Title: Data to support A Survey of the Angular Distortion Landscape in the Coordination Geometries of High-Spin Iron(II) 2,6-Bis(pyrazolyl)pyridine Complexes

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Publication Year: 2024

Description: The iron(II) complexes $[FeL_2][BF_4]_2$ (**1a**; *L* = 4-(3,4-dimethoxyphenylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine) and $[FeL_2][ClO_4]_2$ (**1b**) are high-spin with a highly distorted six-coordinate geometry. This structural deviation from ideal D_{2d} symmetry is caused by an angular Jahn-Teller distortion, which is common in high-spin $[Fe(bpp)_2]^{2+}$ (bpp = di{pyrazol-1-yl}pyridine) derivatives and some related compounds. However, the magnitude of the distortion in **1a** and **1b** is the largest yet discovered in a mononuclear complex. Gas phase DFT calculations identified four minimum or local minimum structural pathways across the distortion landscape, all of which are observed experimentally in different complexes. Small distortions from D_{2d} symmetry are energetically favorable in complexes with electron-donating ligand substituents, and also have smaller energy penalties associated with the lowest energy distortion pathway. Natural population analysis showed these differences reflect greater changes to the Fe–N{pyridyl} σ-bonding as the distortion proceeds, in the presence of more electron-rich pyridyl donors.

Cite as: Capel Berdiell, Izar, Michaels, Evridiki, Munro, Orde Q., and Halcrow, Malcolm A. (2023). Data to support The Most Distorted Coordination Geometry in a Mononuclear Iron(II) Di(pyrazolyl)pyridine Complex. University of Leeds. [Dataset] https://doi.org/10.5518/1452

Related publication: Capel Berdiell, Izar, Michaels, Evridiki, Munro, Orde Q., and Halcrow, Malcolm A. (2024). A Survey of the Angular Distortion Landscape in the Coordination Geometries of High-Spin Iron(II) 2,6-Bis(pyrazolyl)pyridine Complexes. *Inorganic Chemistry*, doi: 10.1021/acs.inorgchem.3c04138.

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2. TERMS OF USE

3. PROJECT AND FUNDING INFORMATION

Title: Exploiting a Spin-Crossover Module in Materials Chemistry and Nanoscience
Dates: 2015-2019
Funding organisation: The Leverhulme Trust
Grant no.: RPG-2015-095

4. CONTENTS

The dataset contains data for this study:

Elemental microanalyses (*microanalysis.zip*).

NMR and electrospray mass spectra (raw and processed data – *NMR-ESMS*.zip)

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

- Structure of *L* at 120 K (CCDC 2260605)
- Structure of **1a** at 120 K (CCDC 2260606)
- Structure of **1b** at 120 K (CCDC 2260607)
- Structure of $[Fe(bpp)_2][CF_3SO_3]_2$ at 120 K (CCDC 2260608)

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

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

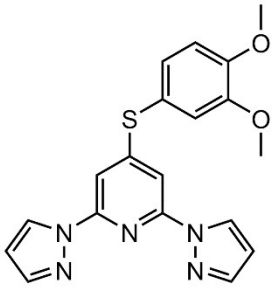
Solution magnetic susceptibility measurements (raw and processed data – *Evans*.zip).

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

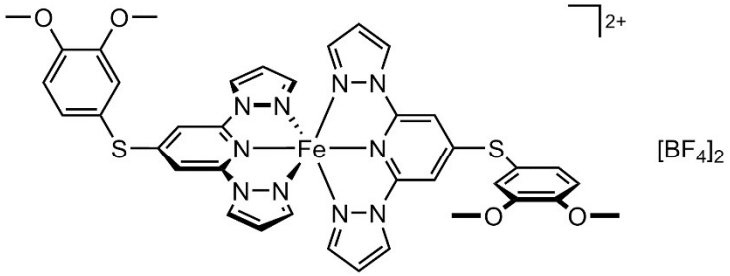
5. METHODS

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

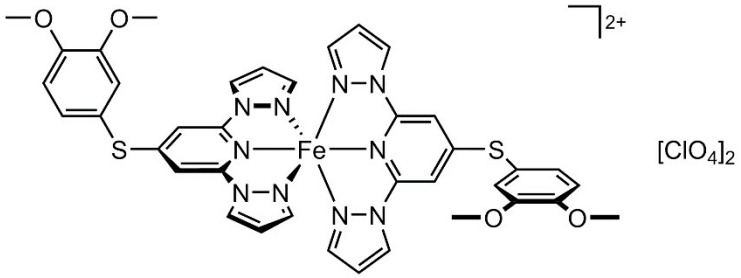
Compounds referred to in this dataset



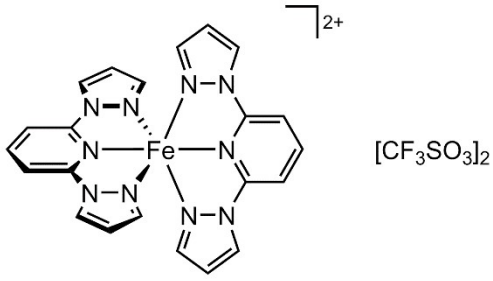
L
4-(3,4-Dimethoxyphenylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine
$C_{19}H_{17}N_5O_2S$



