A Large Dinuclear Fe(II) Triple Helicate Demonstrating a Two-Step Spin Crossover

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Supporting Information

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Experimental:

Synthetic reagents: All reagents and solvents used in this project were obtained from commercial sources and used without further purification.

Synthesis of $[Fe_2L_3](BF_4)$: 0.35 mmol of 4,4'-(1,1'-Biphenyl-4,4'-diyldioxy)dianiline was dissolved in methanol (15 mL). To this a solution of 0.70 mmol 4-thiazolecarboxaldehyde in 5 mL of methanol was added dropwise. The resulting off-white suspension was heated to reflux and stirred overnight under an inert atmosphere. Due to poor solubility of the resulting ligand L, it was decided that the dried product would be used without further purification. To a stirring suspension of L, 0.23mmol Fe(II)BF₄.6H₂O (0.23 mmol) in 10 mL of acetonitrile was added dropwise at room temperature. The reaction mixture was then stirred and heated to reflux for 3 hours, the resulting bright-orange/red clear solution was filtered. Diethyl ether vapour diffusion into this reaction mixture yielded deep red X-ray quality crystals. The crystals were allowed to dry in air (Yield 68%). HR ESI-MS (positive ion mode, CH₃CN, *m/z*): Calc. for $[Fe_2L_3]^{4+}$, 446.8071; exp. found; 446.8000.

Physical Characterisations: High resolution ESI-MS data was obtained on a Waters Xevo QToF mass spectrometer operating in positive ion mode. Calibration of high-resolution masses was achieved using a Waters lock-spray system.

TGA and DSC was measured using a simultaneous thermal analysis NETZSCH STA449 Jupiter instrument. STA measurements were conducted using Argon for both the purge and protective gases; an aluminium crucible and a temperature range of 30 - 473K at a rate of 10K per minute.

Powder X-Ray Diffraction experiments were performed at the Advanced Materials Characterisations Facility at Western Sydney University, using a Bruker D8 Advance XRD with a LYNXEYE XE-T position sensitive detector. Measurements were collected at room temperature from $2.5-60^{\circ} 2\Theta$ with a step size of 0.01° at a rate of 2 seconds per step. Samples were mounted on a low background silicon XRD sample holder using amorphous grease to disperse the sample. Rietveld refinements were carried out using TOPAS Version 6.

Magnetic susceptibility measurements were conducted using a Quantum Design SQUID magnetometer calibrated against a standard palladium sample. The data was collected using filtered single crystals taken directly from diffusion vials. Measurements were collected between 10 K 400 K, holding for 30 minutes at 400K to ensure solvent loss. Measurements were taken under an applied field of 0.5 T at a scan rate of 4 K per minute.

Mössbauer experiments were carried out using a Wissel MVT-1000 Mössbauer spectrometer with a 57 Co/Rh source in a constant-acceleration transmission spectrometer (Topologic Systems) equipped with a closed-cycle helium refrigerator cryostat (Iwatani Co., Ltd.). All isomer shifts are given relative to α -Fe at room temperature.

The X-ray crystallography experiments were performed at the Australian Synchrotron, using silicon double crystal monochromated radiation at 100, 150, 200 and 250 K.^{1,2}The crystal was rotated through Phi angle of 1–360 degrees. Data integration and reduction was undertaken with XDS.³ An empirical absorption correction was then applied using *SADABS* at the Australian Synchrotron.⁴ The structures were solved by direct methods and the full-matrix

least-squares refinements were carried out using a suite of *SHELX* programs^{5,6} via the *OLEX2* graphical interface.⁷ Non-hydrogen atoms were refined anisotropically except where mentioned below. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. The crystallographic data in CIF format has been deposited at the Cambridge Crystallographic Data Centre with CCDC 1997271-1997274. It is available free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Specific refinement details and crystallographic data for each structure are present below in the crystallographic section.

Thermogravimetric Analysis:

The TGA-DSC was carried out for $[Fe_2L_3](BF_4)_4$ after being dried at room temperature (**Fig. S1**) confirms a small amount of solvent loss as indicated with a weight loss (calc. 2.35%).



Fig. S1: TGA-DSC for $[Fe_2L_3](BF_4)_4$ dried at room temperature.

Mass Spectrometry:

The HR ESI-MS was carried out on compound $[Fe_2L_3](BF_4)_4$ dissolved in acetonitrile, the isotopic distribution pattern observed (**Fig. S2**) is consistent with the quadruply charged $[Fe_2L_3]^{4+}$ species, the calculated m/z 446.8000 is in good agreement with the experimental m/z 446.8071.



Fig. S2: HR ESI-MS Spectra of [Fe₂L₃](BF₄)₄

Powder X-Ray Diffraction:

Rietveld refinements were performed in TOPAS version 6 using the SPVII fitting function. The following equations were used to calculate the criteria of fit given below (Y_{0,m} and Y_{c,m} are the observed and calculated data respectively at the data point m, Bkgm = background at data point m, M = the number of data points, P = number of parameters and wm = weighting given to data point m);

Explanation of terms used in fitting;

$$\begin{aligned} \text{R-pattern} & -R_{p} = \frac{\sum |Y_{o,m} - Y_{c,m}|}{\sum Y_{o,m}} \\ \text{R-pattern (background corrected)} & -R_{p'} = \frac{\sum |Y_{o,m} - Y_{c,m}|}{\sum |Y_{o,m} - Bkg_{m}|} \\ \text{R-weighted pattern} & -R_{wp} = \sqrt{R_{p} = \frac{\sum W_{m}(Y_{o,m} - Y_{c,m})^{2}}{\sum W_{m}Y_{o,m}}} \\ \text{R-weighted pattern (background corrected)} & -R_{wp'} = \sqrt{R_{p} = \frac{\sum W_{m}(Y_{o,m} - Y_{c,m})^{2}}{\sum W_{m}Y_{o,m}}} \\ \text{R-expected} & -R_{exp} = \sqrt{R_{p} = \frac{\sum M - P}{\sum W_{m}(Y_{o,m} - Y_{c,m})^{2}}} \\ \text{R-expected (background corrected)} & -R_{exp'} = \sqrt{R_{p} = \frac{\sum M - P}{\sum W_{m}(Y_{o,m} - Bkg_{m})^{2}}} \\ \text{Goodness of fit} - GOF = \frac{R_{wp}}{R_{exp}} \end{aligned}$$

As can be seen the RT PXRD experimental pattern is in excellent agreement with the calculated pattern generated from the crystal structure indicating the single crystal structure is representative of the bulk sample at 250 K.



Fig. S3: Rietveld fit of $[Fe_2L_3](BF_4)_4$ SCXRD at 250K vs PXRD at 293K (RT). The upper portion of the figure shows the overlap of the experimental PXRD pattern (blue) against the calculated pattern generated from the crystal structure (red). The difference plot is shown in grey.

