**Title:** Data to support Iron(II) Complexes of 2,6-*Bis*(imidazo[1,2-a]pyridin-2-yl)pyridine and Related Ligands with Annelated Distal Heterocyclic Donors

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**Organisation(s):** 1. University of Leeds, UK.



**Publication Year:** 2023

**Description:** Following a published synthesis of 2,6-*bis*(imidazo[1,2-a]pyridin-2-yl)pyridine ($L^1$), treatment of $\alpha,\alpha'$-dibromo-2,6-diacetyl-pyridine with 2 equiv 2-aminopyrimidine or 2-aminoquinoline in refluxing acetonitrile respectively gives 2,6-*bis*(imidazo[1,2-a]pyrimidin-2-yl)pyridine ($L^2$) and 2,6-*bis*(imidazo[1,2-a]quinolin-2-yl)pyridine ($L^3$). Solvated crystals of $[Fe(L^1)_2][BF_4]_2$ (**1[BF$_4$]$_2$**) and $[Fe(L^2)_2][BF_4]_2$ (**2[BF$_4$]$_2$**) are mostly high-spin, although one solvate of **1[BF$_4$]$_2$** undergoes thermal spin-crossover on cooling. The iron coordination geometry is consistently distorted in crystals of **2[BF$_4$]$_2$** which may reflect the influence of intramolecular, inter-ligand N$\cdots\pi$ interactions on the molecular conformation. Only 1:1 Fe:$L^3$ complexes were observed in solution, or isolated in the solid state; a crystal structure of $[FeBr(py)_2L^3]Br\cdot xH_2O$ (py = pyridine) is presented. A solvate crystal structure of high-spin $[Fe(L^4)_2][BF_4]_2$ ($L^4$ = 2,6-di{quinolin-2-yl}pyridine; **4[BF$_4$]$_2$**) is also described. The iron(II) complexes are high-spin in solution at room temperature, but **1[BF$_4$]$_2$** and **2[BF$_4$]$_2$** undergo thermal spin-crossover equilibria on cooling. All the compounds exhibit a ligand-based emission in solution at room temperature. Gas phase DFT calculations mostly reproduce the spin state properties of the complexes, but show small anomalies attributed to intramolecular, inter-ligand dispersion interactions in the sterically crowded molecules.

**Cite as:** Kulmaczewski, Rafal and Halcrow, Malcolm A. (2023). Data to support Iron(II) Complexes of 2,6-*Bis*(imidazo[1,2-a]pyridin-2-yl)pyridine and Related Ligands with Annelated Distal Heterocyclic Donors. University of Leeds. [Dataset] https://doi.org/10.5518/1413

**Related publication:** Kulmaczewski, Rafal and Halcrow, Malcolm A. (2023). Iron(II) Complexes of 2,6-*Bis*(imidazo[1,2-a]pyridin-2-yl)pyridine and Related Ligands with Annelated Distal Heterocyclic Donors. *Dalton Transactions*, doi: 10.1039/d3dt02747c

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## 2. TERMS OF USE



## 3. PROJECT AND FUNDING INFORMATION

Title: Understanding and Engineering Function in Switchable Molecular Crystals
Dates: 2013-2018
Funding organisation: EPSRC
Grant no.: EP/K012576/1

## 4. CONTENTS

The dataset contains data for this study:

NMR spectra (raw and processed data – *NMR*.zip).

Electrospray mass spectra (plotted spectra – *ESMS*.zip).

Elemental microanalyses (*microanalysis.zip*).

X-ray Crystallographic data (*crystal*.zip):

- Structure of **1[$BF_4$]$_2$**·MeCN (CCDC 2288873)
- Structure of **1[$BF_4$]$_2$**·*m*$MeNO_2$ (CCDC 2288874)
- Structure of **1[$BF_4$]$_2$**·1.7$MeNO_2$·0.3$Et_2O$ (CCDC 2288875)
- Structure of **1[$BF_4$]$_2$**·1.5MeOH (CCDC 2288876)
- Structure of **2[$BF_4$]$_2$**·1.5MeCN (CCDC 2288877)
- Structure of **2[$BF_4$]$_2$**·$Me_2CO$ (CCDC 2288878)
- Structure of **2[$BF_4$]$_2$**·3.5$MeNO_2$·0.5$Et_2O$ (CCDC 2288879)
- Structure of [$FeBr(py)_2(L^3)$]Br·0.5$H_2O$ (CCDC 2288880)
- Structure of **4[$BF_4$]$_2$**·1.39MeCN·0.125$Et_2O$·0.25$H_2O$ (CCDC 2288881)

X-ray powder diffraction data (measured and simulated – *XRPD*.zip).

