

**Title:** Data to support study of Structural Bifurcation in the High→Low-Spin and Low→High-Spin Phase Transitions Explains the Asymmetric Spin-Crossover in  $[\text{FeL}_2][\text{BF}_4]_2$  (L = 2,6-Di{pyrazol-1-yl}isonicotinonitrile)

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**Rights-holder(s):** Malcolm A. Halcrow

**Publication Year:** 2024

**Description:** The title compound exhibits a cooperative spin-transition with an unusual asymmetric hysteresis. It crystallizes as a mixture of two high-spin polymorphs HS1 and HS2, which convert simultaneously to the low-spin phases LS3 and LS4 on cooling. The HS1 and LS3 fractions increase at the expense of HS2 and LS4 upon repeated scanning, which reflects that HS2 converts to a mixture of LS3 and LS4 on cooling, and LS4 to HS1 and HS2 on rewarming.

**Cite as:** Ahmed, Ahmed, Hall, Amy, Vasili, Hari Babu, Kulmaczewski, Rafal, Kulak, Alexander N., Cespedes, Oscar, Pask, Christopher M., Brammer, Lee, Roseveare, Thomas M., and Halcrow, Malcolm A. (2024): Data to support study of Structural Bifurcation in the High→Low-Spin and Low→High-Spin Phase Transitions Explains the Asymmetric Spin-Crossover in  $[\text{FeL}_2][\text{BF}_4]_2$  (L = 2,6-Di{pyrazol-1-yl}isonicotinonitrile). [Dataset] <https://doi.org/10.5518/1564>

**Related publication:** Ahmed, Ahmed, Hall, Amy, Vasili, Hari Babu, Kulmaczewski, Rafal, Kulak, Alexander N., Cespedes, Oscar, Pask, Christopher M., Brammer, Lee, Roseveare, Thomas M., and Halcrow, Malcolm A. (2024): Structural Bifurcation in the High→Low-Spin and Low→High-Spin Phase Transitions Explains the Asymmetric Spin-Crossover in  $[\text{FeL}_2][\text{BF}_4]_2$  (L = 2,6-Di{pyrazol-1-yl}isonicotinonitrile). *Angewandte Chemie International Edition*, doi: 10.1002/anie.202416924

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## 2. TERMS OF USE

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## 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

Title: Quantifying the Dynamic Response in Metal-Organic Frameworks (MOFs): A Platform for Tuning Chemical Space in Porous Materials  
Dates: 2021-2024  
Funding organisation: EPSRC  
Grant no.: EP/T034068/1

Title: Station I11 Rapid Access Service  
Dates: 2024  
Funding organisation: Diamond Light Source  
Grant no.: CY37697

This work was also funded by the University of Leeds.

#### 4. CONTENTS

The dataset contains data for this study:

Elemental microanalyses (*microanalysis.zip*).

<sup>1</sup>H and <sup>13</sup>C spectra of L, and a paramagnetic <sup>1</sup>H NMR spectrum of the complex (raw and processed data – *NMR.zip*).

Infra-red spectra of the ligand and complexes (*IR.zip*)

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

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

Differential scanning calorimetry data – (*DSC.zip*).

Scanning electron microscopy and optical microscopy images of [FeL<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> crystal samples (*microscopy.zip*)

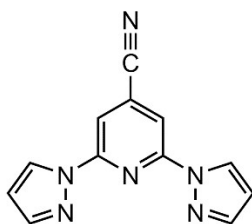
X-ray crystallographic data (*crystal.zip*):

- Structure of L at 120 K (CCDC 2375310).
- Structure of [FeL<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>, HS1 phase at 300 K (CCDC 2380639).
- Structure of [FeL<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>, HS2 phase at 300 K (CCDC 2380640).
- Structure of [FeL<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>, LS3 phase at 120 K (CCDC 2375311).
- Structure of [FeL<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> at 120 K (CCDC 2375312).
- Structure of [FeL<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> at 125 K (CCDC 2375313).
- Structure of [FeL<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> at 120 K (CCDC 2375314).
- Structure of [Ag( $\mu$ -L)]BF<sub>4</sub>·0.5MeNO<sub>2</sub> at 120 K (CCDC 2375315).