Single crystal:

Tables of Crystallographic data:

1 at 100 K:

Table S1:

Empirical formula	$C_{104.5}H_{76.5}B_4F_{16}Fe_2N_{16}O_{6.5}S_6$
Formula weight	2311.61
Temperature/K	100
Crystal system	orthorhombic
Space group	Pna2 ₁
a/Å	19.637(4)
b/Å	27.707(6)
c/Å	19.921(4)
α/\circ	90
β/°	90
γ/°	90
Volume/Å ³	10839(4)
Z	4
$\rho_{calc}g/cm^3$	1.417
μ/mm^{-1}	0.472
F(000)	4718.0
Crystal size/mm ³	$0.02\times0.01\times0.005$
Radiation	MoKa ($\lambda = 0.71073$)
2Θ range for data collection/°	2.518 to 64.492
Index ranges	$\text{-}28 \leq h \leq 28, \text{-}39 \leq k \leq 39, \text{-}29 \leq l \leq 29$
Reflections collected	193699
Independent reflections	34115 [$R_{int} = 0.0455$, $R_{sigma} = 0.0281$]
Data/restraints/parameters	34115/316/1598
Goodness-of-fit on F ²	1.036
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0582, wR_2 = 0.1770$
Final R indexes [all data]	$R_1 = 0.0688, wR_2 = 0.1904$
Largest diff. peak/hole / e Å $^{\text{-}3}$	1.29/-1.01
Flack parameter	0.51(2)

Experimental

Single crystals of **1** at 100 K were formed by Diethyl ether vapour diffusion into a solution of **1** in acetonitrile. A suitable crystal was selected and cold mounted in a carbon dioxide atmosphere in cryotox oil. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
- 3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 100 K

Crystal Data for C_{104.5}H_{76.5}B₄F₁₆Fe₂N₁₆O_{6.5}S₆ (*M* =2311.61 g/mol): orthorhombic, space group Pna2₁ (no. 33), *a* = 19.637(4) Å, *b* = 27.707(6) Å, *c* = 19.921(4) Å, *V* = 10839(4) Å³, *Z* = 4, *T* = 100 K, μ (MoK α) = 0.472 mm⁻¹, *Dcalc* = 1.417 g/cm³, 193699 reflections measured (2.518° ≤ 2 Θ ≤ 64.492°), 34115 unique (*R*_{int} = 0.0455, R_{sigma} = 0.0281) which were used in all calculations. The final *R*₁ was 0.0582 (I > 2 σ (I)) and *wR*₂ was 0.1904 (all data).

Refinement model description

Number of restraints - 316.

Details:

```
1. Twinned data refinement
Scales: 0.49(2)
0.51(2)
2. Fixed Uiso
At 1.2 times of:
 All C(H) groups, All C(H,H) groups
At 1.5 times of:
 All C(H,H,H) groups
3. Restrained distances
02C1-C18C
 1.415 with sigma of 0.01
B03R-F00J = B03R-F02C = B03R-F02D = B03R-F02H = B03R-F0AA = B03R-F02E
 1.32 with sigma of 0.02
 F02E-F0AA
 2.28987 with sigma of 0.02
 F02{-F01I
 2.28987 with sigma of 0.02
 F02{-F03X
 2.28987 with sigma of 0.02
 F03X-F01I
 2.28987 with sigma of 0.02
 F03W-F01H
 2.28987 with sigma of 0.02
 F03W-F02Z
 2.28987 with sigma of 0.02
 F02Z-F01H
 2.28987 with sigma of 0.02
 F02H-F02D
 2.28987 with sigma of 0.02
 F02H-F02C
 2.28987 with sigma of 0.02
 F1AA-B03R
 1.40225 with sigma of 0.01
 F1AA-F0AA
 2.28987 with sigma of 0.01
 F1AA-F02E
 2.28987 with sigma of 0.01
 F1AA-F00J
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2.28987 with sigma of 0.01 FOAA-FO2E 2.28987 with sigma of 0.01 F0AA-F00J 2.28987 with sigma of 0.01 F02E-F00J 2.28987 with sigma of 0.01 F02C-F02D 2.28987 with sigma of 0.01 F02C-F02H 2.28987 with sigma of 0.01 F02C-F00J 2.28987 with sigma of 0.01 F02D-F02H 2.28987 with sigma of 0.01 F02D-F00J 2.28987 with sigma of 0.01 NOAA-C15 1.12 with sigma of 0.02 O1-C7AB 1.45 with sigma of 0.02 F01H-B03P ≈ F01I-B03P with sigma of 0.02 F02Z-B03P ≈ F02{-B03P with sigma of 0.02 B03P-F03W ≈ B03P-F03X with sigma of 0.02 4. Rigid body (RIGU) restrains N039, C02Y, C049 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C8, C9, C10, C11, C21C, C22C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C15C, C16C, C17C, C18C, C19C, C20C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C2, C3, C4, C5, C6, C7 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 $\,$ C9C2, C10C, C11C, C12C, C13C, C14C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 01C, C2, C8C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 01C1, C8C2, C9C2 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C5C, C6C, C7C, C8C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C5C2, C6C2, C7C2, C8C2 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 $\,$ C28C, C29C, C12, C13, C14, C23C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 $\,$ C28C, C29C, C24C, C25C, C26C, C27C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C02Y with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 F02C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 N048, C03T, C046 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 N039 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 NOAA, C15, C16 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 01, C7AB

with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 5. Others Sof(O1C) = 1 - FVAR(1)Sof(O1C1) = FVAR(1)Fixed Sof: O2C1(0.4) C6C2(0.4) H6C2(0.4) C5C2(0.4) H1AA(0.4) H1BB(0.6) H9C(0.4) H9CA(0.6) C8C2(0.4) C7C2(0.4) H7C2(0.4) C9C2(0.4) C1OC(0.4) H10C(0.4) C11C(0.4) H11C(0.4) C12C(0.4) C13C(0.4) H13C(0.4) C14C(0.4) H14C(0.4) C12(0.4) H29D(0.6) H29C(0.4) H28C(0.4) H28D(0.6) C13(0.4) C23C(0.4) H23C(0.4) C14(0.4) H14(0.4) C16C(0.4) H16C(0.4) C17C(0.4) H17C(0.4) C18C(0.4) C19C(0.4) H19C(0.4) C20C(0.4) H20C(0.4) C15C(0.4) O2C(0.6) C2(0.6) C3(0.6) H3(0.6) C4(0.6) H4(0.6) C5(0.6) C6(0.6) H6(0.6) C7(0.6) H7(0.6) C5C(0.6) C6C(0.6) H6C(0.6) C7C(0.6) H7C(0.6) C8C(0.6) C22C(0.6) H22C(0.6) C8(0.6) C9(0.6) H9(0.6) C10(0.6) H10(0.6) C11(0.6) C21C(0.6) H21C(0.6) C24C(0.6) C25C(0.6) H25C(0.6) C26C(0.6)H26C(0.6) C27C(0.6) F01H(0.5) F02Z(0.5) F03W(0.5) F01I(0.5) F02{(0.5) F03X(0.5) F02D(0.5) F02C(0.75) F02H(0.5) F0AA(0.5) F1AA(0.25) F02E(0.5) NOAA(0.5) C15(0.5) C16(0.5) N039(0.75) C02Y(0.75) C049(0.75) H04A(0.75) H04B(0.75) H04C(0.75) O1(0.5) C7AB(0.5) N048(0.75) C03T(0.75) C046(0.75) H04D(0.75) H04E(0.75) H04F(0.75) 6.a Aromatic/amide H refined with riding coordinates: C1C(H1C), C1A(H1A), C1B(H1B), C2B(H2B), C2C(H2C), C2A(H2A), C4C(H4C), C4A(H4A), C4B(H4B), C6B(H6B), C6A(H6A), C7B(H7B), C7A(H7A), C9B(H9B), C9A(H9A), C10B(H10B), C10A(H10A), C12B(H12B), C12A(H12A), C13A(H13A), C13B(H13B), C15B(H15B), C15A(H15A), C16A(H16A), C16B(H16B), C18A(H18A), C18B(H18B), C19A(H19A), C19B(H19B), C21A(H21A), C21B(H21B), C22A(H22A), C22B(H22B), C24A(H24A), C24B(H24B), C25B(H25B), C25A(H25A), C27B(H27B), C27A(H27A), C28A(H28A), C28B(H28B), C29A(H29A), C29B(H29B), C30C(H30C), C31B(H31B), C31A(H31A), C32C(H32C), C32A(H32A), C32B(H32B), C33C(H33C), C6C2(H6C2), C1(H1AA), C1(H1BB), C9C(H9C), C9C(H9CA), C7C2(H7C2), C10C(H10C), C11C(H11C), C13C(H13C), C14C(H14C), C29C(H29D), C29C(H29C), C28C(H28C), C28C(H28D), C23C(H23C), C14(H14), C16C(H16C), C17C(H17C), C19C(H19C), C20C(H20C), C3(H3), C4(H4), C6(H6), C7(H7), C6C(H6C), C7C(H7C), C22C(H22C), C9(H9), C10(H10), C21C(H21C), C25C(H25C), C26C(H26C) 6.b Fitted hexagon refined as free rotating group: C6C2(C5C2,C1,C9C,C8C2,C7C2), C9C2(C10C,C11C,C12C,C13C,C14C), C12(C29C,C28C, c13,c23c,c14), c16c(c17c,c18c,c19c,c20c,c15c), c2(c3,c4,c5,c6,c7), C22C(C8,C9, C10,C11,C21C) 6.c Idealised Me refined as rotating group: C02X(H02A,H02B,H02C), C03L(H03A,H03B,H03C), C049(H04A,H04B,H04C), C046(H04D, H04E,H04F)

Special refinement details:

- The solvent molecule containing the atoms N0AA, C15 and C16 has been modelled isotopically, without hydrogen atoms, due to its low partial occupancy. These have been added to the chemical formula.
- The solvent molecule (MeOH) containing the C7AB carbon atom has been modelled

without hydrogen atoms due to a low partial occupancy and the effect of these hydrogen atoms, generated using a riding model, on the shift value. These have been added to the chemical formula.

1 at 150 K:

Table S2:

Empirical formula	$C_{102.22}H_{75.65}B_4F_{16}Fe_2N_{15}O_{6.25}S_6$
Formula weight	2265.38
Temperature/K	150
Crystal system	orthorhombic
Space group	Pna2 ₁
a/Å	19.690(4)
b/Å	27.779(6)
c/Å	19.967(4)
$\alpha^{\prime \circ}$	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	10921(4)
Z	4
$\rho_{calc}g/cm^3$	1.377
μ/mm^{-1}	0.467
F(000)	4616.0
Crystal size/mm ³	$0.02 \times 0.01 \times 0.005$
Radiation	MoKa ($\lambda = 0.71073$)
2@ range for data collection/°	2.512 to 56.562
Index ranges	$\text{-}26 \leq h \leq 26, \text{-}37 \leq k \leq 37, \text{-}26 \leq l \leq 26$
Reflections collected	170538
Independent reflections	27015 [$R_{int} = 0.0646$, $R_{sigma} = 0.0350$]
Data/restraints/parameters	27015/377/1576
Goodness-of-fit on F ²	1.048
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0571, wR_2 = 0.1733$
Final R indexes [all data]	$R_1 = 0.0693, wR_2 = 0.1901$
Largest diff. peak/hole / e Å ⁻³	0.89/-0.72
Flack parameter	0.53(3)

Experimental

'Same as above'. The crystal was kept at 150 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data 1 at 150K (M = 2263.38 g/mol): orthorhombic, space group Pna2₁ (no. 33), a = 19.690(4) Å, b = 27.779(6) Å, c = 19.967(4) Å, V = 10921(4) Å³, Z = 4, T = 150 K, μ (MoK α) = 0.467 mm⁻¹, *Dcalc* = 1.377 g/cm³, 170538 reflections measured ($2.512^{\circ} \le 2\Theta \le 56.562^{\circ}$), 27015 unique ($R_{int} = 0.0646$, $R_{sigma} = 0.0350$) which were used in all calculations. The final R_1 was 0.0571 (I > 2 σ (I)) and wR_2 was 0.1901 (all data).

Refinement model description

Number of restraints - 377

Details:

```
1. Twinned data refinement
Scales: 0.47(3)
0.53(3)
2. Fixed Uiso
At 1.2 times of:
 All C(H) groups, All C(H,H) groups
At 1.5 times of:
 All C(H,H,H) groups
3. Restrained distances
F00X-F03S
 2.28987 with sigma of 0.02
F00X-F00V
 2.28987 with sigma of 0.02
F00X-F03N
 2.28987 with sigma of 0.02
F03N-F03S
 2.28987 with sigma of 0.02
 F03N-F00V
 2.28987 with sigma of 0.02
 F03S-F00V
 2.28987 with sigma of 0.02
 F0-B03L
 1.40225 with sigma of 0.02
F00X-B03T ≈ F00Y-B03T
with sigma of 0.02
F03N-B03T ≈ F03O-B03T
 with sigma of 0.02
F03S-B03T ≈ F03T-B03T
with sigma of 0.02
4. Restrained angles
N03S-C4AA-C3AA
fixed at 180 with sigma of 0.02
5. Uiso/Uaniso restraints and constraints
Uanis(C03D) \approx Ueq: with sigma of 0.1 and sigma for terminal atoms of 0.2
Uanis(N03S) \approx Ueq, Uanis(F03T) \approx Ueq: with sigma of 0.1 and sigma for
terminal atoms of 0.2
6. Rigid body (RIGU) restrains
C7C, C8C, C9C
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
C11C, C12C, C13C, C14C, C15C, C16C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
C6, C7, C8, C9, C10, C11
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C12, C13, C14, C15, C16, C17
```

with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C22C, C21C, C20C, C19C, C18C, C17C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C28C, C27C, C4, C3, C2, C5 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C27C, C28C, C23C, C24C, C25C, C26C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C5C, C6C, C7C1, C8C1, C9C1, C10C with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C5C, C6C, C7C, C8C, C9C, C1 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 F030 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 FO3N, FO0X, FO3S, BO3T, FOOV with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 F00V, F03T, F00Y, F030 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 FOOM, FO3H, FO, FOAA with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 F00M, F032, F03G, F03M with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C4AA, NO3S, C3AA with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C04C, C03D, N048 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C32B, S2B, C31B with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 C1A, S1A, C2A with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 7. Others Sof (C12) = Sof (H12) = Sof (C13) = Sof (H13) = Sof (C14) = Sof (C15) = Sof (H15) = Sof (C16) = Sof(H16) = Sof(C17) = 1 - FVAR(1)Fixed Sof: F00X(0.5) O7C(0.5) C23C(0.6) C24C(0.6) H24C(0.6) C25C(0.6) H25C(0.6) C26C(0.6) F032(0.75) O03A(0.5) C03D(0.5) F03G(0.75) C10C(0.5) C9C1(0.5) H9C1(0.5) C8C1(0.5) H8C1(0.5) C7C1(0.5) C9C(0.5) H9C(0.5) C8C(0.5)H8C(0.5) C7C(0.5) H6C(0.5) H6CA(0.5) H5C(0.5) H5CA(0.5) C1(0.5) F03M(0.25) F03N(0.75) F03S(0.5) N048(0.5) C04C(0.5) H04A(0.5) H04B(0.5) H04C(0.5) C17C(0.5) C22C(0.5) H22C(0.5) C21C(0.5) H21C(0.5) C20C(0.5) C19C(0.5) H19C(0.5) C18C(0.5) H18C(0.5) C13C(0.6) H13C(0.6) C14C(0.6) C15C(0.6) H15C(0.6) C16C(0.6) H16C(0.6) C11C(0.6) C12C(0.6) H12C(0.6) C2(0.4) H2(0.4) C3(0.4) H3(0.4) C4(0.4) H27C(0.6) H27D(0.4) H28C(0.6) H28D(0.4) C5(0.4) C6(0.4) H6(0.4) C7(0.4) H7(0.4) C8(0.4) C9(0.4) H9(0.4) C10(0.4) H10(0.4) C11(0.4) O8C1(0.5) O7C1(0.5) F03O(0.5) F03T(0.25) F00Y(0.5) F03H(0.25) F0AA(0.5) F0(0.5) C3AA(0.5) N03S(0.5) C4AA(0.5) O1(0.25) 8.a Aromatic/amide H refined with riding coordinates: C29C(H29C), C15A(H15A), C13B(H13B), C31C(H31C), C4A(H4A), C25A(H25A), C32A(H32A), C29A(H29A), C16A(H16A), C12B(H12B), C22A(H22A), C19A(H19A), C22B(H22B), C13A(H13A), C24A(H24A), C7B(H7B), C31B(H31B), C6B(H6B), C25B(H25B), C9B(H9B), C31A(H31A), C27A(H27A), C19B(H19B), C21B(H21B), C21A(H21A), C6A(H6A), C1C(H1C), C7A(H7A), C18A(H18A), C15B(H15B), C27B(H27B), C32C(H32C), C28A(H28A), C24C(H24C), C25C(H25C), C12A(H12A), C16B(H16B), C28B(H28B), C32B(H32B), C10B(H10B), C1A(H1A), C29B(H29B), C9A(H9A), C4C(H4C), C4B(H4B), C18B(H18B), C24B(H24B), C1B(H1B), C2C(H2C), C10A(H10A), C2A(H2A), C9C1(H9C1), C8C1(H8C1), C9C(H9C), C8C(H8C), C6C(H6C), C6C(H6CA), C5C(H5C), C5C(H5CA), C2B(H2B), C22C(H22C), C21C(H21C), C19C(H19C), C18C(H18C), C13C(H13C),

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C15C(H15C), C16C(H16C), C12C(H12C), C2(H2), C3(H3), C27C(H27C),
C27C(H27D),
C28C(H28C), C28C(H28D), C6(H6), C7(H7), C9(H9), C10(H10), C12(H12),
C13(H13),
C15(H15), C16(H16)
8.b Fitted hexagon refined as free rotating group:
C9C(C8C,C7C,C6C,C5C,C1), C17C(C22C,C21C,C20C,C19C,C18C),
C13C(C14C,C15C,C16C,
C11C,C12C), C2(C3,C4,C27C,C28C,C5), C6(C7,C8,C9,C10,C11),
C12(C13,C14,C15,C16,
C17)
8.c Idealised Me refined as rotating group:
C02U(H02A,H02B,H02C), C03Y(H03A,H03B,H03C), C04C(H04A,H04B,H04C)
```