Solid state magnetic susceptibility measurements (raw and processed data – *SQUID*.zip).

Solution magnetic susceptibility measurements (raw and processed data – *Evans*.zip).

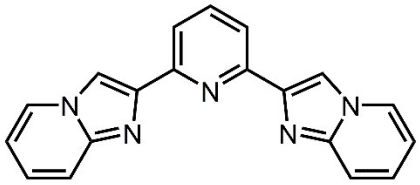
UV/visible absorption and emission spectra (plotted spectra in *Origin* – *UVvis*.zip).

Density functional calculations (*SPARTAN* files – *DFT*.zip)

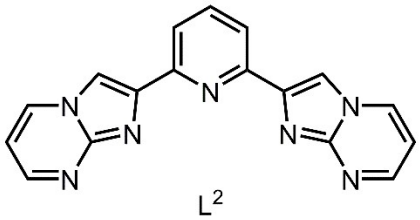
## 5. METHODS

Full details are provided in the related publication, listed above.

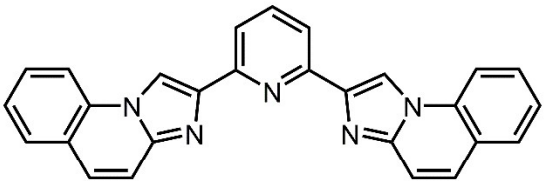
## Organic ligands referred to in this dataset



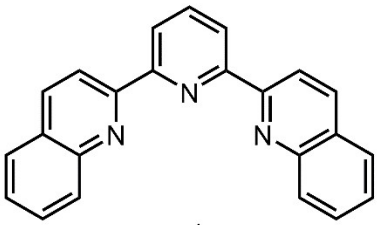
$L^1$
2,6-Bis(imidazo[1,2-a]pyridin-2-yl)pyridine
$C_{19}H_{13}N_5$



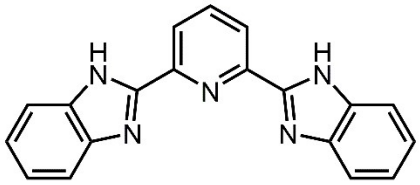
$L^2$
2,6-Bis(imidazo[1,2-a]pyridin-2-yl)pyrimidine
$C_{17}H_{11}N_7$



$L^3$
2,6-Bis(imidazo[1,2-a]quinolin-2-yl)pyridine
$C_{27}H_{17}N_5$

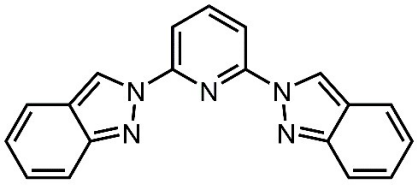


$L^4$
2,6-Di{quinolin-2-yl}pyridine
$C_{23}H_{15}N_3$



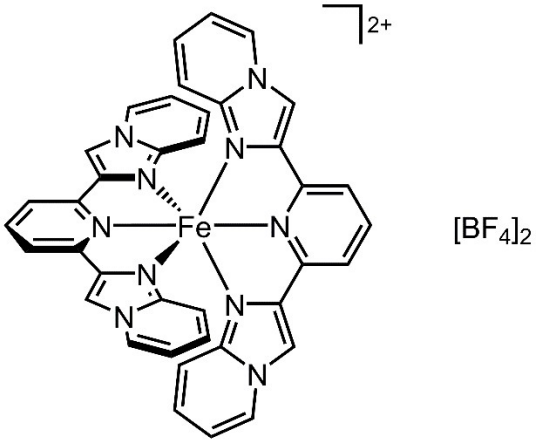
bimpy
2,6-Bis(benzimidazol-2-yl)pyridine
$C_{19}H_{13}N_5$

