

Electronic Supplementary Information (ESI) for: Spin crossover in co-crystallised 2:1 *cis:trans* [Fe^{II}(pldpt)₂(NCS)₂] occurs only in 1/3 of the iron centres

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Experimental details

Methanol was dried by freshly distilling over magnesium and iodine before use. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. Infrared spectra were recorded over the range 4000 – 400 cm⁻¹ with a Perkin-Elmer Spectrum NBX FT-IR spectrophotometer as a potassium bromide pellet. Magnetic data were recorded over the range 300 – 4.2 K with a Quantum Design MPMS5 SQUID magnetometer with an applied field of 1 Tesla by Dr Suresh Narayanaswamy and Professor Jeffery L. Tallon at Industrial Research Limited, Wellington, New Zealand. ⁵⁷Fe Mössbauer spectra were recorded by Dr Guy N. L. Jameson at the University of Otago on a low-field (0.047 T) Mössbauer spectrometer from SEE Co. (Science Engineering & Education Co., MN) equipped with a closed cycle refrigerator system from Janis Research Co. and SHI (Sumitomo Heavy Industries Ltd.). Data were collected in constant acceleration mode in transmission geometry. The zero velocity of the Mössbauer spectra refers to the centroid of the room temperature spectrum of a 25 µm metallic iron foil. Analysis of the spectra was conducted using the WMOSS program (SEE Co., formerly WEB Research Co. Edina, MN). X-ray data were collected with a Bruker APEX II area detector diffractometer at the University of Otago, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects and semi-empirical absorption corrections (SCALE) were applied. The structures were solved by direct methods (SHELXS-97) and refined against all F² data (SHELXL-97).^[1] Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached except those attached to oxygen atoms which were found from the difference map and then fixed with U = 1.2xU(attached atom). All non-hydrogen atoms except the water oxygen O(130) were made anisotropic. ISOR was used on O120.

[1] G. M. Sheldrick, *Acta Crystallographica, Section A* **2008**, A64, 112.

{2 *cis* and 1 *trans* [Fe^{II}(pIdpt)₂(NCS)₂]}·2MeOH·4½H₂O (1·2MeOH·4½H₂O)

To a pale yellow/brown solution of **pIdpt** (50 mg, 0.17 mmol) in methanol/chloroform (1:1, 10 mL), under argon, was added a yellow solution of [Fe(pyridine)₄(NCS)₂] (42 mg, 0.085 mmol) in methanol (5 mL) via a syringe. This gave a deep red solution that on slow evaporation under a stream of nitrogen afforded a red solid. The solid was recrystallised from hot methanol under argon to give 31 mg (49%) of red rod like crystals. Found (air dried sample): C, 54.22; H, 3.31; N, 26.02; S, 8.35. Calcd. for [Fe^{II}(C₁₆H₁₂N₆)₂(NCS)₂] (748.63 gmol⁻¹): C, 54.55; H, 3.23; N, 26.19; S, 8.57%. IR (KBr): 2067 (C≡N), 1601, 1587, 1570 cm⁻¹.

[Fe^{II}(pIdpt)₂(NCS)₂] (2)

To a pale yellow/brown solution of **pIdpt** (100 mg, 0.34 mmol) in methanol/chloroform (1:1, 20 mL), under argon, was added a yellow solution of [Fe(pyridine)₄(NCS)₂] (84 mg, 0.17 mmol) in methanol (10 mL) via a syringe. This gave a deep red solution that on slow evaporation under a stream of nitrogen afforded a red solid. The solid was recrystallised from hot methanol under argon to give 60 mg (48%) of red block like crystals. Found (air dried sample): C, 54.27; H, 3.28; N, 26.17; S, 8.69. Calcd. for [Fe^{II}(C₁₆H₁₂N₆)₂(NCS)₂] (748.63 gmol⁻¹): C, 54.55; H, 3.23; N, 26.19; S, 8.57%. IR (KBr): 2060 (C≡N), 1601, 1587, 1569 cm⁻¹.