Special refinement details:

- Solvent squeeze was applied due to high amounts of small (below 1) peaks of electron density making no chemical sense.

solvent_radius: 1.20 shrink_truncation_radius: 1.20 van der Waals radii:

B C F Fe H N O S 2.00 1.70 1.47 2.00 1.09 1.55 1.52 1.80

Total solvent accessible volume / cell = 727.1 Ang^3 [6.7%] Total electron count / cell = 204.1

gridding: (120,180,120)

Void #	#Grid poi	nts Vol	/A^3 Vol/% Centre of mass (frac) Eigenvectors (frac)
1	43142	181.8	1.7 (0.224, 0.017, 0.242) 1 (0.007, -0.010, 1.000)
			2 (0.985,-0.170,-0.008)
			3 (0.170, 0.985, 0.008)
2	43142	181.8	1.7 (0.276, 0.517, 0.742) 1 (-0.007, -0.010, 1.000)
			2 (0.985, 0.170, 0.008)
			3 (-0.170, 0.985, 0.008)
3	43142	181.8	1.7 (0.724, 0.483, 0.242) 1 (0.007, 0.010, 1.000)
			2 (0.985, 0.170, -0.008)
			3 (-0.170, 0.985, -0.008)
4	43142	181.8	1.7 (0.776,-0.017, 0.742) 1 (-0.007, 0.010, 1.000)
			2 (0.985,-0.170, 0.008)
			3 (0.170, 0.985, -0.008)

Void Vol/Ang^3 #Electrons

1	181.8	51.0
2	181.8	51.0
3	181.8	51.1

4 181.8 51.0

- Water molecule, O1, has been modelled isotopically and without hydrogen atoms due to the low partial occupancy.
- The acetonitrile solvent molecule including atoms NO3S, C4AA, and C3AA has been modelled without hydrogen atoms on C3AA due to the effect of these 0.5 chemically occupied riding model generated protons on the shift value.

1 at 200 K:

Table S3:

Empirical formula	$C_{101.17}H_{72.75}B_4F_{16}Fe_2N_{14.58}O_6S_6$
Formula weight	2239.94
Temperature/K	200
Crystal system	orthorhombic
Space group	Pna2 ₁
a/Å	19.772(4)
b/Å	27.872(6)
c/Å	20.025(4)
$\alpha^{\prime \circ}$	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	11035(4)
Z	4
$\rho_{calc}g/cm^3$	1.348
μ/mm^{-1}	0.461
F(000)	4563.0
Crystal size/mm ³	$0.02 \times 0.01 \times 0.005$
Radiation	MoKa ($\lambda = 0.71073$)
20 range for data collection/°	2.504 to 54.204
Index ranges	$\text{-}25 \leq h \leq 25, \text{-}35 \leq k \leq 35, \text{-}25 \leq l \leq 25$
Reflections collected	151118
Independent reflections	24258 [$R_{int} = 0.0878$, $R_{sigma} = 0.0483$]
Data/restraints/parameters	24258/369/1517
Goodness-of-fit on F ²	1.083
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0888, wR_2 = 0.2465$
Final R indexes [all data]	$R_1 = 0.1037, wR_2 = 0.2745$
Largest diff. peak/hole / e Å ⁻³	1.31/-0.66
Flack parameter	0.38(3)