## Organic ligands referred to in this dataset (continued)



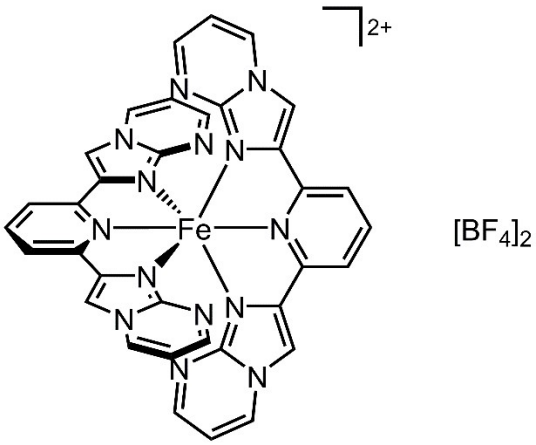
2-bip
2,6-Bis(indazol-2-yl)pyridine
$C_{19}H_{13}N_5$

## Metal complexes referred to in this dataset



$[BF_4]_2$

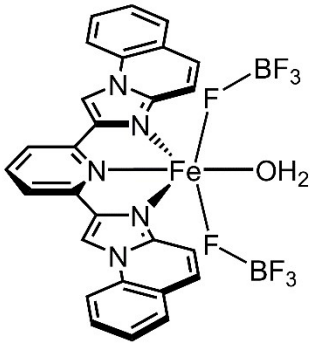
**$1[BF_4]_2$**
$[Fe(L^1)_2][BF_4]_2$
Bis[2,6-bis(imidazo[1,2-a]pyridin-2-yl)pyridine]iron(II) ditetrafluoroborate
$C_{38}H_{26}B_2F_8FeN_{10}$



$[BF_4]_2$

**$2[BF_4]_2$**
$[Fe(L^2)_2][BF_4]_2$
Bis[2,6-bis(imidazo[1,2-a]pyrimidin-2-yl)pyridine]iron(II) ditetrafluoroborate
$C_{34}H_{22}B_2F_8FeN_{14}$

## Metal complexes referred to in this dataset (continued)

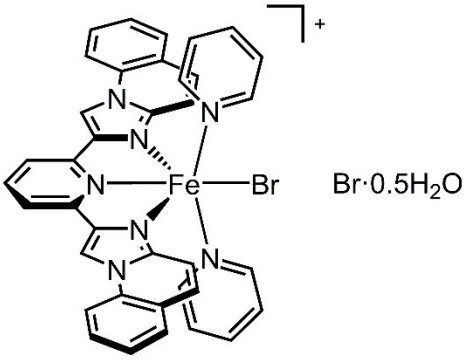



**3'[$BF_4$]$_2$**·$H_2O$

[$FeL^3$][$BF_4$]$_2$·$H_2O$ (analytical formula - the exact connectivity is unknown)

[2,6-Bis(imidazo[1,2-a]quinolin-2-yl)pyridine]bis(pyridine)]iron(II) ditetrafluoroborate hydrate

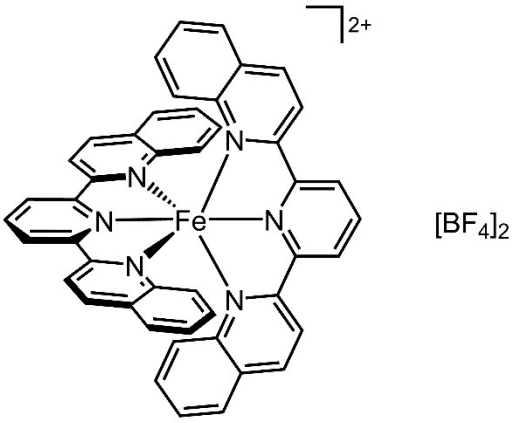
$C_{27}H_{19}B_2F_8FeN_5O$




[$FeBr(pyridine)_2L^3$]Br·$0.5H_2O$

Bromo[2,6-bis(imidazo[1,2-a]quinolin-2-yl)pyridine]bis(pyridine)iron(II) bromide hemihydrate

