This dataset contains:

Analytical characterisation of the new complexes (CHN microanalysis).

^{1}H and ^{13}C NMR spectra of the new organic ligands (raw data).

Paramagnetic ^{1}H NMR spectra of the iron complexes (raw data).

Electrospray mass spectra (plotted spectra).

X-ray Crystallographic data:
- Structure of HL^1 (CCDC 1861171).
- Structure of HL^2 (CCDC 1938350).
- Structure of **1**·6MeCN at 100 K (CCDC 1861172).
- Structure of **1**·6MeCN at 150 K (CCDC 1861173).
- Structure of **1**·6MeCN at 200 K (CCDC 1861174).
- Structure of **1**·6MeCN at 250 K (CCDC 1861175).
- Structure of **2**·xMeCN·yE$_{t2}$O at 125 K (CCDC 1938349).
- Structure of **2**·xMeCN·yE$_{t2}$O at 200 K (CCDC 1938353).
- Structure of **2**·xMeCN·yE$_{t2}$O at 250 K (CCDC 1938352).
- Structure of **3** (CCDC 1861176).
- Structure of **4** (CCDC 1938351).
- Structure of **5**·H_2O (CCDC 1861177).

Solid state magnetic susceptibility measurements (raw and processed data).

Solution magnetic susceptibility measurements (raw NMR spectra and processed data)

X-ray powder diffraction data (measured and simulated).

Mössbauer spectra in this study were run at the Technical University of Kaiserslautern, and those data should be obtained from there (contact Prof Dr V. Schünemann, schuene@physik.uni-kl.de)

Photomagnetic and diffuse reflectance data in this study were measured at the CNRS ICMCB institute, Bordeaux, France. Those data should be obtained from there (contact Dr G. Chastanet, guillaume.chastanet@icmcb.cnrs.fr).
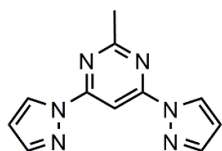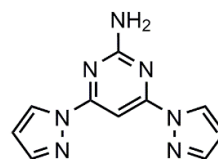
Ligands employed in this study
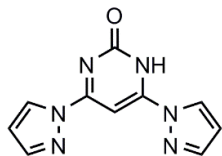
4,6-Di(pyrazol-1-yl)-1H-pyrimid-2-one
$C_{10}H_8N_6O$
HL^1
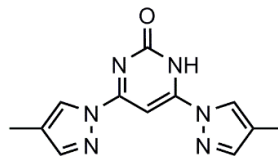
4,6-Di(4-methylpyrazol-1-yl)-1H-pyrimid-2-one
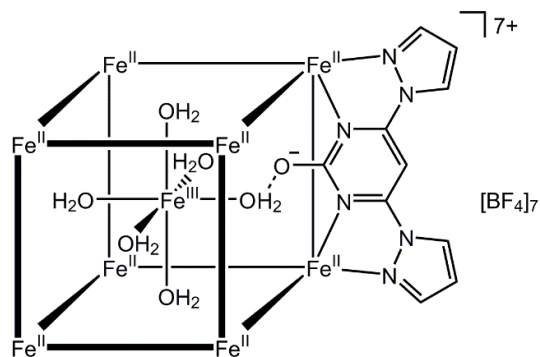$C_{12}H_{12}N_6O$
HL^2

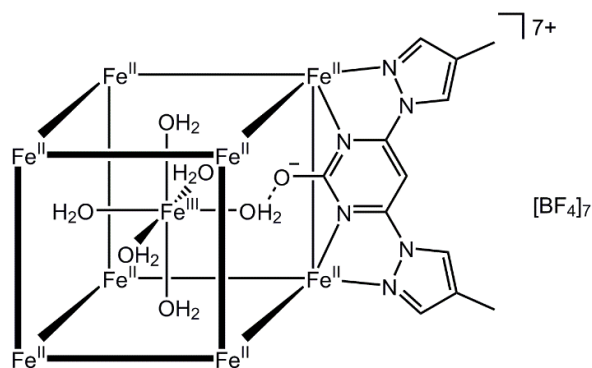**2-Methyl-4,6-di(pyrazol-1-yl)pyrimidine**
$C_{11}H_{10}N_6$
L^3