Experimental

Single crystals of **1** at 200 K were formed by diethyl ether vapour diffusion. A suitable crystal was selected and cold mounted in a CO2 atmosphere in cryotox oil on MX1 of the Australian Synchrotron beamline. The crystal was kept at 200 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
- 3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 1 at 200 K

Crystal Data for C_{101.17}H_{72.75}B₄F₁₆Fe₂N_{14.58}O₆S₆ (*M* =2239.94 g/mol): orthorhombic, space group Pna2₁ (no. 33), *a* = 19.772(4) Å, *b* = 27.872(6) Å, *c* = 20.025(4) Å, *V* = 11035(4) Å³, *Z* = 4, *T* = 200 K, μ (MoK α) = 0.461 mm⁻¹, *Dcalc* = 1.348 g/cm³, 151118 reflections measured (2.504° ≤ 2 Θ ≤ 54.204°), 24258 unique (*R*_{int} = 0.0878, R_{sigma} = 0.0483) which were used in all calculations. The final *R*₁ was 0.0888 (I > 2 σ (I)) and *wR*₂ was 0.2745 (all data).

Refinement model description

Number of restraints - 369

Details:

```
1. Twinned data refinement
Scales: 0.62(3)
0.38(3)
2. Fixed Uiso
At 1.2 times of:
 All C(H) groups, All C(H,H) groups
At 1.5 times of:
 All C(H,H,H) groups
3. Shared sites
{B0, B041}
{B11A, B11}
4. Restrained distances
F00S-F02N
 2.28987 with sigma of 0.02
 F00S-F024
 2.28987 with sigma of 0.02
 B03H-F00S = B03H-F024 = B03H-F02N = B03H-F03U
 1.40225 with sigma of 0.02
02C1 - C19C = 02C1 - C1
 1.4 with sigma of 0.02
 B03H-F00S = B03H-F024 = B03H-F02N = B03H-F03U = B03H-F02O = B03H-F0
 1.40225 with sigma of 0.02
 F9-B03H
 1.40225 with sigma of 0.02
 F03U-F00S
 2.28987 with sigma of 0.02
 F03U-F024
 2.28987 with sigma of 0.02
 F03U-F02N
 2.28987 with sigma of 0.02
 F024-F02N
 2.28987 with sigma of 0.02
 F024-F00S
 2.28987 with sigma of 0.02
 F02N-F00S
 2.28987 with sigma of 0.02
 F020-F9
 2.28987 with sigma of 0.02
```

F020-F00S 2.28987 with sigma of 0.02 F020-F0 2.28987 with sigma of 0.02 F0-F9 2.28987 with sigma of 0.02 FO-FOOS 2.28987 with sigma of 0.02 B0-F1 = B0-F02H = B0-F2 = B0-F0AA1.40225 with sigma of 0.02 B041-F011 = B041-F02G = B041-F03T = B041-F040 1.40225 with sigma of 0.02 FOAA-FO2H 2.28987 with sigma of 0.02 FOAA-F1 2.28987 with sigma of 0.02 FOAA-F2 2.28987 with sigma of 0.02 F1-F2 2.28987 with sigma of 0.02 F2-F02H 2.28987 with sigma of 0.02 F02H-F1 2.28987 with sigma of 0.02 F03T-F02G 2.28987 with sigma of 0.02 F03T-F040 2.28987 with sigma of 0.02 F03T-F011 2.28987 with sigma of 0.02 F011-F02G 2.28987 with sigma of 0.02 F011-F040 2.28987 with sigma of 0.02 F040-F02G 2.28987 with sigma of 0.02 F02Q-F03H 2.28987 with sigma of 0.02 F02Q-F03W 2.28987 with sigma of 0.02 F02Q-F00P 2.28987 with sigma of 0.02 F03W-F00P 2.28987 with sigma of 0.02 F03W-F03H 2.28987 with sigma of 0.02 F03H-F03W 2.28987 with sigma of 0.02 F02P-F03G 2.28987 with sigma of 0.02 F02P-F03V 2.28987 with sigma of 0.02 F000-F02P 2.28987 with sigma of 0.02 F03G-F03V 2.28987 with sigma of 0.02 F03G-F000 2.28987 with sigma of 0.02 F03V-F000 2.28987 with sigma of 0.02 B11-F000 = B11-F02P = B11-F03G = B11-F03V

```
1.40225 with sigma of 0.02
 B11A-F00P = B11A-F02Q = B11A-F03H
 1.40225 with sigma of 0.02
 C7-C6
 1.40225 with sigma of 0.02
 C02W-C02J
 1.40225 with sigma of 0.02
 F000-B11 ≈ F00P-B11
 with sigma of 0.02
 F02P-B11 ≈ F02Q-B11
 with sigma of 0.02
 F03G-B11 ≈ F03H-B11
 with sigma of 0.02
 F03V-B11 ≈ F03W-B11
with sigma of 0.02
5. Uiso/Uaniso restraints and constraints
C7C \approx C7C1: within 1.7A with sigma of 0.04 and sigma for terminal atoms of
0.08
C6C \approx C6C1: within 1.7A with sigma of 0.04 and sigma for terminal atoms of
0.08
F024 \approx F9: within 1.7A with sigma of 0.04 and sigma for terminal atoms of
0.08
Uanis(B0) = Uanis(B041)
Uanis(B11A) = Uanis(B11)
6. Rigid body (RIGU) restrains
C3, C11C, C12C, C13C, C14C, C15C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 \,
 С1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C4, C19C, O2C1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C1, C2, C26C, C27C, C22C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C16C, C17C, C18C, C19C, C20C, C21C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 01C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F024, F0, F9, F02N, F02O, F03U
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F011, F040, B041, F02G, F03T
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F1, F2, B0, F0AA, F02H
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 B11A, F03H, F00P, F02Q, F03W
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 \,
 B11, F03G, F000, F02P, F03V
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 \,
 C049, N03B, C03C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 S1B, C1B, C2B
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 S2A, C30A, C31A
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C4, C19C, O2C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C9C, C7C1, C8C1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C10C, C5C1, C6C1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C26C, C22C, C23C
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
```