$C_{37}H_{28}Br_2FeN_7O_{0.5}$



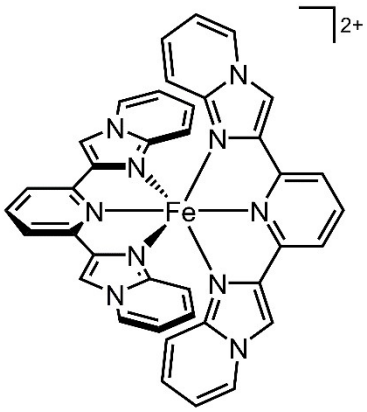

**4[$BF_4$]$_2$**

[$Fe(L^4)_2$][$BF_4$]$_2$

Bis[2,6-bis(quinolin-2-yl)pyridine]iron(II) ditetrafluoroborate

$C_{46}H_{30}B_2F_8FeN_6$

## Molecules in the computational study

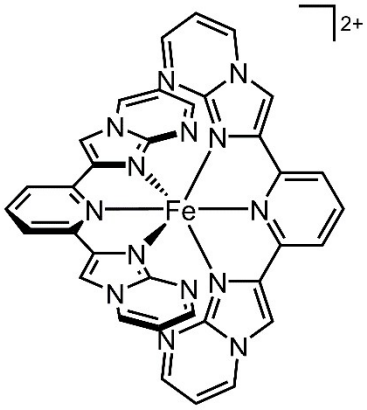



**$1^{2+}$**

$[Fe(L^1)_2]^{2+}$

Bis[2,6-bis(imidazo[1,2-a]pyridin-2-yl)pyridine]iron(II)

$C_{38}H_{26}FeN_{10}$

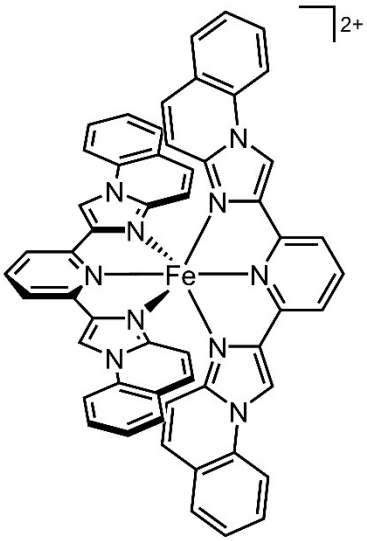



**$2^{2+}$**

$[Fe(L^2)_2]^{2+}$

Bis[2,6-bis(imidazo[1,2-a]pyrimidin-2-yl)pyridine]iron(II)

$C_{34}H_{22}FeN_{14}$



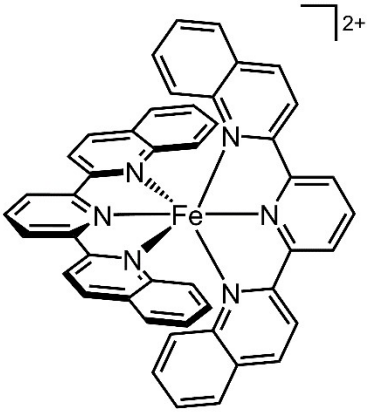

**$3^{2+}$**

$[Fe(L^3)_2]^{2+}$

Bis[2,6-Bis(imidazo[1,2-a]quinolin-2-yl)pyrimidine]iron(II)

$C_{54}H_{34}FeN_{10}$

## Molecules in the computational study (continued)

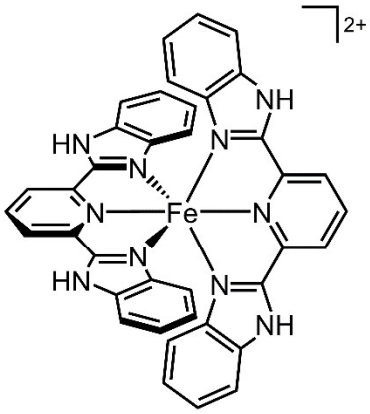



**$4^{2+}$**

$[Fe(L^4)_2]^{2+}$

Bis[2,6-bis(quinolin-2-yl)pyridine]iron(II)

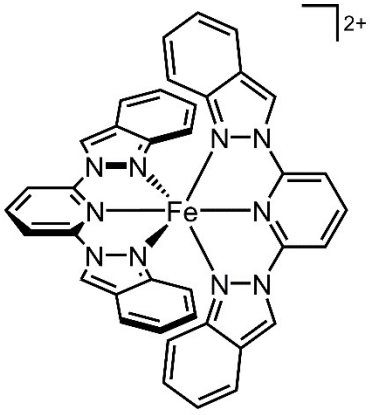
$C_{46}H_{30}FeN_6$




$[Fe(bimpy)_2]^{2+}$

Bis[2,6-bis(benzimidazol-2-yl)pyridine]iron(II)

$C_{38}H_{26}FeN_{10}$




$[Fe(2\text{-}bip)_2]^{2+}$

Bis[2,6-bis(indazol-2-yl)pyridine]iron(II)

$C_{38}H_{26}FeN_{10}$