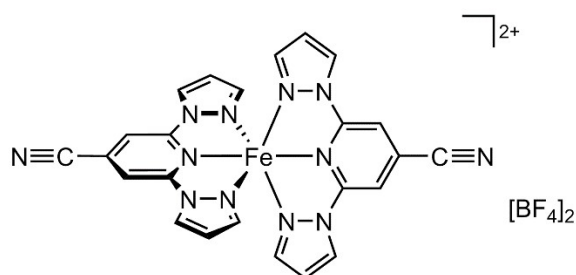
#### 5. METHODS

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

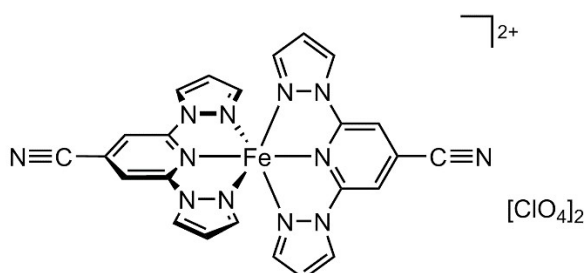
## Compounds referred to in this dataset



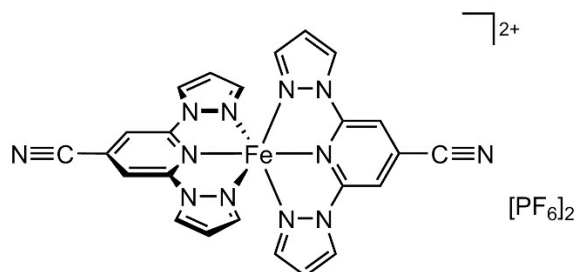
L  
2,6-Di(pyrazol-1-yl)isonicotinonitrile  
 $C_{12}H_8N_6$



$[FeL_2][BF_4]_2$   
Bis[2,6-di(pyrazol-1-yl)isonicotinonitrile]iron(II) di(tetrafluoroborate)  
 $C_{24}H_{16}B_2F_8FeN_{12}$

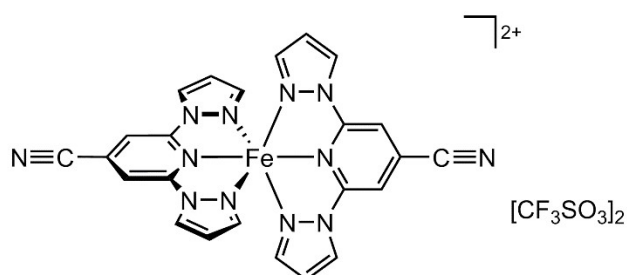


$[FeL_2][ClO_4]_2$   
Bis[2,6-di(pyrazol-1-yl)isonicotinonitrile]iron(II) diperchlorate  
 $C_{24}H_{16}Cl_2FeN_{12}O_8$

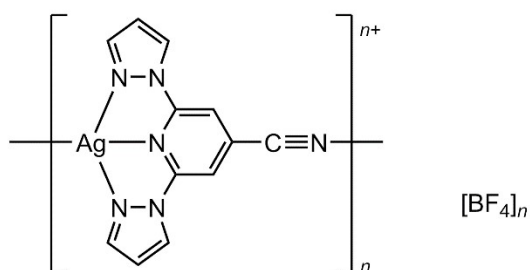


$[FeL_2][PF_6]_2$   
Bis[2,6-di(pyrazol-1-yl)isonicotinonitrile]iron(II) di(hexafluorophosphate)  
 $C_{24}H_{16}F_{12}FeN_{12}P_2$

Compounds referred to in this dataset (continued)



[FeL<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>  
 Bis[2,6-di(pyrazol-1-yl)isonicotinonitrile]iron(II) di(trifluoromethanesulfonate)  
 C<sub>26</sub>H<sub>16</sub>F<sub>6</sub>FeN<sub>12</sub>O<sub>6</sub>S<sub>2</sub>



[Ag(μ-L)]BF<sub>4</sub>  
 Catena-[2,6-di(pyrazol-1-yl)isonicotinonitrile]silver(I) tetrafluoroborate  
 C<sub>12</sub>H<sub>8</sub>AgBF<sub>4</sub>N<sub>6</sub>