7. Others Fixed Sof: C1(0.3) C2(0.3) H2(0.3) C22C(0.3) H2CC(0.3) C23C(0.3) H26C(0.3) H26A(0.7) H27C(0.3) H27A(0.7) C4(0.7) C5(0.7) H5(0.7) O2A(0.6) O2A1(0.4) H10A(0.8) H10C(0.2) C5C1(0.2) C6C1(0.2) H6C1(0.2) C7C1(0.2) H7C1(0.2) C8C1(0.2) H9CA(0.8) H9C(0.2) O2C(0.5) C5C(0.8) C6C(0.8) H6C(0.8) C7C(0.8) H7C(0.8) C8C(0.8) C24C(0.7) H24C(0.7) C25C(0.7) O2C1(0.5) C6(0.25) C7(0.25) H7A(0.25) H7D(0.25) H7E(0.25) N2AA(0.25) C049(0.33333) N03B(0.33333) C03C(0.33333) F011(0.5) F040(0.5) B041(0.5) F02G(0.5) F03T(0.5) F024(0.5) F0(0.5) F9(0.5) F02N(0.5) F02O(0.5) F03U(0.5) B11(0.5) F03G(0.7) F00O(0.7) F02P(0.7) F03V(0.7) F1(0.5) F2(0.5) B0(0.5) F0AA(0.5) F02H(0.5) B11A(0.5) F03H(0.3) F00P(0.3) F02Q(0.3) F03W(0.3) 8.a Aromatic/amide H refined with riding coordinates: C2(H2), C22C(H22C), C26C(H26C), C26C(H26A), C27C(H27C), C27C(H27A), C5(H5), C1A(H1A), C2A(H2A), C3A(H3A), C5A(H5A), C6A(H6A), C8A(H8A), C9A(H9A), C11A(H11A), C12A(H12A), C14A(H14A), C15A(H15A), C17A(H17A), C18A(H18A), C20A(H20A), C21A(H21A), C23A(H23A), C24A(H24A), C26A(H26B), C27A(H27B), C28A(H28A), C30A(H30A), C31A(H31A), C1B(H1B), C2B(H2B), C4B(H4B), C6B(H6B), C7B(H7B), C9B(H9B), C10B(H10B), C12B(H12B), C13B(H13B), C15B(H15B), C16B(H16B), C18B(H18B), C19B(H19B), C21B(H21B), C22B(H22B), C24B(H24B), C25B(H25B), C27B(H27D), C28B(H28B), C29B(H29B), C31B(H31B), C32B(H32B), C1C(H1C), C2C(H2C), C4C(H4C), C10C(H10A), C10C(H10C), C6C1(H6C1), C7C1(H7C1), C9C(H9CA), C9C(H9C), C12C(H12C), C13C(H13C), C3(H3), C21C(H21C), C17C(H17C), C18C(H18C), C20C(H20C), C28C(H28C), C30C(H30C), C31C(H31C), C6C(H6C), C7C(H7C), C24C(H24C) 8.b Fitted hexagon refined as free rotating group: C1(C2,C22C,C23C,C26C,C27C), C10C(C5C1,C6C1,C7C1,C8C1,C9C), C12C(C13C,C14C, C15C,C3,C11C), C21C(C16C,C17C,C18C,C19C,C20C) 8.c Idealised Me refined as rotating group: C02W(H02A,H02B,H02C), C7(H7A,H7D,H7E), C043(H04A,H04B,H04C)

Special refinement details:

- The acetonitrile solvent molecule containing the C049 carbon atom has been modelled without hydrogen atoms due to a low partial occupancy (0.33) and the effect of these hydrogen atoms, generated using a riding model, on the shift value. These have been added to the chemical formula.
- The acetonitrile molecule containing C7 has been modelled isotopically due to a low partial occupancy (0.25).

250 K:

Table S4:

Empirical formula	$C_{101}H_{72.5}B_4F_{15.8}Fe_2N_{14.5}O_6S_6$
Formula weight	2232.73
Temperature/K	250
Crystal system	orthorhombic
Space group	Pccn
a/Å	20.127(4)
b/Å	27.951(6)
c/Å	19.854(4)
α/°	90
β/°	90
$\gamma/^{\circ}$	90
Volume/Å ³	11169(4)
Z	4
$\rho_{calc}g/cm^3$	1.328
μ/mm^{-1}	0.455
F(000)	4553.0
Crystal size/mm ³	$0.02 \times 0.01 \times 0.005$
Radiation	MoKa ($\lambda = 0.71073$)
2Θ range for data collection/ ^c	^o 2.494 to 52.744
Index ranges	$-25 \leq h \leq 25, -34 \leq k \leq 34, -24 \leq l \leq 24$
Reflections collected	141260
Independent reflections	11425 [$R_{int} = 0.1096$, $R_{sigma} = 0.0389$]
Data/restraints/parameters	11425/160/795
Goodness-of-fit on F ²	1.256
Final R indexes [I>=2σ (I)]	$R_1 = 0.0960, wR_2 = 0.2987$
Final R indexes [all data]	$R_1 = 0.1136, wR_2 = 0.3219$
Largest diff. peak/hole / e Å ⁻³	0.92/-0.67

Experimental

Single crystals of **1** at 250 K were formed by diethyl ether vapour diffusion. A suitable crystal was selected and cold mounted in a CO2 atmosphere, uisng cryotox oil on the MX1 beamline of the Australian Synchrotron. The crystal was kept at 250 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

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Crystal structure determination of 1 at 250 K

Crystal Data for C₁₀₁H_{72.5}B₄F_{15.8}Fe₂N_{14.5}O₆S₆ (*M* =2232.73 g/mol): orthorhombic, space group Pccn (no. 56), *a* = 20.127(4) Å, *b* = 27.951(6) Å, *c* = 19.854(4) Å, *V* = 11169(4) Å³, *Z* = 4, *T* = 250 K, μ (MoK α) = 0.455 mm⁻¹, *Dcalc* = 1.328 g/cm³, 141260 reflections measured (2.494° ≤ 2 Θ ≤ 52.744°), 11425 unique (*R*_{int} = 0.1096, R_{sigma} = 0.0389) which were used in all calculations. The final *R*₁ was 0.0960 (I > 2 σ (I)) and *wR*₂ was 0.3219 (all data).

Refinement model description

Number of restraints - 160

Details:

```
1. Fixed Uiso
At 1.2 times of:
 All C(H) groups, All C(H,H) groups
At 1.5 times of:
 All C(H,H,H) groups
2. Shared sites
{B01T, B01U}
3. Restrained distances
F00W-B01T ≈ F00X-B01U
with sigma of 0.02
F01C-B01T ≈ F0AA-B01U
with sigma of 0.02
 F01P-B01T ≈ F01Q-B01U
with sigma of 0.02
 B01T-F01W ≈ B01U-F01X
with sigma of 0.02
 F00W-F01C ≈ F00X-F0AA
 with sigma of 0.04
 F00W-F01P ≈ F00X-F01Q
 with sigma of 0.04
 F00W-F01W ≈ F00X-F01X
 with sigma of 0.04
 F01C-F01P ≈ F0AA-F01Q
 with sigma of 0.04
F01C-F01W ≈ F0AA-F01X
 with sigma of 0.04
F01P-F01W ≈ F01Q-F01X
with sigma of 0.04
4. Uiso/Uaniso restraints and constraints
C12 \approx C021: within 1.7A with sigma of 0.04 and sigma for terminal atoms of
0.08
Uanis(B01T) = Uanis(B01U)
5. Rigid body (RIGU) restrains
 CO1Q, CO1Y, CO1V, CO1G, CO1X, CO1R
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
CO1U, CO1L, N1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F010, F00F, B01Z, F01D, F01J
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F01C, F00W, B01T, F01P, F01W
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C12, C021, N023
```

