a**. The reflections' positions are marked with bars and the difference curve is shown at the bottom. Top: Pattern of **1a**, calculated from single crystal data (dotted red line).



**Figure S2** Comparison of the observed powder pattern ( $\lambda = \text{Mo K}\alpha_1$ ) of **3c** (black dotted line) with the calculated patterns of the corresponding chromium (**3b** red dotted line) and cobalt (**3a** green dotted line) complexes. The arrow indicates the approximate position of the first low-angle reflections.



**Figure S3.** The calculated spin density distribution of the broken-symmetry spin states for **1b-3d** molecular fragments extracted from experimental X-ray structures using B3LYP/de2-TZVP. Positive and negative spin densities are represented by yellow and cyan surfaces, respectively. The respective the isotropic exchange parameters  $J$  calculated with eq. 5 are also listed.

**Table S1** Crystallographic data

| Abbreviation                                                                         | <b>1b</b>                                                       | <b>3a</b>                                                         | <b>3b</b>                                                         | <b>3d</b>                                                         |
|--------------------------------------------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|
| Formula                                                                              | C <sub>20</sub> H <sub>27</sub> FeN <sub>4</sub> O <sub>6</sub> | C <sub>46</sub> H <sub>44</sub> CoFeN <sub>6</sub> O <sub>9</sub> | C <sub>46</sub> H <sub>44</sub> CrFeN <sub>6</sub> O <sub>9</sub> | C <sub>22</sub> H <sub>24</sub> AgFeN <sub>6</sub> O <sub>4</sub> |
| Formula weight /g mol <sup>-1</sup>                                                  | 475.3                                                           | 939.65                                                            | 924.37                                                            | 600.18                                                            |
| Crystal system                                                                       | orthorhombic                                                    | triclinic                                                         | triclinic                                                         | orthorhombic                                                      |
| <i>T</i> /K                                                                          | 293(2)                                                          | 100(2)                                                            | 293(2)                                                            | 100(2)                                                            |
| Space group                                                                          | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>           | <i>P</i> $\bar{1}$                                                | <i>P</i> $\bar{1}$                                                | <i>I</i> ba2                                                      |
| <i>a</i> /Å                                                                          | 7.3393(6)                                                       | 11.2605(7)                                                        | 11.2435(6)                                                        | 12.8506(6)                                                        |
| <i>b</i> /Å                                                                          | 13.1519(18)                                                     | 11.2605(7)                                                        | 13.6516(7)                                                        | 12.7677(6)                                                        |
| <i>c</i> /Å                                                                          | 21.8069(18)                                                     | 14.1826(9)                                                        | 14.4148(6)                                                        | 14.4195(8)                                                        |
| $\alpha$ /°                                                                          | 90                                                              | 97.156(5)                                                         | 96.464(4)                                                         | 90                                                                |
| $\beta$ /°                                                                           | 90                                                              | 106.096(5)                                                        | 106.508(4)                                                        | 90                                                                |
| $\gamma$ /°                                                                          | 90                                                              | 92.685(5)                                                         | 93.240(4)                                                         | 90                                                                |
| <i>V</i> /Å <sup>3</sup>                                                             | 2104.9(4)                                                       | 2048.8(2)                                                         | 2098.75(18)                                                       | 2365.8(2)                                                         |
| <i>Z</i>                                                                             | 4                                                               | 2                                                                 | 2                                                                 | 4                                                                 |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                                             | 0.981                                                           | 0.930                                                             | 0.994                                                             | 1.092                                                             |
| Data/restraints/parameters                                                           | 3364/9/292                                                      | 8052/12/582                                                       | 7393/7/588                                                        | 4886/1/155                                                        |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | 0.0489/0.1063                                                   | 0.0370/0.0853                                                     | 0.0562/0.1212                                                     | 0.0175/0.0429                                                     |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all)                                 | 0.0797/0.1141                                                   | 0.0622/0.0853                                                     | 0.1154/0.1356                                                     | 0.0210/0.0436                                                     |
| CCD deposit number                                                                   |                                                                 |                                                                   |                                                                   |                                                                   |