Crystallographic data**Table S1: Crystallographic data for 1 and 2.**

	1		2	
Empirical formula	C _{34.67} H _{29.67} Fe N ₁₄ O _{2.17} S ₂		C ₃₄ H ₂₄ Fe N ₁₄ S ₂	
Formula weight	797.03		748.64	
Temperature	89(2) K		91(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Triclinic		Triclinic	
Space group	P-1		P-1	
Unit cell dimensions	a = 8.3788(8) Å	a = 87.501(4)°	a = 9.0442(5) Å	α = 101.242(2)°
	b = 18.0665(17) Å	b = 82.316(4)°	b = 9.3305(4) Å	β = 98.868(2)°
	c = 18.9973(18) Å	g = 76.712(4)°	c = 10.5023(5) Å	γ = 90.785(2)°
Volume	2773.4(5) Å ³		857.98(7) Å ³	
Z	3		1	
Density (calculated)	1.432 Mg/m ³		1.449 Mg/m ³	
Absorption coefficient	0.575 mm ⁻¹		0.610 mm ⁻¹	
F(000)	1233		384	
Crystal size	0.60 x 0.08 x 0.06 mm ³		0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.16 to 26.49°		2.00 to 25.50°	
Index ranges	-7<=h<=10, -21<=k<=22, -23<=l<=23		-10<=h<=10, -8<=k<=11, -12<=l<=12	
Reflections collected	30644		7123	
Independent reflections	11196 [R(int) = 0.0733]		3122 [R(int) = 0.0332]	
Completeness to theta = 26.50°	97.3 %		97.8 %	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	0.9663 and 0.5091		0.7454 and 0.6674	
Refinement method	Full-matrix least-squares on F ²		Full-matrix least-squares on F ²	
Data / restraints / parameters	11196 / 6 / 732		3122 / 0 / 232	
Goodness-of-fit on F ²	1.029		1.071	
Final R indices [I>2σ(I)]	R1 = 0.0676, wR2 = 0.1656		R1 = 0.0382, wR2 = 0.0967	
R indices (all data)	R1 = 0.1366, wR2 = 0.1978		R1 = 0.0492, wR2 = 0.1037	
Largest diff. peak and hole	1.951 and -1.097 e.Å ⁻³		0.330 and -0.503 e.Å ⁻³	

Structure description of 2

The red blocks of **2** crystallise in the triclinic space group P-1. The asymmetric unit contains one half of the molecule with Fe(1) on a centre of inversion. The bond lengths and angles are consistent with those expected for HS iron(II) [Fig. S1 and Table S2).

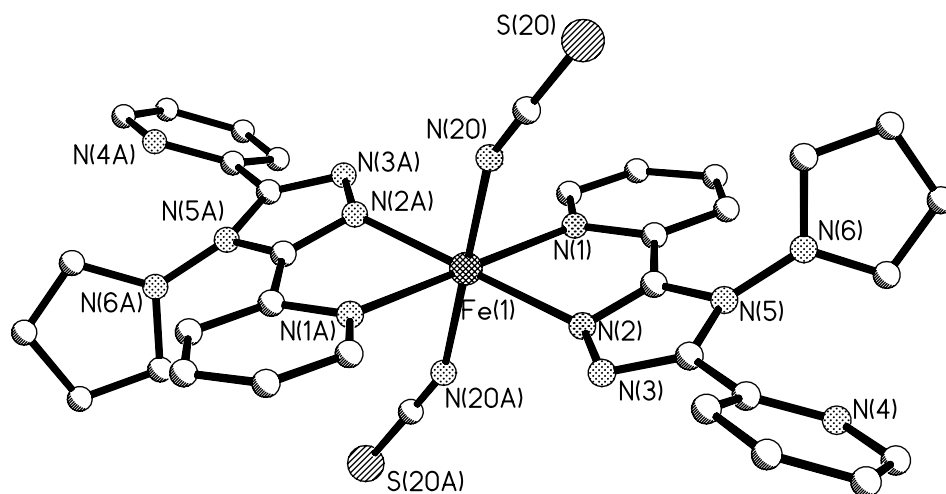


Figure S1: Perspective view of **2**. Hydrogen atoms have been omitted for clarity.