with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 N023, C021, C12 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 FOAA, BO1T, FO1X, FO1Q, FO0X with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 F01W, F00W, B01U, F01C, F01P with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004 6. Others Fixed Sof: F00W(0.6) C010(0.5) F01C(0.5) C01Q(0.5) C01Y(0.5) H01Y(0.5) C01X(0.5) H01X(0.5) C01G(0.5) C01R(0.5) H01R(0.5) C01V(0.5) H01V(0.5) O01H(0.5) F01P(0.5) C01S(0.5) B01T(0.5) F01W(0.5) C021(0.25) C022(0.5) H022(0.5) N023(0.25) C024(0.5) H024(0.5) C12(0.25) H12A(0.25) H12B(0.25) H12C(0.25) C01W(0.5) H01W(0.5) C0AA(0.5) C01Z(0.5) H01Z(0.5) C1AA(0.5) H1AA(0.5) C01H(0.5) C2AA(0.5) O01I(0.5) C0(0.5) H00U(0.5) H00A(0.5) H01B(0.5) H01A(0.5) C01T(0.5) C2(0.5) H2(0.5) C1(0.5) H1(0.5) F01X(0.5) F01Q(0.5) B01U(0.5) F0AA(0.5) F00X(0.3) 7.a Aromatic/amide H refined with riding coordinates: C00I(H00I), C00J(H00J), C00K(H00K), C00L(H00L), C00M(H00M), C000(H000), C00Q(H00Q), C00R(H00R), C00T(H00T), C00V(H00V), C00Y(H00Y), C00Z(H00Z), C012(H012), C013(H013), C014(H014), C015(H015), C016(H016), C017(H017), C019(H019), C01E(H01E), C01F(H01F), C01Y(H01Y), C01X(H01X), C01R(H01R), C01V(H01V), C01I(H01I), C01K(H01K), C01M(H01M), C01N(H01N), C022(H022), C024(H024), C01W(H01W), C01Z(H01Z), C1AA(H1AA), C00U(H00U), C00U(H00A), CO1B(H01B), CO1B(H01A), C2(H2), C1(H1) 7.b Fitted hexagon refined as free rotating group: C01Q(C01Y,C01X,C01G,C01R,C01V), C01W(C0AA,C01Z,C1AA,C01H,C2AA), C0(C00U,C01B, C01T, C2, C1) 7.c Idealised Me refined as rotating group: C01U(H01C, H01D, H01G), C12(H12A, H12B, H12C)

Unit Cell Isomeric Distribution:

100 K:



Fig S4. Schematic representation of the distribution of isomers in the unit cell of **1** at 100 K, showing helicates whose centroids fit in the unit cell. Cationic helicates with the opposite absolute configurations are shown as $\Delta - \Delta$ (right handed – green) and $\Lambda - \Lambda$ (left handed – red), with Fe(II) atoms displayed in a space filling representation.

250 K:



Fig 5. Schematic representation of the distribution of isomers in the unit cell of 1 at 250 K, showing helicates whose centroids fit in the unit cell. Cationic helicates with the opposite absolute configurations are shown as $\Delta - \Delta$ (right handed – green) and $\Lambda - \Lambda$ (left handed – red), with Fe(II) atoms displayed in a space filling representation.



Fig S6. Schematic representation of the measurement of the torsion angle representing the twist of the ligand, measuring the angle with which the ligand wraps around the axis containing the two Fe(II) centres. This figure is shown perpendicular to the intranuclear axis.



Figure S7. Schematic representation of the measurement of the torsion angle representing the twist of the ligand, measuring the angle with which the ligand wraps around the axis containing the two Fe(II) centres. This figure is shown along the intranuclear axis.



Figure S8: Schematic representation of the distribution of LS (purple) and MS (orange) Fe(II) centres of **1** throughout the lattice at 200 K.



Figure S9: Overlapping images of the Fe2 half of the [LS-LS] 100 K (purple) and [LS-MS] 200 K structures (yellow), demonstrating the major change in conformation with SCO is occurring at the flexible benzene-O-benzene region of **L**.

Table S5: Edge-to-face π - π distances in 1 at 100 K, presenting the length for the C-H^{...}Benzene centroid contacts that act to stabilise a highly strained helical architecture.

Contact	H23C	H18B	H18A C	H15A…C	H13CC	H15B…C	H16CC	H6C2 C	H6A	H27B…C
(edge	···C23	····C-	15C-	11B-	11A-	10C-	17B-	5B-C6B-	C1-	28C-
Hbenzene	A-	17A-	C16C-	C12B-	C12A-	C11C-	C18B-	C7B-	C9C-	C29C-
centroid)	C24A-	C18A-	C17C-	C13B-	C13A-	C12C-	C19B-	C8B-	C5C2-	C12C-
	C25A-	C19A-	C17C-	C14B-	C14A-	C13C-	C20B-	C9B-	C8C2-	C14-C-
	C26A-	C20A-	C19C-	C15B-	C15A-	C14C-	C21B-	C10B	C7C2-	C23C-
	C27A-	C21A-	C20C	C16B	C16A	C92C	C22B		C6C2	C13
	C28A	C22A								
Distance	3.078	2.916	3.324	2.891	2.710	3.580	3.090	2.585	2.941	3.445
(Å)										

Table S6: Selected	variable-temperature	single-crystal X-ray	diffraction p	parameters for compound 1.	

Compound	Space group	Fe Fe (Å)	Twist*	Σ (°)	Fe-N (Å)
			N _{bonding} -Fe-Fe-		
			$N_{bonding}(^{\circ})$		
100 K	$Pna2_1$	19.322	273.717	Fe01 - 56.32	Fe01 - 1.992
				Fe02 - 58.943	Fe02 - 1.995
150 K	$Pna2_1$	19.319	273.263	Fe01 - 59.516	Fe01 - 2.009
				Fe02 - 60.313	Fe02 - 1.996
200 K	$Pna2_1$	19.317	271.058	Fe01 - 61.947	Fe01 - 2.01
				Fe02 - 70.845	Fe02 - 2.094
250 K	Pccn	19.352	268.758	70.917	2.098
*See above for description on	the calculation of the light	gand twist.			

⁵⁷Fe Mössbauer spectroscopy

Temperature (K)	78 K		200 K		298 K		
Doublet	LS	HS	LS	HS	LS	HS	
Isomer Shift	0.3342	0.9375	0.3371	0.9474	0.3375	0.7500	
$(\mathbf{mm}\cdot\mathbf{s}^{-1})$							
Quadrupole	0.2334	1.6921	0.1605	1.4996	0.1964	1.0803	
splitting (mm [·] s ⁻ ¹)							
Amplitude	3882.9251	796.8336	3738.4790	4066.0284	1962.0857	2125.5928	
	± 292.4	± 158.06	± 449.3	± 350.3	± 684.15	± 548.00	
Mössbauer γ	77.5	22.5	50.1	49.9	36.3	63.7	
(%)							
SQUID yHS	30.7		53.4		69.1		
(%)							

Table S7. Variable temperature ⁵⁷Fe Mössbauer results for compound 1.

Literature Survey of Dinuclear Triple Helicates Exhibiting SCO:

Table S8.

