The dataset contains:

Analytical characterisation of the complexes (CHN microanalysis)

X-ray Crystallographic data:

- Structure of L^1 (CCDC 2099823)
- Structure of L^2 (CCDC 2099824)
- Structure of L^4 (CCDC 2099825)
- Structure of L^5 (CCDC 2099826)
- Structure of $[Fe(L^1)_4(OH_2)_2][ClO_4]_2 \cdot 2MeCN$ (**1[ClO$_4$]$_2$**·2MeCN – CCDC 2099827)
- Structure of $[Fe(NCS)_2(L^1)_2(OH_2)_2][ClO_4]_2 \cdot L^1$ (**2**·L^1 – CCDC 2099828)
- Structure of $[Cu(\mu\text{-}L^1)_2(OH_2)_2][BF_4]_2 \cdot 2MeCN$ (**3[BF$_4$]$_2$**·2MeCN – CCDC 2099829)
- Structure of $[Fe(L^2)_2][ClO_4]_2 \cdot 2MeNO_2$ (**4[ClO$_4$]$_2$**·$2MeNO_2$ – CCDC 2099835)
- Structure of $[Fe(L^3)_2][ClO_4]_2 \cdot 2H_2O$ (**5[ClO$_4$]$_2$**·$2H_2O$ – CCDC 2099836)
- Structure of $[Fe(L^3)_2][ClO_4]_2 \cdot 2MeCN$ (**5[ClO$_4$]$_2$**·2MeCN – CCDC 2099837)
- Structure of $[Co(L^3)_2][BF_4]_2 \cdot H_2O$ (**6[BF$_4$]$_2$**·H_2O – CCDC 2099838)
- Structure of $[Fe(L^4)_2][ClO_4]_2 \cdot 3MeNO_2$ (**7[ClO$_4$]$_2$**·$3MeNO_2$ phase 1 – CCDC 2099839)
- Structure of $[Fe(L^4)_2][ClO_4]_2 \cdot 3MeNO_2$ (**7[ClO$_4$]$_2$**·$3MeNO_2$ phase 2 – CCDC 2099840)
- Structure of $[Fe(L^4)_2][ClO_4]_2 \cdot x MeNO_2$ (**7[ClO$_4$]$_2$**·xMeNO$_2$; $x \approx 0.93$ – CCDC 2099869)
- Structure of $[Fe(L^4)_2][ClO_4]_2 \cdot H_2O$ (**7[ClO$_4$]$_2$**·H_2O – CCDC 2099841)
- Structure of $[Fe(L^5)_2][BF_4]_2$ (**8[BF$_4$]$_2$** – CCDC 2099842)
- Structure of $[Fe(L^5)_2][BF_4]_2 \cdot MeCN \cdot H_2O$ (**8[BF$_4$]$_2$**·MeCN·H_2O – CCDC 2099843)
- Structure of $[Fe(L^5)_2][BF_4]_2 \cdot y MeCN$ (**8[BF$_4$]$_2$**·yMeCN; $x \approx 2.3$ – CCDC 2099844)

plus

- Structure of uncertain formula, either $[Fe(L^3)_2][ClO_4]X \cdot 2H_2O$ (**5[ClO$_4$]X**·$2H_2O$, X^- = a monoatomic anion) or $[Fe(L^3)(L^3\text{–H})]ClO_4 \cdot 3H_2O$ ([**5–H]ClO$_4$**·$3H_2O$ – not deposited with the CCDC)

X-ray powder diffraction data (measured and simulated)

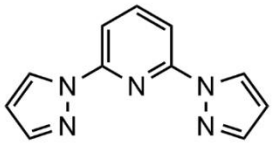
^{1}H NMR spectra (raw data and plotted spectra).

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

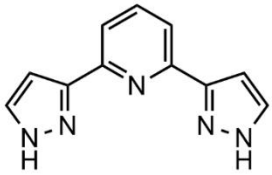
Solution magnetic susceptibility measurements (raw spectra and calculated χ_MT values).