2-Amino-4,6-di(pyrazol-1-yl)pyrimidine
$C_{10}H_9N_7$
L^4

Complexes employed in this study

$[\{Fe(OH_2)_6\}Fe_8(\mu\text{-}L^1)_{12}][BF_4]_7$
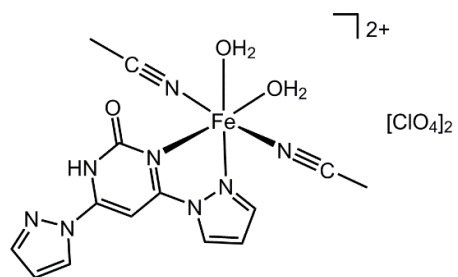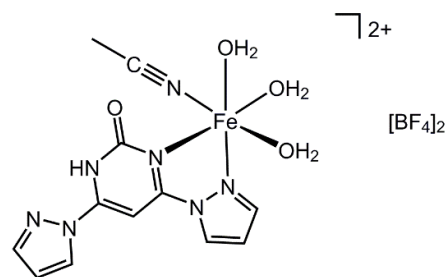$C_{120}H_{96}B_7F_{28}Fe_9N_{72}O_{18}$
1

$[\{Fe(OH_2)_6\}Fe_8(\mu\text{-}L^2)_{12}][BF_4]_7$
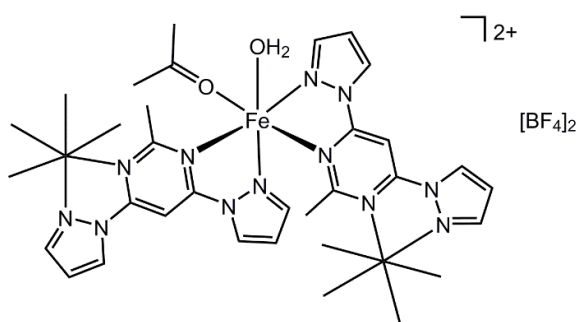$C_{144}H_{144}B_7F_{28}Fe_9N_{72}O_{18}$
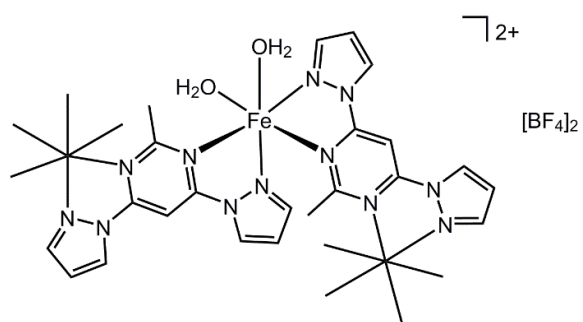**2**

Complexes employed in this study (continued)

[Fe(H*L*^{1})(OH$_2$)$_2$(NCCH$_3$)$_2$][ClO$_4$]$_2$
C$_{14}$H$_{18}$Cl$_2$FeN$_8$O$_{11}$
3

[Fe(H*L*^{1})(OH$_2$)$_3$(NCCH$_3$)][BF$_4$]$_2$
C$_{12}$H$_{17}$B$_2$F$_8$FeN$_7$O$_4$
4

catena-[Fe(μ-*L*^{3})(OH$_2$)(OC{CH$_3$}$_2$)][BF$_4$]$_2$
C$_{14}$H$_{18}$B$_2$F$_8$FeN$_6$O$_2$
5

catena-[Fe(μ-*L*^{3})(OH$_2$)$_2$][BF$_4$]$_2$
C$_{11}$H$_{14}$B$_2$F$_8$FeN$_6$O$_2$
5b