Compound	Space	FeFe	Twist	Phase	Nature of SCO
	group	(Å)	N _{bonding} -Fe-Fe-	change	
		10.222	N _{bonding} (°)	V	
I - [LS-LS]	$Pna2_1$	19.322	271.324	Yes	Full, two-step
From this			272.925		
paper.			270.905		
1 [MG]	Deen	10.252	AV - 2/3./17	٠,	6.2
1 - [M5]	PCCII	19.552	270.229		
			267.002		
			$\Delta v = 268.758$		
$2a^8 - [I S - HS]$	IArcd	9 728	106.021	No	Incomplete (Half)
C1 ⁻	14100	5.720	106.021	110	meompiete (man)
CI .			121.612		
			Av – 111.290		
2a - [HS-HS]	$I4_1cd$	9.749	101.796	٠,	د ,
			118.518		
			103.464		
			Av - 107.926		
2a' –	$I4_1cd$	• >	" - solvatomorph	No	Complete
Solv.			of 2a		
2b	$I4_1cd$	9.670	105.480	No	Incomplete (half)
Br - [LS-HS]			120.827		-
			107.815		
			Av - 111.374		
2b'	$I4_1cd$	9.668	" - solvatomorph	No	Complete
Solv. – [LS-			of 2b		
LS]					
$3a^9 - [LS-LS]$	C2/c	11.396	196.936	No	Complete
PF_6^-			198.479		
			198.479		
			Av – 197.965		
3b – [LS-HS]	P-1	11.556	187.784	No	Complete
BF_4			191.579		
			191.353		
2 [1.0.110]	D 1	11.504	Av - 190.2387	N	T 1.
3c - [LS-HS]	P-I	11.584	192.406	No	Incomplete
CIO_4			190.482		(Half)
			180.993		
	$P2_{1/c}$	3 851	Av - 109.901	No	Incomplete
-10^{-10}	1 2]/C	5.651		110	(Half)
$\frac{104}{4a - [\text{HS-HS}]}$	$P2_1/c$	4.036		No	(fiail) (;
ClO_4^-	1 21/0	4.050		110	
4b - [LS-HS]	P-1	3,870	84.519	No	Incomplete (Half)
BF4 ⁻		2.2.70	88.492		(Hysteresis)
			86.774		
			Av - 86.595		
5 ¹¹ - [LS-LS]	$P2_{1}/n$	11.35	181.732	no	Full (hysteresis)

			175.005		
			179.127		
			Av - 178.621		
$6^{12}a - [LS-LS]$	Pccn	14.847	131.694	No	Complete
			129.083		
			131.694		
			Av – 130.824		
6b - [LS-HS]	P-1	15.002	132.731	No	Complete
			137.843		
			130.174		
	-		Av - 133.583		
6b – [HS-HS]	P-1	15.223	124.622	د،	23
			132.176		
			128.295		
- 12		11.500	Av - 128.364		
7a ¹³	C2/c	11.720	177.369	No	Incomplete
			177.369		
			169.169		
	D 1	11.700	Av - 1/4.636		
/b	P-I	11.780	176.379	No	Incomplete
			1/6.564		
			1/3.011		
7.	D 1	11.620	AV - 1/5.518	N.	The second secon
/c	P-1	11.620	103.///	No	Incomplete
			176.935		
			1/8.269		
	D 1	11 220	AV - 1/2.994	N.	Committee
$\delta^{14} - [LS-LS]$	P-1	11.330	166.405	No	Complete
			109.535		
			1/2./09		
0 [LC MC]	D 1	11.260	AV - 109.349	No	62
8 - [LS-MS]	P-1	11.300	188.400	INO	
			104.024		
			191.700 Av. 188.202		
0.0 ¹⁵ [US	$C^{2/a}$	11 500	AV - 188.293	2 stop	Incomplete
9a – [113- USI	$C_{2/\ell}$	11.500	177.202	2-step	meompiete
115]			177.202		
			$A_{\rm V} = 177.705$		
9b = [I S I S]	P_1	11 341	170.420	No	Complete
70 [LS-LS]	1 -1	11.541	170.420	110	complete
			172 137		
			Av = 172.243		
9b - [HS-HS]	٠,	11 568	178 303	٤,	· · ·
		11.000	175 278		
			178 198		
			Av - 177.259		
$10^{16*} -$	C2/c	9,163	219.457	No	Incomplete
••		2.100	165.239		
			219.457		
			Av - 201.384		
$11^{17} - \Pi S$ -	$P2_{1/c}$	11.45	172.245	No	Incomplete
HS]			171.481		
1			170.043		
	1	1		1	

			Av - 171.256		
12 ¹⁸	P-1	15.440	156.202 155.628 153.384 Av - 155.071	No	Complete
13 ¹⁹ ** (3 SCO derivatives)	-	-	-	-	SCO
14 ²⁰ – [LS-LS]	P2 ₁ /c	6.857	1.380 0.168 0.530 Av - 0.693	No	Unknown (high temp SCO - not finished)
15 ²¹ – [LS-LS]	<i>P</i> 2 ₁ / <i>c</i>	10.682	188.983 177.233 175.953 Av - 180.723	No	Complete
15 - [LS— HS]	<i>P</i> 2 ₁ / <i>c</i>	10.609	187.371 164.030 169.569 Av – 173.657	د،	۶ ۶
16 ²² **					Incomplete
17 ²³ – (L6 Fe-Eu)	P-1	8.542	277.375 277.985 278.679 Av - 278.013	No	Incomplete
17 ²⁴ – (L6 Fe-Eu)	C2/c	9.143	253.013 279.427 282.444 Av - 271.628	No	Complete
17 ²⁴ - (L5 - Fe-Ln)	P-1	9.190	276.999 278.329 266.908 Av - 274.079	No	Unknown (high temp SCO - not finished)

Note: 2a and 2a' are distinct solvatomorphs

*This structure is for the complex of Fe(II) with the ligand structure 2c from this paper, while the structure showing SCO used ligand 2a, these differing by an ethyl group toward the centre of the ligand, so this has been used as an estimate for the crystal structure. **No structural data obtained for this compound.

Notes on Table S8 above;

- The restrictions for compounds included in this table is to be a dinuclear triple helicate architecture that displays spin crossover.

Magnetic susceptibility:



Figure S10: A χ mT vs T plot for compound **1**, the dots represent the experimental magnetic susceptibility values and the solid line shows the best least squares fit between calculated and experimental data. The method for the least squares fitting method was followed as the reported method²⁵.

	Value	Standard Error
(xmT) _{LH}	$2.09407 \text{ cm}^{3}\text{Kmol}^{-1}$	0.07041
(xmT) _{HH}	$7.5 \text{ cm}^3 \text{Kmol}^{-1}$	0.29738
T _{e1}	400 K	9.90167
T _{e2}	124.35102 K	2.74121
(χmT) _R	2.07503 cm ³ Kmol ⁻¹	0.009
ΔS_1	16.105605 JK ⁻¹ mol ⁻¹	1.6965
ΔS_2	23.96496 JK ⁻¹ mol ⁻¹	1.29325
ΔH_1	3.22112101 kJmol ⁻¹	182.39549
ΔH_2	2.98006773 kJmol ⁻¹	99.69068

For a detailed explanation of these parameters see the method above²⁵.

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