Table S2. Selected bond lengths [Å] and angles [°] for **2**.

Fe(1)-N(20)	2.107(2)
Fe(1)-N(2)	2.1701(18)
Fe(1)-N(1)	2.215(2)
<hr/>	
N(20)-Fe(1)-N(2) ^a	95.32(7)
N(20)-Fe(1)-N(2)	84.68(7)
N(20)-Fe(1)-N(1) ^a	92.31(7)
N(20)-Fe(1)-N(1)	87.69(7)
N(2) ^a -Fe(1)-N(1)	104.46(7)
N(2)-Fe(1)-N(1)	75.54(7)
C(20)-N(20)-Fe(1)	158.49(18)
N(20)-C(20)-S(20)	179.1(2)

Symmetry transformations used to generate equivalent atoms:

^a = -x+1,-y+1,-z+1

Packing analysis plots for 1·2MeOH·4½H₂O

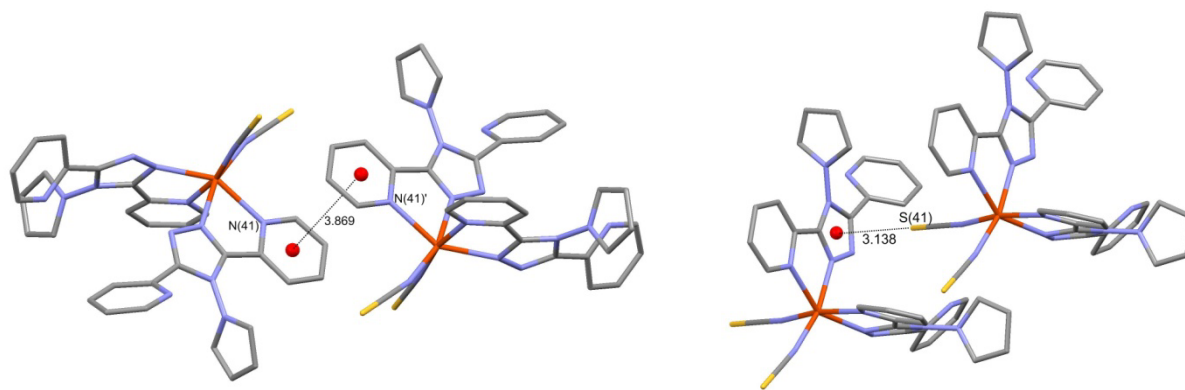


Figure S2: Views of $\pi \cdots \pi$ stacking (left) and $S \cdots \pi$ interaction (right) in $\{[\text{Fe}(\text{pldpt})_2(\text{NCS})_2]_3\} \cdot 2\text{MeOH} \cdot 4\frac{1}{2}\text{H}_2\text{O}$. Note: these are two separate images.

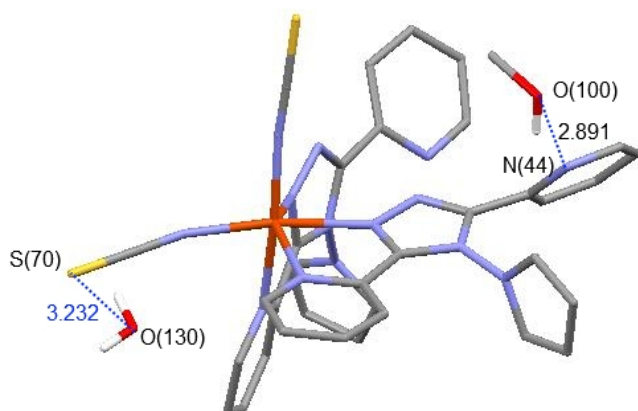


Figure S3: View of hydrogen bonding between solvent molecules and the *cis* isomer of 1·2MeOH·4½H₂O. Hydrogen atoms other than those on solvent molecules have been omitted for clarity.