DFT calculations (*SPARTAN* files)

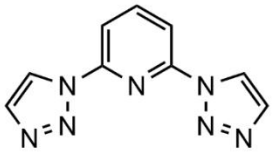
Ligands referred to in this study



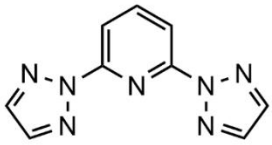
2,6-Di(pyrazol-1-yl)pyridine
$C_{11}H_9N_5$
1-bpp



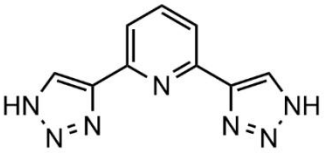
2,6-Di(1*H*-pyrazol-3-yl)pyridine
$C_{11}H_9N_5$
3-bpp



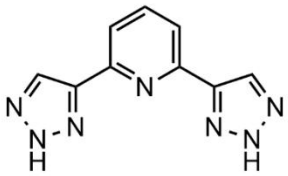
2,6-Di(1,2,3-triazol-1-yl)pyridine
$C_9H_7N_7$
L^1



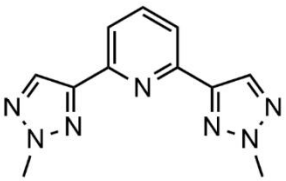
2,6-Di(1,2,3-triazol-2-yl)pyridine
$C_9H_7N_7$
L^2



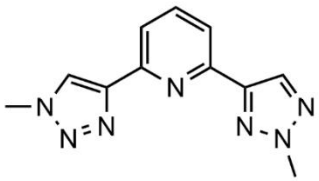
2,6-Di(1*H*-1,2,3-triazol-4-yl)pyridine
$C_9H_7N_7$
L^3



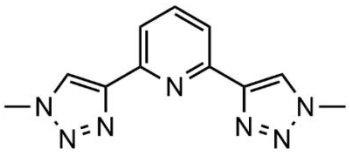
2,6-Di(2*H*-1,2,3-triazol-4-yl)pyridine
$C_9H_7N_7$
$L^{3'}$



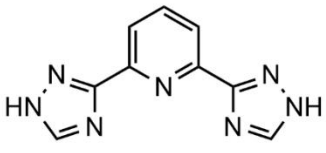
2,6-Di(2-methyl-1,2,3-triazol-4-yl)pyridine
$C_{11}H_{11}N_7$
L^4



2-(1-Methyl-1,2,3-triazol-4-yl)-6-
(2-methyl-1,2,3-triazol-4-yl)pyridine
$C_{11}H_{11}N_7$
L^5