1a
$[Fe\mathit{L}_2][BF_4]_2$
Bis[4-(3,4-dimethoxyphenylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine]iron(II) di-tetrafluoroborate
$C_{38}H_{34}B_2F_8FeN_{10}O_4S_2$

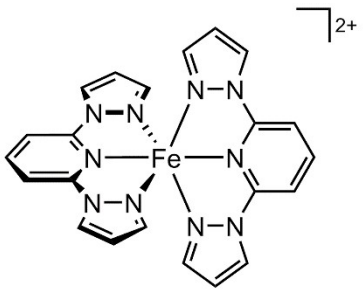


1b
$[Fe\mathit{L}_2][ClO_4]_2$
Bis[4-(3,4-dimethoxyphenylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine]iron(II) diperchlorate
$C_{38}H_{34}Cl_2FeN_{10}O_{12}S_2$

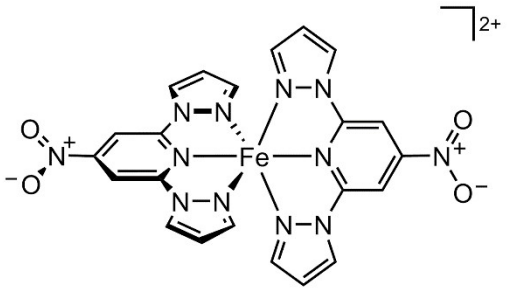


$[Fe(bpp)_2][CF_3SO_3]_2$
Bis[2,6-di(pyrazol-1-yl)pyridine]iron(II) di(trifluoromethanesulfonate)
$C_{24}H_{18}F_6FeN_{10}O_6S_2$

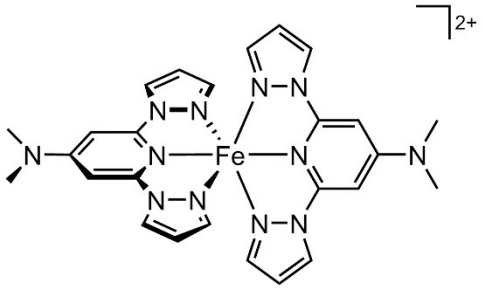
Complex cations studied by DFT calculations



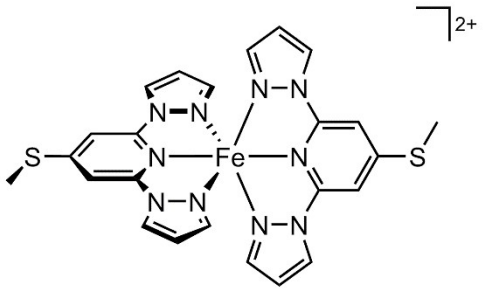
$[Fe(bpp)_2]^{2+}$
Bis[2,6-di(pyrazol-1-yl)pyridine]iron(II)
$[C_{22}H_{18}FeN_{10}]^{2+}$



$[Fe(bpp^{NO_2})_2]^{2+}$
Bis[4-nitro-2,6-di(pyrazol-1-yl)pyridine]iron(II)
$[C_{22}H_{16}FeN_{12}O_4]^{2+}$

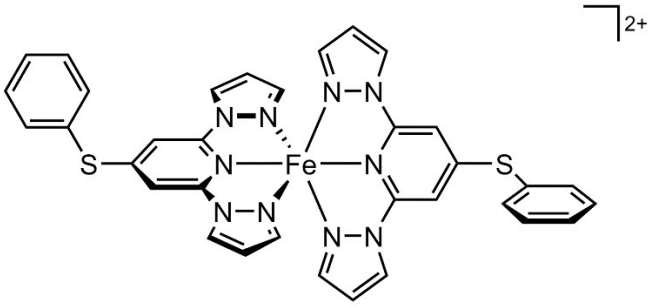


$[Fe(bpp^{NMe_2})_2]^{2+}$
Bis[4-(dimethylamino)-2,6-di(pyrazol-1-yl)pyridine]iron(II)
$[C_{26}H_{28}FeN_{12}]^{2+}$

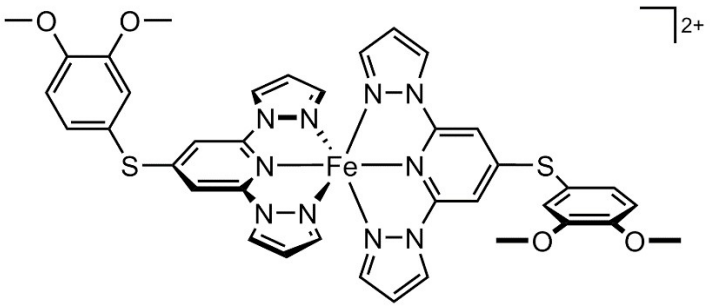


$[Fe(bpp^{SMe})_2]^{2+}$
Bis[4-(methylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine]iron(II)
$[C_{24}H_{22}FeN_{10}S_2]^{2+}$

Complex cations studied by DFT calculations (continued)



$[Fe(bpp^{SPh})_2]^{2+}$
Bis[4-(phenylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine]iron(II)
$[C_{34}H_{26}FeN_{10}S_2]^{2+}$



$[FeL_2]^{2+}$
Bis[4-(3,4-dimethoxyphenylsulfanyl)-2,6-di(pyrazol-1-yl)pyridine]iron(II)
$[C_{38}H_{34}FeN_{10}O_4S_2]^{2+}$