Magnetochemistry data on 2

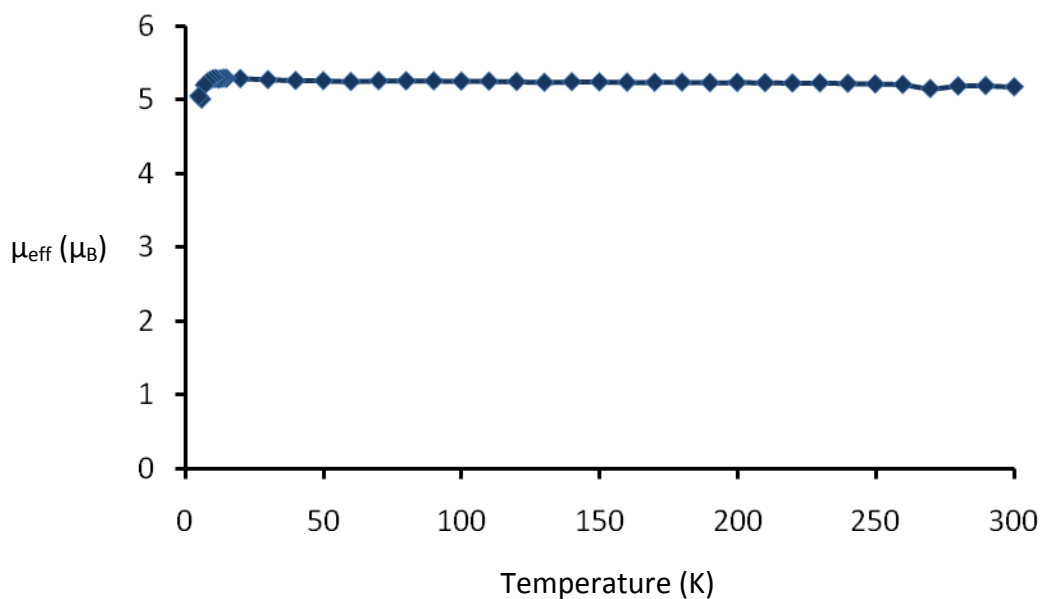


Figure S4: Plot of effective magnetic moment vs. temperature for 2. Blue dots are data points; solid line simply joins data points.

Mössbauer data on 2

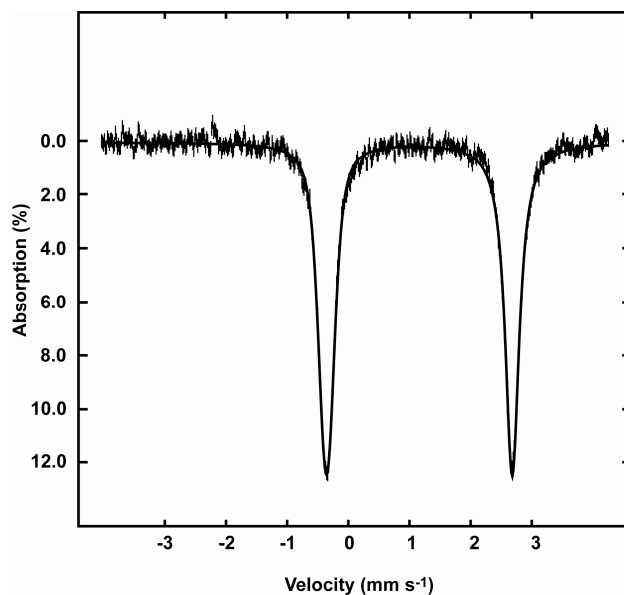


Figure S5: Mössbauer spectrum of 2 measured at 4.4 K and 0.047 Tesla. The solid line corresponds to a single quadrupole doublet with parameters: $\delta = 1.16 \text{ mm s}^{-1}$ and $\Delta E_{\text{q}} = 3.04 \text{ mm s}^{-1}$.