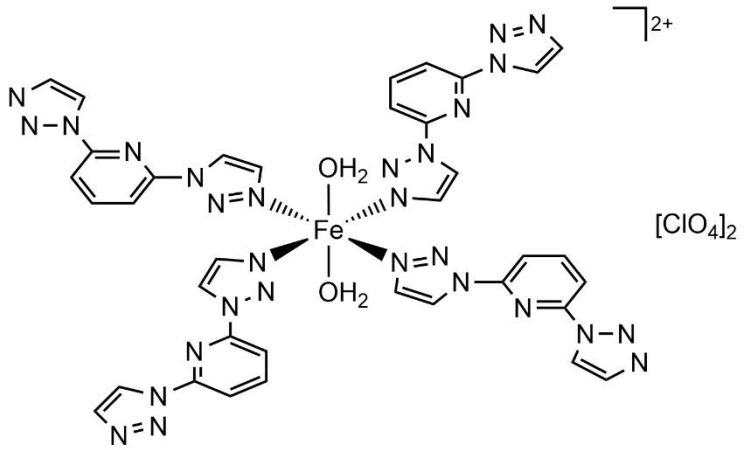


2,6-Di(1-methyl-1,2,3-triazol-4-yl)pyridine
$C_{11}H_{11}N_7$
$b3tp^{Me}$

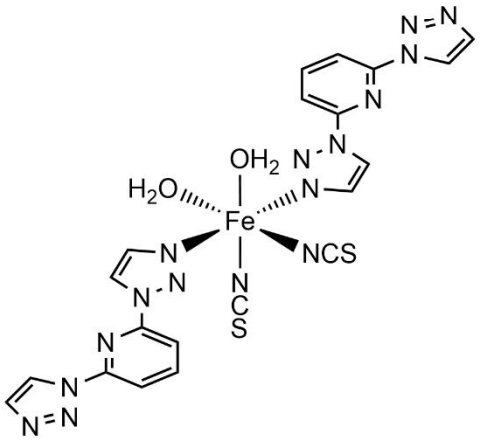


2,6-Di(1*H*-1,2,4-triazol-3-yl)pyridine
$C_9H_7N_7$
$b4tp^{H}$

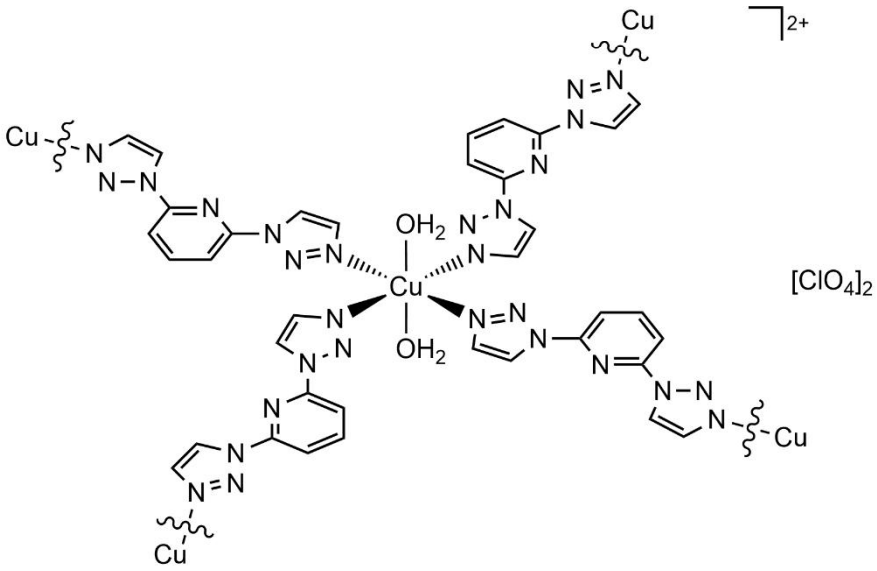
Complexes referred to in this study



Tetrakis[2,6-bis(1,2,3-triazol-1-yl)pyridine]diaqua-iron(II) diperchlorate
$C_{36}H_{32}Cl_2FeN_{28}O_{10}$
1[ClO$_4$]$_2$

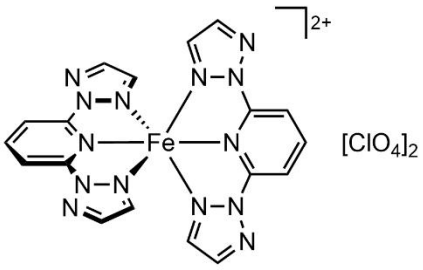


Di(isothiocanato)bis[2,6-bis(1,2,3-triazol-1-yl)pyridine]diaqua-iron(II)
$C_{20}H_{18}FeN_{16}O_2S_2$
2

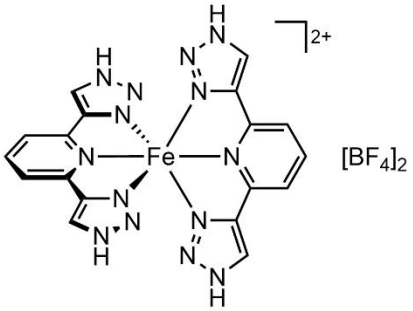


Bis[2,6-bis(1,2,3-triazol-1-yl)pyridine]diaqua-copper(II) di(tetrafluoroborate)
$C_{18}H_{18}B_2CuF_8N_{14}O_2$
3[BF$_4$]$_2$

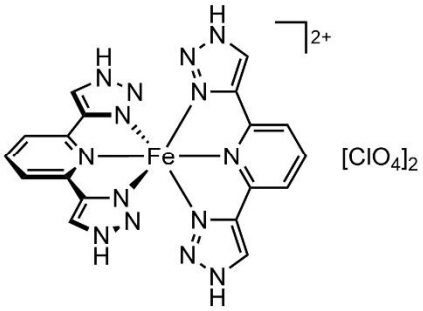
Complexes referred to in this study (continued)



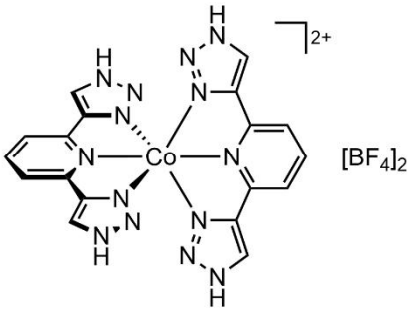
Bis[2,6-bis(1,2,3-triazol-2-yl)pyridine]iron(II) diperchlorate
$C_{18}H_{14}Cl_2FeN_{14}O_8$
4[ClO$_4$]$_2$



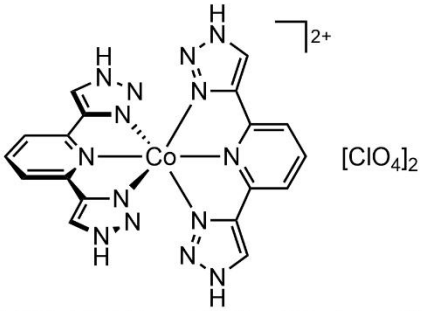
Bis[2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridine]iron(II) di(tetrafluoroborate)
$C_{18}H_{14}B_2F_8FeN_{14}$
5[BF$_4$]$_2$



