Supplementary Information

An octahedral tetrachlorido Fe(II) complex with aminopyrazinium ligands from a serendipitous redox synthesis exhibiting magnetic exchange through non-covalent 3-D architectures

Elizabeth K. Rusbridge, Yan Peng, Annie K. Powell, David Robinson and Anthony J. Fitzpatrick*

a School of Science and Technology, Nottingham Trent University, Nottingham, UK
b Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, 76131 Karlsruhe, Germany.
c Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

*Email: anthony.fitzpatrick@ntu.ac.uk.

1. Synthesis
2. UV-Vis experiments
3. X-ray
4. Magnetic Measurements
5. Computational

1. Synthesis

2-Aminopyrazine (1 mmol, 0.095 g) was added to salicylaldehyde (1 mmol, 0.122 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in a deep purple colour immediately. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 35.3 mg, 11.5 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to 3-methoxysalicylaldehyde (1 mmol, 0.152 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in a deep purple colour immediately. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 9.9 mg, 2.5 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to 5-chlorosalicylaldehyde (1 mmol, 0.156 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in a deep purple colour immediately. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 67.4 mg, 17.3 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to propionaldehyde (1 mmol, 0.058 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in an orange colour. The solution was filtered after 20 min stirring
and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 61.7 mg, 21.3 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to phenylacetaldehyde (1 mmol, 0.120 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in an orange colour. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 11.5 mg, 3.5 %

2-Aminopyrazine (1 mmol, 0.095 g) was added to benzaldehyde (1 mmol, 0.106 g) in 1:1 methanol/acetonitrile (20 mL) and stirred for 10 min. Ferric chloride hydrate (2 mmol, 0.541 g) was then added to this solution resulting in an orange colour. The solution was filtered after 20 min stirring and small purple rectangular plate-like crystals formed after several days of slow solvent evaporation. The crystals were then washed with acetone. Yield: 25.7 mg, 8.9 %

IR (cm\(^{-1}\)): 639, 775, 1014, 1207, 1292, 1351, 1417, 1619, 1657, 3050, 3147, 3309

Elemental Calc. (Found): C, 24.65 (23.20), H, 3.10 (3.01), N, 21.56 (20.49)

2. UV-Vis Experiments

Fig S1: UV-Vis of salicylaldehyde oxidation at 2x10\(^{-4}\) M. 0 µl corresponds to the appropriate salicylaldehyde and 2-aminopyrazine only being present in the cuvette. Then additions of 2x10\(^{-5}\) M
FeCl$_3$H$_2$O in aliquots of 100 µL over 10 additions, followed by the addition of 1 mL of the same solution to the cuvette.

3. X-ray data analysis.

A suitable crystal was selected and mounted on an Xcalibur, Sapphire3, Gemini diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimisation.

Empirical formula $\text{C}_8\text{H}_{12}\text{Cl}_4\text{FeN}_6$

Formula weight 389.88

Temperature/K 149.99(10)

Crystal system triclinic

Space group P-1

\begin{align*}
a/\text{Å} & \quad 7.1768(5) \\
b/\text{Å} & \quad 7.3352(5) \\
c/\text{Å} & \quad 7.8852(6) \\
\alpha/^\circ & \quad 115.541(7) \\
\beta/^\circ & \quad 110.288(7) \\
\gamma/^\circ & \quad 96.890(6) \\
\text{Volume/Å}^3 & \quad 333.02(5) \\
Z & \quad 1 \\
\rho_{\text{calc}}/\text{g/cm}^3 & \quad 2.172 \\
\mu/\text{mm}^{-1} & \quad 1.363 \\
F(000) & \quad 225.0 \\
\text{Radiation} & \quad \text{MoKα (λ = 0.71073)} \\
\text{2θ range for data collection/°} & \quad 6.384 \text{ to } 58.958 \\
\text{Index ranges} & \quad -6 \leq h \leq 9, \ -9 \leq k \leq 7, \ -9 \leq l \leq 10 \\
\text{Reflections collected} & \quad 2663 \\
\text{Independent reflections} & \quad 1524 \ [R_{\text{int}} = 0.0235, \ R_{\text{sigma}} = 0.0382] \\
\text{Data/restraints/parameters} & \quad 1524/0/88 \\
\text{Goodness-of-fit on } F^2 & \quad 0.823 \\
\text{Final R indexes [I>=2σ(I)]} & \quad R_1 = 0.0323, \ wR_2 = 0.1016
Final R indexes [all data] \( R_1 = 0.0363 \), \( wR_2 = 0.1082 \)

Largest diff. peak/hole / e Å\(^3\) 0.64/-0.46

Fig. S2: \( \pi-\pi \) stacking in 1. The displaced motif occurs between the complexes in red while the sandwich-type stacking motif occurs between the white and red complexes.
4. Magnetic Measurements

All measurements were carried out on a Quantum Design MPMS® SQUID XL-7. The sample was restrained in an eicosane matrix. DC magnetic susceptibility was carried out between 300 and 2 K in an applied field of 1000 Oe. AC susceptibility was carried out under 3 Oe AC field with various applied DC fields at 2 K. (see Fig S4.)
Fig S4: AC susceptibility for complex 1 at 2 K.
5. Computational details.

Geometries were optimised using density functional theory (DFT) with the ωB97X-D functional\(^1\) and Stuttgart-Bonn TZVP basis set and pseudopotential\(^2\) (the 6-311G(d) basis set is used for H, C, N and Cl atoms\(^3,4\)). Gas-phase geometries were optimised with and without symmetry, allowing the \(\text{C}_i\) symmetry of the molecule to break. Harmonic vibrational frequencies were calculated to confirm the geometries as true minima. Further geometry optimisations including solvent effects were performed using the polarisable continuum solvent (PCM) model\(^5-7\) with a dielectric constant, \(\varepsilon\), of 78.39. Ligand dissociation energies were calculated by optimising the geometries of the different fragments (see figures S5 and S6, below). All calculations were performed with the Q-Chem software.\(^8\)

**Figure S5.** Molecular orbitals calculated using DFT at the gas-phase, symmetry broken geometry. SOMO-1 (top left); SOMO (top right); LUMO (bottom left); LUMO+1 (bottom right).
Figure S6. Molecular orbitals calculated using DFT with the optimised geometry within a polarisable continuum solvent (water). SOMO-1 (top left); SOMO (top right); LUMO (bottom left); LUMO+1 (bottom right).
References