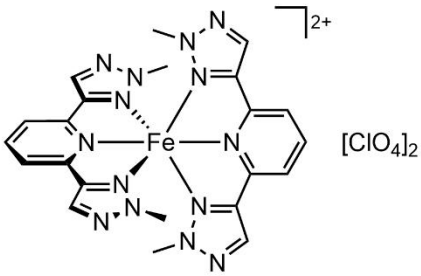
Bis[2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridine]iron(II) diperchlorate
$C_{18}H_{14}Cl_2FeN_{14}O_8$
5[ClO$_4$]$_2$



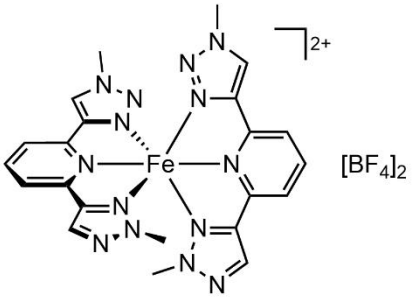
Bis[2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridine]cobalt(II) di(tetrafluoroborate)
$C_{18}H_{14}B_2CoF_8N_{14}$
6[BF$_4$]$_2$



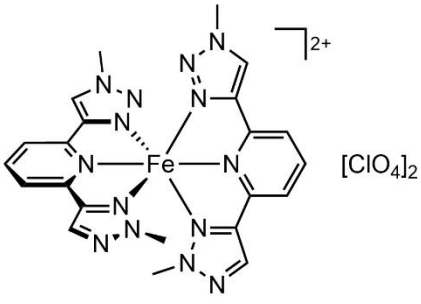
Bis[2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridine]cobalt(II) diperchlorate
$C_{18}H_{14}Cl_2CoN_{14}O_8$
6[ClO$_4$]$_2$



Bis[2,6-bis(2-methyl-1,2,3-triazol-4-yl)pyridine]iron(II) diperchlorate
$C_{22}H_{22}Cl_2FeN_{14}O_8$
7[ClO$_4$]$_2$

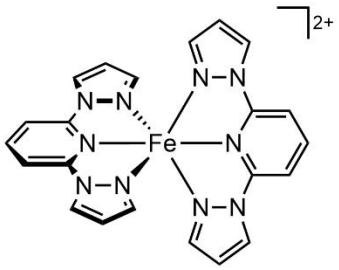


Bis[2-(1-methyl-1,2,3-triazol-4-yl)-6-(2-methyl-1,2,3-triazol-4-yl)pyridine]-iron(II) di(tetrafluoroborate)
$C_{22}H_{22}B_2F_8FeN_{14}$
8[BF$_4$]$_2$

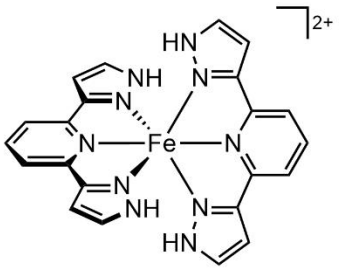


Bis[2-(1-methyl-1,2,3-triazol-4-yl)-6-(2-methyl-1,2,3-triazol-4-yl)pyridine]-iron(II) diperchlorate
$C_{22}H_{22}Cl_2FeN_{14}O_8$
8[ClO$_4$]$_2$

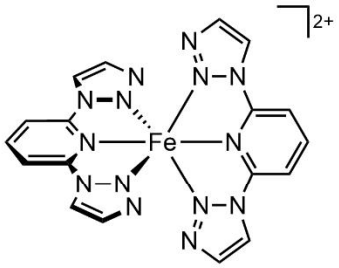
Complex cations studied by DFT calculations



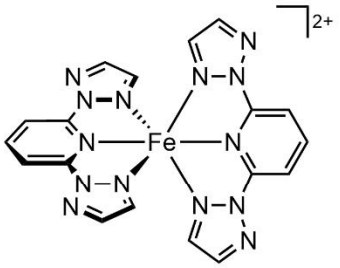
Bis[2,6-bis(pyrazol-1-yl)pyridine]iron(II)
$C_{22}H_{18}FeN_{10}$
$[Fe(1\text{-bpp})_2]^{2+}$



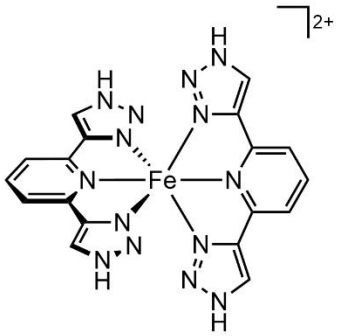
Bis[2,6-bis(1*H*-pyrazol-3-yl)pyridine]iron(II)
$C_{22}H_{18}FeN_{10}$
$[Fe(3\text{-bpp})_2]^{2+}$



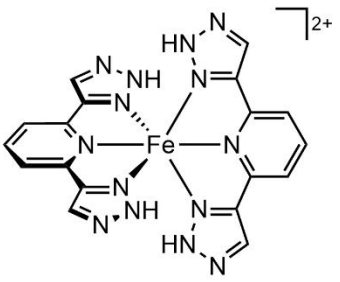
Bis[2,6-bis(1,2,3-triazol-1-yl)pyridine]iron(II)
$C_{18}H_{14}FeN_{14}$
$[Fe(L^1)_2]^{2+}$



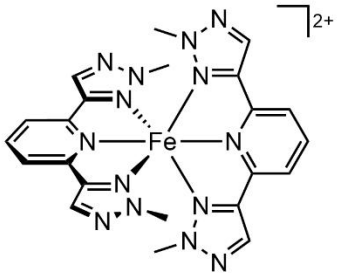
Bis[2,6-bis(1,2,3-triazol-2-yl)pyridine]iron(II)
$C_{18}H_{14}FeN_{14}$
$[Fe(L^2)_2]^{2+}$



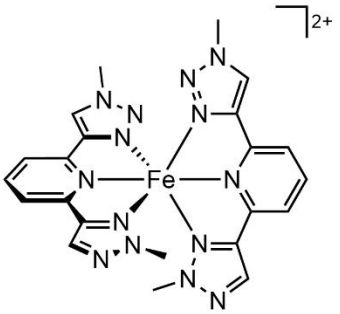
Bis[2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridine]iron(II)
$C_{18}H_{14}FeN_{14}$
$[Fe(L^3)_2]^{2+}$



Bis[2,6-bis(2*H*-1,2,3-triazol-4-yl)pyridine]iron(II)
$C_{18}H_{14}FeN_{14}$
$[Fe(L^{3'})_2]^{2+}$

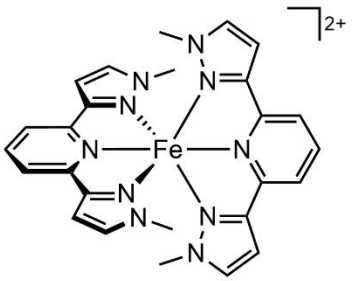


Bis[2,6-bis(2-methyl-1,2,3-triazol-4-yl)pyridine]iron(II)
$C_{22}H_{22}FeN_{14}$
$[Fe(L^4)_2]^{2+}$

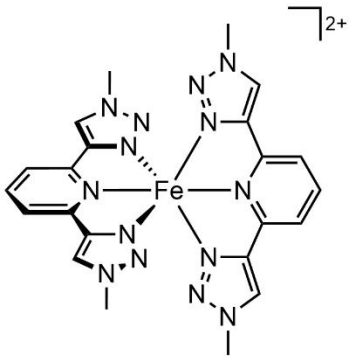


Bis[2-(1-methyl-1,2,3-triazol-4-yl)-6-
(2-methyl-1,2,3-triazol-4-yl)pyridine]iron(II)
$C_{22}H_{22}FeN_{14}$
$[Fe(L^5)_2]^{2+}$

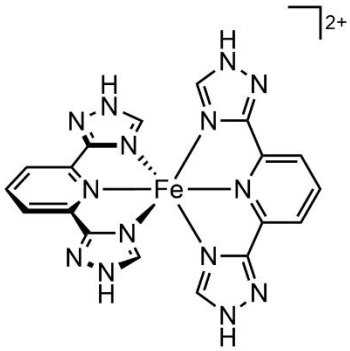
Complex cations studied by DFT calculations (continued)



Bis[2,6-bis(1-methylpyrazol-3-yl)pyridine]iron(II)
$C_{26}H_{26}FeN_{10}$
$[Fe(3\text{-}bpp^{Me})_2]^{2+}$



Bis[2,6-bis(1-methyl-1,2,3-triazol-4-yl)pyridine]iron(II)
$C_{22}H_{22}FeN_{14}$
$[Fe(b3tp^{Me})_2]^{2+}$



Bis[2,6-bis(1*H*-1,2,4-triazol-3-yl)pyridine]iron(II)
$C_{18}H_{14}FeN_{14}$
$[Fe(b4tp^{H})_2]^{2+}$